COPOLYMER SEALANT COMPOSITIONS AND METHOD FOR MAKING

Inventors: Navjot Singh, Clifton Park, NY (US); John Thomas Leman, Niskayuna, NY (US); John M. Whitney, Niskayuna, NY (US); Herman Otto Krabbenhoft, Scotia, NY (US)

Assignee: General Electric Company, Niskayuna, NY (US)

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

Appl. No.: 10/199,661
Filed: Jul. 22, 2002

Abstract

Condensation curable poly(fluoroorganosiloxane-poly(silarylene)siloxane block copolymer compositions having a glass transition temperature not exceeding about -54°C. and excellent solvent resistance have been found useful as sealants. Polyalkoxysilylorganosiloxane compounds, such as 1,4-bis[trimethoxysilyl(ethyl)]benzene have been found to be effective as cross-linkers.

25 Claims, No Drawings
COPOLYMER SEALANT COMPOSITIONS AND METHOD FOR MAKING

This application is a division of application Ser. No. 09/626,768, filed Jul. 27, 2000, which is hereby incorporated by reference in its entirety, now U.S. Pat. No. 6,451,954.

The present invention is based on work sponsored under NASA's High Speed Research Contract NASI 20220, with Boeing under subcontract ZA0073 Task 22, Subtask 4.2.2.4.

BACKGROUND OF THE INVENTION

The present invention is directed to copolymer compositions useful in the preparation of fuel tank sealants. More particularly, the present invention relates to condensation curable poly(fluoroorganosiloxane-poly(silarylene) siloxane block copolymer compositions and the use of polyalkoxysiloxylorganic compounds as cross-linkers to facilitate the condensation cure of poly(fluoroorganosiloxane-poly(silarylene)siloxane block copolymers.

As shown by Smith, U.S. Pat. No. 3,109,826, bis (alkoxysilyl) hydrocarbons, such as 1,2-bis(triethoxysilyl) ethane, can be used as cross-linkers in combination with a metal salt to effect the neutral condensation cure of hydroxy end-blocked polydiorganosiloxanes. However, the resulting cured silicone compositions have been found to be problematic as aircraft fuel tank sealants, as they do not have the required solvent or fuel resistance. It is known that fluorosilicones, for example, made by polymerizing tris [(trifluoropropyl)methyl]cyclosiloxane, can provide excellent fuel resistance. However, fluorosilicones often do not meet the wide temperature stability requirements needed in aircraft sealants, such as temperatures in a range between -54°C and 177°C over an extended period of time. In addition, fluorosilicones are subject to depolymerization which can result in the formation of low molecular weight cyclics.

In an effort to enhance the thermal stability of fluorosilicones, non-siloxane groups, such as p-silphenylene, have been inserted into the polyfluorosiloxane backbone, as shown by Grassie and Beattie, "The Thermal Degradation of Polysiloxanes: Part 7", Polymer Degradation and Stabilization 8:177-193 (1984). It is also reported by Dvornic and Lenz, Macromolecules, 25, 3769 (1992), that copolymers having a glass transition temperature (Tg) of -51°C can be made by reacting methyl[3,3,3-trifluoropropyl]silanediol and 1,4-bis(dimethylhydroxysilyl)benzene.

While fluorosilicones have improved thermal stability, fluorosilicone compositions have been found to have a glass transition temperature which does not satisfy the minimum -54°C. Tg flexibility requirements of aircraft fuel tank sealants.

Experience also has shown that in addition to being sensitive to depolymerization, condensation curable fluoro-silicone compositions often suffer from an incomplete cure using a conventional curing catalyst, such as a tin salt, and a standard neutral condensation curable cross-linker, for example a polyalkoxysilane. One possible explanation, as discussed by Fujiki, U.S. Pat. No. 5,236,997, is that the steric hindrance or electronic effects of bulky terminal trifluoropropyl groups inhibit crosslinking of the network.

Accordingly, depolymerization resistant silicone base copolymers which could be compounded to a fuel resistant condensation curable silicone composition convertible to the elastomeric state upon cure exhibiting stability over an operable temperature in a range between about -54°C or below and at least about 177°C over an extended period of time are constantly being sought which also exhibit low temperature flexibility, in addition to high temperature stability.

BRIEF SUMMARY OF THE INVENTION

The present invention provides a condensation curable poly(fluoroorganosiloxane-poly(silarylene)siloxane block copolymer exhibiting a glass transition temperature not exceeding about -54°C.

In yet another embodiment of the present invention, there is provided a neutral condensation curable poly (fluoroorganosiloxane-siloxy-poly(silarylene)siloxane block copolymer sealant composition comprising

(a) a poly(fluoroorganosiloxane-poly(silarylene)siloxane block copolymer,
(b) a cross-linker, and
(c) a condensation catalyst.

In yet another embodiment of the present invention, there is provided a method for making a neutral condensation curable poly(fluoroorganosiloxane-siloxy-poly(silarylene)siloxane block copolymer sealant composition which comprises

(a) effecting reaction between bis(diorganohydroxy silyl)arylene and poly(fluoroalkylorganocyclopolsiloxane to form a condensation curable poly(fluoroorganosiloxane-siloxy-poly(silarylene)siloxane block copolymer,
(b) shearing the copolymer, and
(c) blending a cross-linker and a condensation catalyst with the copolymer to form a sealant.

DETAILED DESCRIPTION OF THE INVENTION

The poly(fluoroorganosiloxane-poly(silarylene)siloxane block copolymer, or “block copolymers” within the scope of the present invention, can be used to make aircraft fuel tank sealants having property profiles which include a glass transition temperature (Tg) of about -54°C or below and can be made by the ring opening polymerization of a poly(fluoroalkylorganocyclopolsiloxane in the presence of a bis(diorganohydroxy silyl)arylene.

As used hereinafter, the term “bis(diorganohydroxy silyl)arylene”, or “bis(hydroxy silyl)arylene” is shown by the formula,

\[-(\text{HO})-(\text{R})\text{Si}=\text{O}, -(\text{R})\text{Si}-(\text{O}),\]

and the term “silarylenesiloxy” can be represented by the formula,

\[-(\text{R})\text{Si}(\text{O})\text{Si}(\text{R})\text{O} \ldots , -(\text{R})\text{Si}(\text{O})\text{Si}(\text{R})\text{O} \ldots .\]

where Q is a C12-12, divalent aromatic organic radical, and R is a C1-1 radical. Preferably, the bis (diorganohydroxy silyl)arylene is 1,4-bis (dimethylhydroxy silyl)benzene.

“Poly(fluoroalkylorganocyclopolsiloxane”, sometimes expressed as “poly(fluoroalkyl)cyclic siloxane” is shown by the following formula:

\[-(\text{R})\text{Si}(\text{O})\text{Si}(\text{R})\text{O} \ldots .\]
where \( R^1 \) is a C\(_{3-8}\) polyfluoroalkyl radical, \( R^2 \) is a C\(_{1-12}\) organic radical, and \( a \) is an integer in a range between about 3 and about 8 inclusive, and preferably 3 or 4. Poly(fluoroalkylorganocyclosiloxanes) can be used in a proportion in a range between about 0.5 and about 4 moles, and preferably in a range between about 1 and about 2 moles, per mole of bis(dioorganohydroxy)silyl)aryl radical. Reaction to form the copolymer is typically effected with agitation under neat conditions or in the presence of an inert organic solvent, for example, toluene, at temperatures in a range between about 60°C and about 150°C. Reaction is typically effected for a time period in a range between about 30 minutes and about 2 hours, and preferably, in a range between about 45 minutes and about 1.5 hours. It is preferred to operate within an inert atmosphere, for example, under a nitrogen blanket. Typically, there is also present an initiator, for example, an alkali hydroxide (e.g. sodium hydroxide) or an alkali fluorosilanolate (e.g. sodium fluorosilanolate) in a range between about 5 parts per million (ppm) and about 50 ppm, based on the weight of reaction mixture, and a quencher, for example, phosphoric acid or silyl phosphate in a range between about 10 ppm and about 60 ppm, based on the weight of reaction mixture, and preferably in a range between about 0.1 and about 10 parts by weight unless otherwise indicated.

\[ \text{Under a nitrogen blanket. Typically, there is also present an } \]

\[ \text{between about 5 parts and about 15 parts by weight per 100 } \]

\[ \text{by weight unless otherwise indicated.} \]

The copolymer can be used in combination with an effective amount of a condensation catalyst, such as a tin compound, to effect the neutral condensation cure of block copolymers comprising blocks of poly(fluoroorganosiloxanes) and other groups. The block copolymers are referred to as "block copolymer" into a curable sealant base, or masterbatch under shearing conditions. Shearing can be effected at a temperature in a range between about 25°C and about 200°C, preferably, in a range between about 100°C and about 150°C, at atmospheric pressure, and preferably under inert conditions, such as under an inert gas, for example, nitrogen, in a mixer, for example, a double-planet mixer. Shearing can be carried out over a period in a range between about 15 minutes and about 4 hours, preferably in a range between about 1 hour and about 2 hours.

The block copolymer can be blended with a filler which can include a reinforcing filler, such as fumed silica, or a combination thereof with an extending filler, such as diatomaceous earth, precipitated silica, ground quartz, or calcium carbonate. It is preferred to use fumed silica which has been pretreated with an effective amount of a cyclic siloxane, such as octamethylcyclotetrasiloxane, or a mixture thereof with an organosilazane, such as hexamethyldisilazane. A proportion of filler in a range between about 0 parts and about 30 parts by weight, per 100 parts of block copolymer can be used. Preferably, the filler is present in a range between about 5 parts and about 15 parts by weight per 100 parts of block copolymer. A heat stabilizer, such as iron oxide, in a range between about 0.1 and about 10 parts by weight, per 100 parts of block copolymer has been found to be effective.

After blending of the masterbatch ingredients, the mixture can be degassed under reduced pressure, and the resulting paste can be stored.

The neutral condensation curable poly(fluoroorganosiloxane-poly(silylene)siloxane copolymer sealant compositions can be made by blending the block copolymer masterbatch with an effective amount of a condensation catalyst and a suitable bis(polyalkoxysilyl)organocross-linker, referred to hereinafter sometimes as "cross-linker". "Neutral" as used herein refers to a sealant composition which is substantially acid-free and substantially base-free.

Suitable condensation catalysts are present in a range between about 0.1 and about 2 parts, per 100 parts of block copolymer.

In order that skilled in the art will be better able to practice the present invention, the following examples are given by way of illustration and not by way of limitation. All parts are by weight unless otherwise indicated.

**Example 1**

A poly(fluoroorganosiloxane-poly(silylene)siloxane block copolymer useful in making a condensation curable sealant composition was prepared as follows:

A mixture of 2.26 grams (g) (0.010 mole) of 1,4-bis(dimethylhydroxy)silyl)benzene and 9.42 g (0.020 mole) of tris(trifluoropropyl)methyl)cyclosiloxane was heated with stirring to about 150°C under a nitrogen atmosphere. There was then added 0.04 g of sodium fluorosilanolate. After 60 minutes at 150°C, there was added to the mixture 0.065 g of a silyl phosphate. The reaction mixture was maintained with stirring for an additional at 150°C and then allowed to cool. Based on method of preparation, there was obtained a block copolymer, including chemically combined blocks of 1,4-dimethyl-silylphenylsiloxanesiloxane units and blocks of methyl(3,3,3-trifluoropropyl)siloxanesiloxane units. A silicon-29 nuclear magnetic resonance spectrum indicated the 1,4-
were obtained, where the respective cross-linked compositions are denoted by their previously identified cross-linkers, namely BTMSEB, BTSE and BTMSHEX:

<table>
<thead>
<tr>
<th>Test Period</th>
<th>Tensile Strength (psi)</th>
<th>Elongation (%)</th>
<th>100% Modulus</th>
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<tbody>
<tr>
<td>A</td>
<td>BTMSEB 250</td>
<td>196</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>BTSE 227</td>
<td>212</td>
<td>87</td>
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<tr>
<td></td>
<td>BTMSHEX 227</td>
<td>178</td>
<td>110</td>
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<tr>
<td>B</td>
<td>BTMSEB 273</td>
<td>213</td>
<td>100</td>
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<tr>
<td></td>
<td>BTSE 239</td>
<td>385</td>
<td>115</td>
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<td></td>
<td>BTMSHEX 268</td>
<td>196</td>
<td>116</td>
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<tr>
<td>C</td>
<td>BTMSEB 151</td>
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<td>BTMSHEX 192</td>
<td>92</td>
<td>—</td>
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<tr>
<td>D</td>
<td>BTMSEB 291</td>
<td>212</td>
<td>111</td>
</tr>
<tr>
<td></td>
<td>BTSE 253</td>
<td>386</td>
<td>122</td>
</tr>
<tr>
<td></td>
<td>BTMSHEX 279</td>
<td>191</td>
<td>121</td>
</tr>
</tbody>
</table>

The above results show that the copolymers of the present invention are depolymerization resistant and provide neutral condensation curable compositions which are useful as solvent resistant sealants.

The crosslinker in the present invention can be employed in non-corrosive cure systems to fabricate elastomers useful as fuel resistant sealing materials, electronic encapsulation, and in applications requiring chemically resistant materials. Particularly, the crosslinkers can be used for preparation of fuel tank sealants.

While typical embodiments have been set forth for the purpose of illustration, the foregoing description should not be deemed to be a limitation on the scope of the invention. Accordingly, various modifications, adaptations, and alternatives may occur to one skilled in the art without departing from the spirit and scope of the present invention.

What is claimed:

1. A condensation curable poly(fluoroorgano)siloxane-poly(silylene)siloxane block copolymer exhibiting a glass transition temperature not exceeding about -54° C.

2. The copolymer in accordance with claim 1, wherein the copolymer exhibits a weight average molecular weight in the range between about 60,000 and about 190,000.

3. The copolymer in accordance with claim 1, wherein the copolymer is depolymerization resistant.

4. The copolymer in accordance with claim 1, wherein the copolymer exhibits a weight average molecular weight in the range between about 0.5 moles and about 4 moles, per mole of bis(diorganohydroxysilyl)arylene.

5. The copolymer in accordance with claim 2, wherein the copolymer exhibits a weight average molecular weight in the range between about 0.5 moles and about 4 moles, per mole of bis(diorganohydroxysilyl)arylene.

6. The copolymer in accordance with claim 2, wherein the copolymer comprises the reaction product of a bis(diorganohydroxysilyl)arylene chemically combined with a poly(fluoroalkylyorganosilyl)alkylpolysiloxane.

7. The copolymer in accordance with claim 2, wherein the copolymer comprises the reaction product of a bis(diorganohydroxysilyl)arylene chemically combined with a poly(fluoroalkylyorganosilyl)alkylpolysiloxane.
The copolymer in accordance with claim 7, wherein the bis(diorganohydroxy)silyl)arylene comprises 1,4-bis(dimethylhydroxysilyl)benzene.

The copolymer in accordance with claim 2, wherein the poly(fluoroalkylorgano)cyclopolysiloxane comprises the formula

$$[(\text{R}^1)(\text{R}^2)\text{SiO}]_n$$

(III)

where $\text{R}^1$ is a C$_{\text{6-12}}$ polyfluoroalkyl radical, $\text{R}^2$ is a C$_{\text{1-12}}$ organic radical, and "a" is an integer in a range between about 3 and about 8 inclusive.

The copolymer in accordance with claim 9, wherein the poly(fluoroalkylorgano)cyclopolysiloxane comprises the reaction product of 1,4-bis(dimethylhydroxysilyl)benzene chemically combined with tris[(trifluoropropyl)methyl]cyclosiloxane.

A depolymerization resistant condensation curable poly(fluoroorgano)siloxane-poly(silarylene)siloxane block copolymer exhibiting a glass transition temperature not exceeding about $-54^\circ$ C. and a weight average molecular weight in the range between about 60,000 and about 190,000, wherein the copolymer comprises the reaction product of 1,4-bis(dimethylhydroxysilyl)benzene chemically combined with tris[(trifluoropropyl)methyl]cyclosiloxane.

A method for making a poly(fluoroorgano)siloxane-poly(silarylene)siloxane block copolymer comprising effecting a reaction between bis(diorganohydroxsiyl)arylene and poly(fluoroalkylorgano)cyclopolysiloxane.

The method in accordance with claim 12, wherein the reaction further comprises an initiator.

The method in accordance with claim 14, wherein the initiator is present in a range between about 5 parts per million and about 50 parts per million.

The method in accordance with claim 14, wherein the initiator comprises an alkali fluorosilanolate.

The method in accordance with claim 12, wherein the reaction further comprises a quencher which is present in a range between about 10 parts per million and about 60 parts per million.