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Silicone rubber having reduced compression set.

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Description

The present invention relates to silicone rubber particularly to silicone rubber containing a spinel composition and more particularly to silicone rubber having reduced compression set.

Background of the Invention

It is known from U.S. 3,817,910 to Viksne, that compression set of heat curable silicone rubber can be improved by incorporating alkaline earth metal silicates in curable organopolysiloxane compositions. Spinel compositions, such as iron-manganese spinels are described in U.S. 4,604,375 to Soled et. al. and 4,618,597 to Fiaito. These spinel compositions are used as catalysts in the conversion of CO/H₂ to alpha-olefins.

Therefore, it is an object of the present invention to provide curable organopolysiloxane compositions having reduced compression set. Another object of the present invention is to provide silicone rubber having reduced compression set. Still another object of the present invention is to provide a process or preparing organopolysiloxane compositions which when cured have reduced compression set. A further object of the present invention is to provide a process for preparing silicone rubber having reduced compression set.

Summary of the Invention

The foregoing objects and others which will become apparent from the following description are accomplished in accordance with this invention, generally speaking by providing heat curable organopolysiloxanes comprising

(a) an organopolysiloxane having an average of at least two Si-bonded aliphatically unsaturated monovalent hydrocarbon radicals, per molecule
(b) an organohydrogenpolysiloxane having at least two silicon-bonded hydrogen atoms per molecule,
(c) a platinum catalyst which is capable of promoting the addition of silicon-bonded hydrogen atoms to the aliphatically unsaturated monovalent hydrocarbon radicals, and
(d) an iron-manganese spinel.

The resultant composition when cured to a silicone elastomeric exhibits reduced compression set.

Description of the Invention

The organopolysiloxanes employed as component (a) in the compositions of this invention generally contain recurring units of the formula

\[ R_nSiO_{4-n} \]

where R is selected from the group consisting of monovalent hydrocarbon radicals and halogenated monovalent hydrocarbon radicals and x is an integer of from 1 to 3 with an average of from 1.7 to 2.1.

It is preferred that the monovalent hydrocarbon radicals and halogenated monovalent hydrocarbon radicals represented by R each contain from 1 to 18 carbon atoms. Examples of suitable hydrocarbon radicals are alkyl radicals, such as the methyl, ethyl, n-propyl, iso-propyl, 1-n-butyl, 2-n-butyl, iso-butyl, tert-butyl, n-pentyl, iso-pentyl, neo-pentyl and tert-pentyl radicals; hexyl radicals such as the n-hexyl radical; heptyl radicals, such as the n-heptyl radical; octyl radicals, such as the n-octyl radical and iso-octyl radicals, such as the 2,2,4-trimethylpentyl radical; nonyl radicals, such as the n-nonyl radical; decyl radicals, such as the n-decyl radical; dodecyl radicals, such as the n-dodecyl radical; octadecyl radicals, such as the n-octadecyl radical; alkenyl radicals, such as the vinyl, allyl, methallyl and butadienyl radicals; cycloalkyl radicals, such as the cyclopentyl, cyclohexyl and cycloheptyl radicals and methylcyclohexyl radicals; aryl radicals, such as the phenyl, napthyl and anthryl and phenanthryl radical; alkaryl radicals, such as o-, m- and p-tolyl radicals, xylyl radicals and ethylphenyl radicals; and aralkyl radicals, such as the benzyl radical and the o- and p-phenylethyl radicals.

Examples of substituted monovalent hydrocarbon radicals represented by R are halogenated hydrocarbon radicals such as the haloalkyl radicals, the 3,3,3-trifluoro-n-propyl radical, the 2,2,2,2',2'-hex-
affluoroisopropyl radical and the heptafluoroisopropyl radical, and haloaryl radicals, such as the o-, m- and p-chlorophenyl radicals.

Examples of hydrocarbon radicals having aliphatic unsaturation are vinyl, allyl, methallyl and butadienyl radicals, with vinyl being the preferred radical.

The organopolysiloxanes employed in the compositions of this invention preferably have a viscosity of from 5 to 10,000,000 mPa·s at 25 °C and more preferably from 40 to 1,000,000 mPa·s at 25 °C.

The organopolysiloxanes employed herein are produced by the hydrolysis and condensation of the corresponding hydrolyzable silanes. These organopolysiloxanes are preferably linear polymers containing diorganosiloxane units of the formula R₂SiO₂; however these polymers may also contain minor amounts of other units, such as R₅SiO₃ units, R₇SiO₅₃ and/or SiO₄ units, in which R is the same as above.

The preferred organopolysiloxane is a diorganopolysiloxane having the formula

\[
\begin{align*}
\text{R-SiO} &= \text{SiO} \quad \text{Si-R} \\
\text{R} &= \text{R}
\end{align*}
\]

where R is the same as above with the proviso that an average of at least two R's per molecule are aliphatic unsaturated hydrocarbon radicals having from 2 to 8 carbon atoms such as an alkanyl radical, for example vinyl, allyl, methallyl and butadienyl radicals and n is the same as above.

Examples of organopolysiloxanes which may be employed are dimethylpolysiloxanes, methylphenylpolysiloxanes, methylvinylpolysiloxanes, and copolymers of such units, such as copolymers containing dimethyl- and phenylmethylsiloxane units, copolymers containing dimethyl- and methylvinylsiloxane units and copolymers containing phenylmethyl-dimethyl- and vinylmethylsiloxane units. The terminal groups of the organopolysiloxanes may be, for example, trimethylsiloxyl groups, dimethylvinylsiloxyl groups, dimethylphenylsiloxyl groups, trivinylsiloxyl groups, allyldimethylsiloxyl groups and the like.

The organopolysiloxanes are represented by formula (I) above, with the proviso that the organopolysiloxane contains an average of at least two aliphatically unsaturated groups per molecule. The preferred organopolysiloxanes are represented by formula (II) where the terminal units are aliphatically unsaturated groups, such as the vinyl, allyl, methallyl or butadienyl groups.

Organohydrogenpolysiloxanes employed in the compositions of this invention generally consist of units of the general formula

\[
\frac{R'_n SiO_{4-m}}{2}
\]

where R' represents hydrogen, a monovalent hydrocarbon radical or a halogenated monovalent hydrocarbon radical having from 1 to 18 carbon atoms, in which at least two and preferably three Si-bonded hydrogen atoms are present per molecule and m is 1, 2 or 3. Preferred compounds are those consisting of R'SiO₂-units, R₂SiO₃- and R₄SiO₅-units, in which an Si-bonded hydrogen atom is present for each 3 to 100 silicon atoms and R' is the same as above. The examples of the R radicals mentioned above are also examples of the R' radicals. It is preferred that the organohydrogenpolysiloxanes have a viscosity of from 10 to 50,000 mPa·s and more preferably from 100 to 20,000 mPa·s at 25 °C.

The organohydrogenpolysiloxanes may also contain monovalent hydrocarbon radicals having aliphatic unsaturation as well as Si-bonded hydrogen atoms in the same molecule.

It is preferred that the organohydrogenpolysiloxanes contain from 0.002 to 1.7% by weight of Si-bonded hydrogen atoms, and the silicon valences not satisfied by hydrogen atoms or siloxane oxygen atoms are satisfied by unsubstituted or substituted monovalent hydrocarbon radicals free of aliphatic unsaturation.

The amount of organohydrogenpolysiloxane III employed in the composition of this invention may vary over a broad range. Preferably the amount of organohydrogenpolysiloxane employed may be such that from 0.5 to 5 or 0.8 to 2.0 Si-bonded hydrogen atoms are present per aliphatically unsaturated radical bonded to a silicon atom contained in organopolysiloxane (I). Theoretically, one Si-bonded hydrogen atom is equivalent to one olefinic double bond. For many purposes, however, it may be desirable to employ an excess of either the organopolysiloxane (I) or the organohydrogenpolysiloxane (III) to facilitate the completion of the reaction or to insure that the reaction product still contains either unreacted Si-bonded hydrogen.
atoms or Si-bonded aliphatically unsaturated groups.

The organohydrogenpolysiloxanes having an average of at least 2 Si-bonded hydrogen atoms per molecule are preferably present in the compositions of this invention in an amount of from about 0.5 to 15 Si-bonded hydrogen atoms per aliphatically unsaturated group.

The platinum catalyst employed in this invention may consist of finely dispersed platinum as well as platinum compounds and/or platinum complexes which have been used heretofore to promote the addition of Si-bonded hydrogen atoms to compounds having aliphatically unsaturated groups.

Examples of catalysts which can be used in this invention are finely dispersed platinum on carriers, such as silicon dioxide, aluminum oxide or activated charcoal, platinum halides, such as PtCl₄, chloroplatinic acid and N₂PtCl₄·nH₂O, platinum-olefin complexes, for example, those with ethylene, propylene or butadiene, platinum-alcohol complexes, platinum-styrene complexes such as those described in U.S. 4,394,317 to McAfee et al. platinum-alcoholate complexes, platinum-acetylacetone, reaction products comprising chloroplatinic acid and monoketones, for examples, cyclohexanone, methyl ethyl ketone, acetone, methyl-n-propyl ketone, disobutyl ketone, acetoephonone and mesityl oxide, as well as platinum-vinylsiloxane complexes, such as platinum-divinyltetramethylsilisiloxane complexes with or without a detectable amount of inorganic halogen. The platinum-vinylsiloxane complexes are described, for example, in U.S. 3,715,334; 3,775,452 and 3,814,730 to Karstedt.

Mixtures of various platinum catalysts, for example, a mixture consisting of the reaction product of chloroplatinic acid and cyclohexanone and a platinum-divinyltetramethylsilisiloxane complex which is free of detectable inorganic halogen may be used in the compositions of this invention.

The platinum catalyst is generally employed in an amount of from about 0.5 to 300 ppm by weight and more preferably from about 2 to 50 ppm by weight calculated as platinum and based upon the weight of the silicone compounds.

The iron-manganese spinels useful in reducing compression set in silicone elastomers have the empirical formula FeₓMnᵧO₉, where x and y are integer or decimal values, other than zero, with the proviso that the sum of x + y is 3 and the ratio of y/z is 2:1 to 19:1 and more preferably the iron to manganese atomic ratio is 3:1 to 7:1. The spinel exhibits a powder x-ray diffraction pattern substantially isostructural with Fe₉O₄ and having a surface area greater than about 30 m²/g. The composition can be comprised of a mixture of single phase spinels of different iron-manganese atomic ratios.

The term "spinel" is meant a crystal structure whose general stoichiometry corresponds to A₂B₂O₄, where A and B can be the same or different cations. Spinels contain an approximately cubic close-packed arrangement of oxygen atoms with 1/8 of the available tetrahedral interstices and 1/2 of the octahedral interstices filled, and can exhibit hundreds or different phases. Further description of the spinel structure can be found in "Structural Inorganic Chemistry" by A.F. Wells, Third Edition, Oxford Press, and the article "Crystal Chemistry and Some Magnetic Properties of Mixed Metal Oxides with the Spinel Structure" by G. Blasse, Phillips Research Review Supplement, Volume 3, pp 1-30 (1964). By the term "isostructural" is meant crystallizing in the same general structure type such that the arrangement of the atoms remain very similar with only minor change in unit cell constants, bond energies and angles. The term "single phase spinel" means one structural and composition formula, corresponding to a single spinel material into which all of the metal components are incorporated, and exhibiting one characteristic x-ray diffraction pattern.

Examples of various spinels corresponding to the formulas are Fe₀.₉₇Mn₀.₀₃O₄, Fe₀.₈₅Mn₀.₁₅O₄, Fe₀.₆₂₅Mn₀.₃₇₅O₄, and Fe₀.₂₆Mn₀.₇₄O₄.

In general, the physical properties of the spinels are similar to those of magnetite and include a melting point above 1400 °C and a brownish-red color.

The iron-manganese spinels employed in this invention have a BET surface area of over 30 m²/g and generally from 50 to 100 m²/g with 100 m²/g being an average surface area, as determined by the well known BET surface area measurement technique described in the reference JACS 60, p 309 (1938) by S. Brunover, P.H. Emmett, and G. Teller. This range of surface area generally corresponds to a particle size range of from about 100 to 200 angstroms.

The spinels employed in this invention may be prepared by dissolving iron salts and manganese salts, in a water-soluble salt form such as nitrates, sulfates, chlorides, acetates and the like in water. An alpha-hydroxy carboxylic acid is added to the aqueous solution of the iron and manganese salts together with sufficient base such as ammonium hydroxide, sodium hydroxide, or potassium hydroxide to solubilize the resulting acid salts. The amount of base added is sufficient to keep the pH in the range of from 5 to 7. The resultant solution is evaporated, for example by air drying or under reduced pressure at an elevated temperature. The residue from the evaporation step is heated at a temperature of from 100 °C and more preferably from 100 °C to 350 °C for about 1 to 24 hours in air to provide a substantially single spinel phase which is isostructural with Fe₉O₄.
The amount of spinels employed in this composition is not critical and may vary over a broad range. Thus, the amount of spinels employed may range from 0.5 to 30% by weight based on the weight of the organopolysiloxane (I) and more preferably from 1 to 20% by weight based on the weight of the organopolysiloxane (I).

Fillers which may be incorporated in the compositions of this invention are reinforcing fillers, i.e., fillers having a surface area of at least 50 m²/g. Examples of such fillers are precipitated silicon dioxide having a surface area of at least 50 m²/g and/or pyrogenically produced silicon dioxide. Examples of other reinforcing fillers are the aerogels, alumina, carbon blacks and graphite.

A portion of the fillers can be semi- or non-reinforcing fillers, i.e., fillers which have a surface area of less than 50 m²/g. Examples of semi-or non-reinforcing fillers are metal oxides, metal nitrides, cork, organic resins, polytetrafluoroethylene, polychlorotrifluoroethylene, polyvinyl chloride, carbon black, graphite, bentonite, diatomaceous earth, crushed quartz, mica, metal fibers, glass beads, bubbles or fibers and mixtures thereof. Preferred examples of metal oxides are zinc oxide, ferric oxide, alumina and titanium oxide. The fillers may also be treated with, for example, triorganoalkoxysilanes, such as trimethyllethoxysilane to coat the surfaces with organosiloxyl groups.

The amount of fillers which may be incorporated in the compositions of this invention is not critical and may vary over a wide range. Thus, the amount of filler may range from 1 to 80% by weight, preferably from 5 to 75% by weight, and more preferably from 10 to 50% by weight, based on the weight of the composition, i.e., the weight of the organopolysiloxane, the organohydrogenpolysiloxane, the platinum catalyst, the spinel and the filler.

Other additives which may be incorporated in the compositions of this invention include pigments, other compression set additives, oxidation inhibitors, plasticizers, adhesion promoters, base stabilizer and other materials commonly employed as additives in the silicone rubber art. Such additives are preferably present in an amount below about 15% by weight based on the weight of the composition.

In the preparation of the organopolysiloxane compositions of this invention, the organopolysiloxane (I) containing aliphatic unsaturation may be mixed with the organohydrogenpolysiloxane (III), the spinel and then the desired amount of platinum catalyst is added, or the organopolysiloxane (I) may be mixed with the desired amount of platinum catalyst and spinel and then the organohydrogenpolysiloxane (III) is added. A preferred method is to premix the platinum catalyst with the organopolysiloxane (I) having aliphatic unsaturation and then combine the resultant mixture with the spinel and then the organohydrogenpolysiloxane (III).

The compositions of this invention may be prepared by mixing the components on a roller mill, a kneader or a Banbury mixer. These compositions are heated to a temperature up to 500 °C.

Generally, these compositions are heated to temperatures of from 50 °C to 300 °C and more preferably to a temperature of from 100 °C to 200 °C to form the silicone elastomers. The time required for cross-linking varies depending on such things as the reactants employed and the amount and type of catalyst employed.

In some cases, it is desirable to employ a diluent for the catalyst and/or reactants. The diluent should be inert to the reactants and catalyst under the reaction conditions. Examples of suitable diluents are organopolysiloxanes such as trimethylsiloxy-terminated dimethylpolysiloxanes and organic solvents which vaporize at low temperatures. Examples of suitable organic solvents are chlorinated hydrocarbons such as trichloroethylene. When organic solvents are employed, they are preferably employed in an amount of less than 20% by weight based on the weight of the organopolysiloxane composition.

The addition of the Si-bonded hydrogen atoms to the aliphatically unsaturated groups may be inhibited or at least controlled by the addition of other inhibitors to the composition. Various compounds which may be used to inhibit platinum catalyzed addition reactions are benzotriazole; acetylenic compounds such as acetylenically unsaturated secondary or tertiary alcohols and siloxanes such as 1,3-divinyl1,1,3,3-tetramethyl-disiloxane. Other compounds which may be employed are tetramethylquandine acetate, ethylenically unsaturated isocyanurate, phenylhydrazine, a diaziridine, dithiocarbamic acids, thiuram monosulfides, hydrazine 2-mercaptopbenzothiazole and the like.

The amounts of inhibitor used may be varied depending on such characteristics as the type and amount of platinum catalyst used, the degree of inhibition desired to be imparted to the platinum catalyst and often the type of unsaturated polysiloxane and hydrogenopolysiloxane employed. Generally, the amount of inhibitor employed can range from 0.001 to 6% by weight and more preferably from 0.01 to 5% by weight based on the weight of the composition.

The compositions of this invention can be used for any application where heat curing is possible. These compositions are especially useful as coating compositions and as encapsulating materials for semiconductors. In addition, these compositions may be used as adhesive repellent coatings and as fabric coatings. Also, these compositions may be used in injection molding equipment.
The heat curable organopolysiloxane compositions of this invention have excellent storage stability at room temperature. In addition, the curing system of this invention can serve to control the rate of curing of a platinum catalyzed curing system.

In the following examples, all parts are by weight unless otherwise specified and the parts of platinum catalyst are based on the weight of elemental platinum. All temperatures are at 25 °C unless otherwise stated.

Preparation of Platinum Compounds

(A) Preparation of platinum-vinylsiloxane complex.
About 20 parts of sodium bicarbonate were added to a mixture containing 10 parts of H₂PtCl₆ • 6H₂O, 20 parts of 1,3-divinyl-1,1,3,3-tetramethyldisiloxane and 50 parts of ethanol. The mixture was heated for 30 minutes to boiling under reflux while stirring, then allowed to stand for 15 hours and subsequently filtered. The volatile constituents were distilled off from the filtrate at about 16 hPa (abs.) About 17 parts of a liquid were obtained as residue and the liquid was dissolved in benzene. The solution was filtered and the benzene was distilled off from the filtrate. The residue was blended with a dimethylpolysiloxane having dimethylvinylsiloxane units as terminal units and having a viscosity of 1400 mPa•s at 25 °C as diluent, in an amount such that the mixture contains 0.1% by weight of platinum, calculated as the element.

(B) Preparation of dicyclopentadiene-platinum dichloride.
About 0.2 g of dicyclopentadiene-platinum dichloride is dissolved in 20 ml of methylene chloride. The solution is mixed with a dimethylpolysiloxane having terminal vinyl(dimethyl)siloxyl units and a viscosity of 1000 mPa•s at 23 °C. The mixture is stirred at room temperature and at 1 bar until the methylene chloride evaporates. The resultant mixture contains 0.12% of platinum, calculated as elemental platinum.

(C) Preparation of ammonium platinum complex.
An aminofunctional silicone composition is prepared by heating a mixture containing about 226.4 parts of octamethylcyclotrisiloxane, 22.4 parts of β-(aminoethyl)-gamma-aminopropytrimethoxysilane and 0.29 parts of potassium hydroxide to a temperature of 145 °C for three hours. After cooling the liquid product to room temperature, 0.29 parts of acetic acid are added to neutralize the potassium hydroxide. The product is filtered and a liquid product having a viscosity of about 40 mPa•s at 25 °C is recovered. About 28.8 parts of the aminofunctional silicone composition prepared above are added to a reactor under an atmosphere of nitrogen. About 100 parts of isopropanol, 1.04 parts of chloroplatinic acid hexahydrate, and 45 parts of toluene are added to the reactor and the reaction mixture is stirred for 30 minutes at 27 °C. The resultant transparent orange colored product contains 0.16% by weight of platinum.

Example 1

Organopolysiloxane compositions are prepared by mixing an organopolysiloxane with a platinum catalyst, fumed silica and an iron-manganese spinel at room temperature. The resultant mixture is then mixed with an organohydrogenpolysiloxane for about ten (10) minutes and then molded. The formulations are shown in Table I.
### TABLE I

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Formulations, parts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Dimethylpolysiloxane, vinyl terminated (20,000 mPa·s)</td>
<td>50.3</td>
</tr>
<tr>
<td>Fumed silica</td>
<td>19.7</td>
</tr>
<tr>
<td>Ground quartz</td>
<td>28.3</td>
</tr>
<tr>
<td>Iron-manganese spinel (Ferro F-6331)</td>
<td>1.0</td>
</tr>
<tr>
<td>Methylhydrogenpolysiloxane (0.23 weight percent silicon-bonded hydrogen - 50 mPa·s)</td>
<td>1.6</td>
</tr>
<tr>
<td>Platinum catalyst (A)</td>
<td>.00068</td>
</tr>
</tbody>
</table>

### TABLE II

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Formulations, parts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
</tr>
<tr>
<td>Dimethylpolysiloxane, vinyl terminated (20,000 mPa·s)</td>
<td>55.8</td>
</tr>
<tr>
<td>Fumed silica</td>
<td>15.3</td>
</tr>
<tr>
<td>Ground Quartz</td>
<td>27.8</td>
</tr>
<tr>
<td>Iron-manganese spinel (Ferro F-6331)</td>
<td>1.0</td>
</tr>
<tr>
<td>Methylhydrogenpolysiloxane (0.23 weight percent silicon-bonded hydrogen - 50 mPa·s)</td>
<td>1.2</td>
</tr>
<tr>
<td>Platinum catalyst (A)</td>
<td>.00042</td>
</tr>
</tbody>
</table>

Each of the formulations shown in Tables I and II are molded and cured for 5 minutes at 177 °C. The physical properties of the cured formulations are illustrated in Table III.

### TABLE III

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Formulations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Tensile strength, MPa (p.s.i.)</td>
<td>7.4 (1076)</td>
</tr>
<tr>
<td>100% Modulus, MPa (p.s.i.)</td>
<td>3.6 (515)</td>
</tr>
<tr>
<td>Elongation, (%)</td>
<td>314</td>
</tr>
<tr>
<td>Tear Die B, KN/m (p.p.i.)</td>
<td>22.8 (130)</td>
</tr>
<tr>
<td>Durometer, Shore A</td>
<td>71</td>
</tr>
<tr>
<td>Compression Set, (%) 22 hours/177 °C</td>
<td>31</td>
</tr>
</tbody>
</table>

### EXAMPLE 2

The following formulations are prepared in accordance with the procedure described in Example 1. The formulations are shown in Table IV.
TABLE IV

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Formulations, parts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Dimethylpolysiloxane, vinyl terminated (20,000 mPa*s)</td>
<td>71.6</td>
</tr>
<tr>
<td>Fumed silica</td>
<td>26.2</td>
</tr>
<tr>
<td>Iron-manganese spinel (Ferro F-6331)</td>
<td>1</td>
</tr>
<tr>
<td>Methylhydrogenpolysiloxane (0.23 weight percent silicon bonded hydrogen - 50 mPa*s)</td>
<td>2.2</td>
</tr>
<tr>
<td>Platinum catalyst (A)</td>
<td>.00065</td>
</tr>
</tbody>
</table>

Each of the formulations shown in Table IV are molded and cured for 5 minutes at 177 °C. The physical properties of these cured formulation are illustrated in Table V.

TABLE V

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Formulations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Tensile strength, MPa (p.s.i.)</td>
<td>6.4 (923)</td>
</tr>
<tr>
<td>100% Modulus, MPa (p.s.i.)</td>
<td>0.5 (78)</td>
</tr>
<tr>
<td>Elongation, (%)</td>
<td>585</td>
</tr>
<tr>
<td>Tear Die B, KN/m (p.p.i.)</td>
<td>16.1 (92)</td>
</tr>
<tr>
<td>Durometer, Shore A</td>
<td>32</td>
</tr>
<tr>
<td>Compression Set, (%)</td>
<td>18</td>
</tr>
<tr>
<td>22 hours/177 °C</td>
<td>38</td>
</tr>
</tbody>
</table>

The molded formulations are heated for 5 minutes at 177 °C and then oven cured for 1 hour at 177 °C. The physical properties are illustrated in Table VI.

TABLE VI

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Formulations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Tensile strength, MPa (p.s.i.)</td>
<td>8.3 (1210)</td>
</tr>
<tr>
<td>100% Modulus, MPa (p.s.i.)</td>
<td>0.6 (88)</td>
</tr>
<tr>
<td>Elongation, (%)</td>
<td>638</td>
</tr>
<tr>
<td>Tear Die B, KN/m (p.p.i.)</td>
<td>17.0 (97)</td>
</tr>
<tr>
<td>Durometer, Shore A</td>
<td>32</td>
</tr>
<tr>
<td>Compression Set, (%)</td>
<td>16</td>
</tr>
<tr>
<td>22 hours/177 °C</td>
<td>38</td>
</tr>
</tbody>
</table>

Example 3

The following formulations are prepared in accordance with the procedure described in Example 1. The formulations are shown in Table VII.
TABLE VII

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Formulations, parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylpolysiloxane, vinyl terminated (20,000 mPa·s)</td>
<td>68.4</td>
</tr>
<tr>
<td>Fumed silica (Min-U-Sil)</td>
<td>30.5</td>
</tr>
<tr>
<td>Iron-manganese spinel (Ferro F-6331)</td>
<td>1</td>
</tr>
<tr>
<td>Methylhydrogenpolysiloxane (0.23 weight percent silicon-bonded hydrogen - 50 mPa·s)</td>
<td>1.1</td>
</tr>
<tr>
<td>Platinum catalyst (A)</td>
<td>0.00046</td>
</tr>
</tbody>
</table>

Each of the formulations shown in Table VII are molded and cured for 5 minutes at 177 °C. The physical properties of these formulations are illustrated in Table VIII.

TABLE VIII

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Formulations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
</tr>
<tr>
<td>Tensile strength, MPa (p.s.i.)</td>
<td>8.2 (1193)</td>
</tr>
<tr>
<td>100% Modulus, MPa (p.s.i.)</td>
<td>0.7 (106)</td>
</tr>
<tr>
<td>Elongation, (%)</td>
<td>833</td>
</tr>
<tr>
<td>Tear Die B, KN/m (p.p.i.)</td>
<td>43.4 (248)</td>
</tr>
<tr>
<td>Durometer, Shore A</td>
<td>37</td>
</tr>
<tr>
<td>Compression Set, (%)</td>
<td></td>
</tr>
<tr>
<td>22 hours/177 °C</td>
<td>39</td>
</tr>
<tr>
<td>70 hours/177 °C</td>
<td>67</td>
</tr>
</tbody>
</table>

The molded formulations are heated for 5 minutes at 177 °C and then oven cured for 1 hour at 177 °C. The physical properties are illustrated in Table IX.

TABLE IX

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Formulations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E</td>
</tr>
<tr>
<td>Tensile strength, MPa (p.s.i.)</td>
<td>7.9 (1152)</td>
</tr>
<tr>
<td>100% Modulus, MPa (p.s.i.)</td>
<td>0.7 (106)</td>
</tr>
<tr>
<td>Elongation, (%)</td>
<td>748</td>
</tr>
<tr>
<td>Tear Die B, KN/m (p.p.i.)</td>
<td>43.8 (250)</td>
</tr>
<tr>
<td>Durometer, Shore A</td>
<td>37</td>
</tr>
<tr>
<td>Compression Set, (%)</td>
<td></td>
</tr>
<tr>
<td>22 hours/177 °C</td>
<td>32</td>
</tr>
<tr>
<td>70 hours/177 °C</td>
<td>71</td>
</tr>
</tbody>
</table>

Example 4

The procedure of Example 1 is repeated except that .0012 parts of the platinum catalyst prepared according to (B) above as platinum metal are substituted for the platinum catalyst (A). The physical properties of the molded and cured formulations are essentially the same as those shown in Table III.
Example 5

The procedure of Example 1 is repeated except that .002 parts of the platinum catalyst prepared according to (O) above as platinum metal are substituted for the platinum catalyst prepared according to (A) above. The physical properties of the molded and cured formulations are essentially the same as those shown in Table III.

Claims

1. An organopolysiloxane composition which is capable of curing to an elastomer having reduced compression set which comprises:
   (a) an organopolysiloxane having an average of at least two silicon-bonded aliphatically unsaturated hydrocarbon radicals per molecule;
   (b) an organohydrogenpolysiloxane having an average of at least two silicon-bonded hydrogen atoms per molecule;
   (c) a platinum catalyst which is capable of promoting the addition of Si-bonded hydrogen atoms to aliphatically unsaturated hydrocarbon radicals; and
   (d) an iron-manganese spinel.

2. The composition of claim 1, wherein the organopolysiloxane (a) contains recurring units of the formula

\[ \frac{R_xSiO_{4-x}}{2} \]

where R is selected from the group consisting of monovalent hydrocarbon radicals having from 1 to 18 carbon atoms and halogenated monovalent hydrocarbon radicals having from 1 to 18 carbon atoms, in which an average of at least two of the monovalent hydrocarbon radicals contain aliphatic unsaturation per molecule and x is an integer of from 1 to 3, with an average value of from 1.7 to 2.1.

3. The composition of claims 1 or 2, wherein the organopolysiloxane (a) has a viscosity of from 5 to 10,000,000 mPa·s at 25 °C.

4. The composition of one of claims 1 to 3, wherein the organohydrogenpolysiloxane (b) has the formula

\[ \frac{R'_mSiO_{4-m}}{2} \]

where R' is selected from the group consisting of hydrogen, a monovalent hydrocarbon radical and a halogenated monovalent hydrocarbon radical, in which an average of at least two Si-bonded hydrogen atoms are present per molecule and m is 1, 2 or 3.

5. The composition of one of claims 1 to 4, wherein the organohydrogenpolysiloxane (b) has a viscosity of from 10 to 50,000 mPa·s at 25 °C.

6. The composition of one of claims 1 to 5, wherein the organopolysiloxane composition contains a filler.

7. The composition of one of claims 1 to 6, wherein the iron-manganese spinel (d) has the empirical formula

\[ Fe_yMn_zO_{4y} \]

where y and z have integer or decimal values other than zero, with the proviso that the sum of y + z is 3 and the ratio of y/z is 2:1 to 19:1.
8. The composition of one of claims 1 to 7, wherein the iron-manganese spinel (d) has a ratio of y/z of from 3:1 to 19:1.

9. The composition of one of claims 1 to 8, wherein the iron-manganese spinel (d) has a ratio of y/z of from 3:1 to 7:1.

10. The composition of one of claims 1 to 9, wherein the iron-manganese spinel (d) has the formula $\text{Fe}_{2.85}\text{Mn}_{0.15}\text{O}_4$, $\text{Fe}_{2.85}\text{Mn}_{0.75}\text{O}_x$, $\text{Fe}_{2.97}\text{Mn}_{0.03}\text{O}_4$ or $\text{Fe}_{2.65}\text{Mn}_{0.35}\text{O}_4$.

11. The composition of one of claims 1 to 10, wherein the iron-manganese spinel (d) is a mixture of iron-manganese spinels of different iron-manganese atomic ratios.

12. A process for preparing the organopolysiloxane composition of one of claims 1 to 11 which comprises mixing an iron-manganese spinel with a composition containing:
   (a) an organopolysiloxane having an average of at least two silicon-bonded aliphatically unsaturated hydrocarbon radicals per molecule;
   (b) an organohydrogenpolysiloxane having an average of at least two silicon-bonded hydrogen atoms per molecule and
   (c) a platinum catalyst which is capable of promoting the addition of Si-bonded hydrogen atoms to aliphatically unsaturated hydrocarbon radicals.

13. The process of claim 12, wherein the organopolysiloxane composition is heated to a temperature up to 500 °C.

14. The process of claim 13, wherein the organopolysiloxane composition is heated to a temperature of from 50 °C to 300 °C.

Patentansprüche

1. Organopolysiloxanzusammensetzung, welche in der Lage ist, zu einem Elastomer mit verringertem Druckverformungsrest zu härten, umfassend:
   (a) ein Organopolysiloxan mit im Durchschnitt mindestens zwei Siliciumgebundenen, aliphatisch ungesättigten Kohlenwasserstoffresten pro Molekül;
   (b) ein Organowasserstoffpolysiloxan mit im Durchschnitt mindestens zwei Silicium-gebundenen Wasserstoffatomen pro Molekül;
   (c) einen Platinkatalysator, welche in der Lage ist, die Addition von Si-gebundenen Wasserstoffatomen an aliphatisch ungesättigte Kohlenwasserstoffreste zu fördern; und
   (d) einen Eisen-Mangan-Spinell.

2. Zusammensetzung nach Anspruch 1, wobei das Organopolysiloxan (a) wiederkehrnde Einheiten der Formel $R_x\text{SiO}_{4-x/2}$

   enthält, worin R aus der einwertige Kohlenwasserstoffreste mit 1 bis 18 Kohlenstoffatomen und halogenierte einwertige Kohlenwasserstoffreste mit 1 bis 18 Kohlenstoffatomen umfassenden Gruppe gewählt ist, wobei im Durchschnitt mindestens zwei der einwertigen Kohlenwasserstoffreste eine aliphatische Ungesättigkeit pro Molekül enthalten, und x eine ganze Zahl von 1 bis 3 ist, mit einem Durchschnittswert von 1,7 bis 2,1.

3. Zusammensetzung nach Anspruch 1 oder 2, wobei das Organopolysiloxan (a) eine Viskosität von 5 bis 10 000 000 mPa·s bei 25 °C aufweist.

4. Zusammensetzung nach einem der Ansprüche 1 bis 3, wobei das Organowasserstoffpolysiloxan der Formel

11
entspricht, worin R' aus der Wasserstoff, einen einwertigen Kohlenwasserstoffrest und einen halogenierten einwertigen Kohlenwasserstoffrest umfassenden Gruppe gewählt ist, wobei im Durchschnitt mindestens zwei Si-gebundene Wasserstoffatome pro Molekül vorliegen, und m 1,2 oder 3 ist.

5. Zusammensetzung nach einem der Ansprüche 1 bis 4, wobei das Organowasserstoffpolysiloxan (b) eine Viskosität von 10 bis 50 000 mPa·s bei 25 °C aufweist.

6. Zusammensetzung nach einem der Ansprüche 1 bis 5, wobei die Organopolysiloxanzusammensetzung einen Füllstoff enthält.

7. Zusammensetzung nach einem der Ansprüche 1 bis 6, wobei der Eisen-Mangan-Spinell (d) die empirische Formel
\[
\text{Fe}_x\text{Mn}_y\text{O}_4
\]
besitzt, worin y und z von 0 verschiedene ganze Zahlen oder Dezimalwerte bedeuten, mit der Maßgabe, daß die Summe aus y + z 3 ist und das Verhältnis von y/z 2:1 bis 19:1 beträgt.

8. Zusammensetzung nach einem der Ansprüche 1 bis 7, wobei der Eisen-Mangan-Spinell (d) ein Verhältnis von y/z von 3:1 bis 19:1 aufweist.

9. Zusammensetzung nach einem der Ansprüche 1 bis 8, wobei der Eisen-Mangan-Spinell (d) ein Verhältnis von y/z von 3:1 bis 7:1 aufweist.

10. Zusammensetzung nach einem der Ansprüche 1 bis 9, wobei der Eisen-Mangan-Spinell (d) die Formel
\[
\text{Fe}_{2.85}\text{Mn}_{0.15}\text{O}_4, \text{Fe}_{2.26}\text{Mn}_{0.75}\text{O}_4, \text{Fe}_{2.97}\text{Mn}_{0.03}\text{O}_4 \text{ oder Fe}_{2.85}\text{Mn}_{0.97}\text{O}_4
\]
aufweist.


12. Verfahren zur Herstellung der Organopolysiloxanzusammensetzung nach einem der Ansprüche 1 bis 11, umfassend das Vermischen eines Eisen-Mangan-Spinells mit einer Zusammensetzung, enthaltend:
   (a) ein Organopolysiloxan mit im Durchschnitt mindestens zwei Silicium-gebundenen, aliphatisch ungesättigten Kohlenwasserstoffresten pro Molekül;
   (b) ein Organowasserstoffpolysiloxan mit im Durchschnitt mindestens zwei Silicium-gebundenen Wasserstoffatomen pro Molekül; und
   (c) einen Platinkatalysator, welche in der Lage ist, die Addition von Si-gebundenen Wasserstoffatomen an aliphatisch ungesättigte Kohlenwasserstoffresten zu fördern.

13. Verfahren nach Anspruch 12, wobei die Organopolysiloxanzusammensetzung auf eine Temperatur bis zu 500 °C erhitzt wird.

14. Verfahren nach Anspruch 13, wobei die Organopolysiloxanzusammensetzung auf eine Temperatur von 50 bis 300 °C erhitzt wird.

50. Revendications

1. Composition d’organopolysiloxane qui est capable de durcir pour donner un élastomère ayant une déformation permanente réduite qui comprend:
   (a) un organopolysiloxane ayant en moyenne au moins deux radicaux hydrocarbonés aliphatiquement insaturés liés à du silicium par molécule ;
   (b) un organohydrogénapolysiloxane ayant en moyenne au moins deux atomes d’hydrogène liés à du silicium par molécule ;
(c) un catalyseur de platine qui est capable d'accélérer l'addition d'atomes d'hydrogène liés à du Si sur des radicaux hydrocarbonés aliphatiquement insaturés ; et
(d) une spinelle fer-manganèse.

2. Composition selon la revendication 1, dans laquelle l'organopolysiloxane (a) contient des unités récurrentes de formule

\[ R_x S_i O_4 - x \]

\( \frac{2}{2} \)

dans laquelle R est sélectionné parmi le groupe composé de radicaux hydrocarbonés monovalents ayant de 1 à 18 atomes de carbone et de radicaux hydrocarbonés monovalents halogénés ayant de 1 à 18 atomes de carbone, dans lesquels une moyenne d'au moins deux des radicaux hydrocarbonés monovalents contiennent une insaturation aliphatique par molécule et x est un nombre entier compris entre 1 et 3, avec une valeur moyenne comprise entre 1,7 et 2,1.

3. Composition selon la revendication 1 ou 2, dans laquelle l'organopolysiloxane (a) a une viscosité comprise entre 5 et 10.000.000 mPa.s à 25 °C.

4. Composition selon l'une des revendications 1 à 3, dans laquelle l'organohydrogénopolysiloxane (b) répond à la formule

\[ R'_m S_i O_4 - m \]

\( \frac{2}{2} \)

dans laquelle R' est sélectionné parmi le groupe composé de l'hydrogène, d'un radical hydrocarboné monovalent et d'un radical hydrocarboné monovalent halogéné, dans lequel une moyenne d'au moins 2 atomes d'hydrogène liés au Si sont présents par molécule et m vaut 1, 2 ou 3.

5. Composition selon l'une des revendications 1 à 4, dans laquelle l'organohydrogénopolysiloxane (b) a une viscosité comprise entre 10 et 50.000 mPa.s à 25 °C.

6. Composition selon l'une des revendications 1 à 5, dans laquelle la composition organopolysiloxane contient une charge.

7. Composition selon l'une des revendications 1 à 6, dans laquelle la spinelle fer-manganèse (d) répond à la formule empirique

Fe\(_y\)Mn\(_z\)O\(_x\)

dans laquelle y et z ont des valeurs entières ou décimales autres que 0, avec la condition que la somme y + z vaut 3 et le rapport de y/z est compris entre 2:1 et 19:1.

8. Composition selon l'une des revendications 1 à 7, dans laquelle la spinelle fer-manganèse (d) a un rapport de y/z compris entre 3:1 et 19:1.

9. Composition selon l'une des revendications 1 à 8, dans laquelle la spinelle fer-manganèse (d) a le rapport de y/z compris entre 3:1 et 7:1.

10. Composition selon l'une des revendications 1 à 9, dans laquelle la spinelle fer-manganèse (d) a la formule Fe\(_{2,85}\)Mn\(_{0,15}\)O\(_4\), Fe\(_{2,26}\)Mn\(_{0,74}\)O\(_4\), Fe\(_{2,87}\)Mn\(_{0,03}\)O\(_4\), ou Fe\(_{2,828}\)Mn\(_{0,372}\)O\(_4\)
11. Composition selon l'une des revendications 1 à 10, dans laquelle la spinelle fer-manganèse (d) est un mélange de spinelle fer-manganèse de différents rapports atomiques fer-manganèse.

12. Procédé de préparation de la composition organopolysiloxane de l'une des revendications 1 à 11 qui comprend le mélange d'une spinelle fer-manganèse avec une composition contenant :
   (a) un organopolysiloxane ayant en moyenne au moins deux radicaux hydrocarbonés aliphatiquement insaturés liés à du silicium par molécule ;
   (b) un organohydrogénopolysiloxane ayant en moyenne au moins deux atomes d'hydrogène liés à du silicium par molécule et
   (c) un catalyseur au platine qui est capable d'accélérer l'addition d'atomes d'hydrogène liés à du Si sur des radicaux hydrocarbonés insaturés aliphatiques.

13. Procédé selon la revendication 12, dans lequel la composition organopolysiloxane est chauffée à une température allant jusqu'à 500 °C.

14. Procédé selon la revendication 13, dans lequel la composition organopolysiloxane est chauffée à une température comprise entre 50 °C et 300 °C.