Condenation curable poly(fluoroorgano)siloxane-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. Polyalkoxysilylorgano compounds, such as 1,4-bis[trimethoxysilyl(ethyl)]benzene have been found to be effective as cross-linkers.
1. COPOLYMER SEALANT COMPOSITIONS AND METHOD FOR MAKING

2. CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a divisional 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 polyalkoxysilylorganic compounds as cross-linkers to facilitate the condensation cure of poly(fluoroorganosiloxane-siloxane-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 having improved thermal stability of fluorosilicones, non-siloxane groups, such as p-silphenylene, have been inserted into the polyfluorosiloxane backbone, such copolymers have been found to have a glass transition temperature which does not satisfy the minimum ~54°C. Tg for 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.

A further embodiment of the present invention provides a method for making a poly(fluoroorganosiloxane-siloxane-poly(silarylene)siloxane block copolymer comprising effecting reaction between a bis(diorganohydroxysilyl)arylene and a poly(fluoroalkylorgano)cyclopolydimethylsiloxane.

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

(a) effecting reaction between bis(diorganohydroxysilyl) arylene and poly(fluoroalkylorgano)cyclopolydimethylsiloxane to form a condensation curable poly(fluoroorganosiloxane-siloxane-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 copolymers, 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(fluoroalkylorgano)cyclopolydimethylsiloxane in the presence of a bis(diorganohydroxysilyl)arylene.

As used hereinafter, the term "bis(diorganohydroxysilyl)arylene", or "bis(hydroxysilyl)arylene" is shown by the formula,

(HO)-(R)Si-OQ,

and the term "silarylensiloxy" can be represented by the formula,

-(R)SiOQSi(R)2O-,

where Q³ is a C(6,12) divalent aromatic radical, and R is a C(1,4)-alkyl radical. Preferably, the bis (diorganohydroxysilyl)arylene is 1,4-bis(dimethylhydroxysilyl)benzene.

"Poly(fluoroalkylorgano)cyclopolydimethylsiloxane", sometimes expressed as "poly(fluoroalkyl)cyclic siloxane" is shown by the following formula:

[(R)³]OQ³
under a nitrogen blanket. Typically, there is also present an between about 5 parts and about 15 parts by weight per 100 parts but are not limited to, for example, methyl, ethyl, propyl, which is substantially acid-free and substantially base-free.

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.

C(2.12) alkyl radicals which are included within R are, for example, methyl, ethyl, propyl and butyl; C(3.12) polyfluoroalkyl radicals which are included within R^2, include but are not limited to, for example, trifluoropropyl units; tridecafluoro-1,1,2,2-tetrahydroxyl units, nonafluoro-1,1,2,2-tetrahydroxyethyl units, and perfluoro-1,1,2,2-tetrahydroxyl units. Radicals included within R^2 include, but are not limited to, for example, methyl, ethyl, propyl, butyl, and phenyl units.

Among the hydrocarbon radicals included within Q are dialkylene radicals such as dimethylene, trimethylene, tetramethylene, pentamethylene, and hexamethylene. Also included are divalent arylene radicals, for example, phenylene, tolylene, xylene, naphthylene, naphthylene. Divalent aromatic radicals included within Q are for example phenylene, tolylene, xylene and naphthylene.

The cross-linker can be used in combination with an effective amount of a condensation catalyst, such as a tin catalyst, to effect the neutral condensation cure of block copolymers comprising blocks of [polyfluoroorganoglycol]organoglycol units chemically combined with poly(silylarylene)siloxane groups. The block copolymers are referred to as polyfluoroorganosiloxane-poly(silylarylene) siloxane block copolymers. The sealant composition of the present invention is preferably made by initially compounding the poly-fluoroorganoglycol-siloxane-poly(silylarylene) siloxane block copolymer, or “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-planetary mixer.

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 organosiloxane, 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 polyfluoroorganoglycol-siloxane-poly(silylarylene)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)organo cross-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. A copolymer and include, for example, organo-metal compounds such as dibutyltin dicetate, dimethyltin diocanoate, dibutyltin dilaurate, stannous octoate, dimethyltin hydroxyoleate, or combinations thereof.

Some of the preferred bis(polyalkoxysilyl)organo cross-linkers included within formula (I) are, for example, 1,2-bis(1,4-bis[(triethoxysilyl)ethyl]phenylene-siloxane, 1,4-bis[tris(trifluoropropyl)methyl]phenylene-siloxane, the reaction mixture was maintained at a temperature in a range between about 25°C and 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 0.05 g of a silyl phosphate. The reaction mixture was maintained with stirring to about 150°C. Under a nitrogen atmosphere. There was then added 0.04 g of sodium fluorosilanolate.
phenylendimethylsiloxane:methyl(3,3,3-trifluoropropyl)
disiloxane ratio to be 1:5.7 as compared to the theoretical of
1:6. Based on gel permeation chromatography (GPC), its
weight averaged molecular weight was 151,297; number
average molecular weight = 90,292; differential scanning
calorimetry (DSC) indicated a Tg of -63°C, measured at a
rate of 10°C per minute.

EXAMPLE 2

A viscous red sealant paste useful in making condensation
curable sealant compositions was prepared as follows from a
block copolymer made in accordance with the method of
Example 1. The block copolymer was initially compounded
in a Baker-Perkins double-planetary mixer for 1 hour under
a nitrogen blanket with a silazane/ octamethylcyclotetrasiloxane treated fumed silica, and red
iron oxide. A homogeneous filler dispersion was prepared
based on the use of 1324 parts of block copolymer, 105 parts
of a bis(polyalkoxysily1) C(6.1z) hydrocarbon cross-
linker and 100 parts of the above block copolymer red
iron oxide. A homogeneous filler dispersion was prepared
using 4 inch x 5 inch x 0.08 inch sheets. The sheets were
allowed to cure to the elastomeric state for a minimum of 7
tears after standard cure. The following results
were obtained, where the respective cross-linked condensa-
tions were prepared by blending in a Semco 388 mixer, 4
parts of a bis(polyalkoxysily1) C(2-z) hydrocarbon cross-
linker and 100 parts of the above block copolymer red
sealant paste contained in a Semco cartridge. The respective
neutral condensation curable sealant compositions are iden-
tified in the tables below by the particular bis
(polyalkoxysily1)Q cross-linker, where Q is as previously
defined in Example 1. Several neutral condensation curable sealant compositions were prepared by blending in a Semco 388 mixer, 4
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defined in Example 1. Particularly, the crosslinkers can be used for preparation of
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 alter-
natives 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(fluoroorganosiloxy)siloxane-
based sealant composition containing a poly(fluoroalkylorgano)cyclopolysiloxane.
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 2, wherein the
copolymer exhibits a weight average molecular weight in
the range between about 60,000 and about 190,000.
4. The copolymer in accordance with claim 1, wherein the
copolymer is depolymerization resistant.
5. The copolymer in accordance with claim 2, wherein the
copolymer is depolymerization resistant.
6. The copolymer in accordance with claim 2, wherein the
copolymer comprises the reaction product of a bis
(diorganohydroxysily1)arylene chemically combined with a
poly(fluoroalkylorgano)cyclopolysiloxane.
7. The copolymer in accordance with claim 2, wherein the
copolymer comprises the reaction product of a bis
(diorganohydroxysily1)arylene chemically combined with a
poly(fluoroalkylorgano)cyclopolysiloxane.

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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
tank sealants. Particularly, the crosslinkers can be used for preparation of
fuel tank sealants.

A viscous red sealant paste useful in making condensation
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iron oxide. A homogeneous filler dispersion was prepared
using 4 inch x 5 inch x 0.08 inch sheets. The sheets were
allowed to cure to the elastomeric state for a minimum of 7
tears after standard cure.

Shearing was maintained for 2 hours while applying heat
and vacuum to the system. The planetary mixer was main-
tained at a temperature of 150°C. A viscous red sealant
paste was then discharged while slightly above room tem-
perature into a 4 liter (l) Semco® 1350 apparatus of PRC
Desoto Inc of Mount Laurel, N.J. and then dispensed into 6
ounce Semco cartridges.

Several neutral condensation curable sealant compositions were prepared by blending in a Semco 388 mixer, 4
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the range between about 60,000 and about 190,000.
3. The copolymer in accordance with claim 2, wherein the
copolymer is depolymerization resistant.
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5. The copolymer in accordance with claim 2, wherein the
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The above results show that the copolymers of the present
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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.

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Particularly, the crosslinkers can be used for preparation of
fuel tank sealants.
8. The copolymer in accordance with claim 7, wherein the bis(diorganohydroxysilyl)arylene comprises 1,4-bis(dimethylhydroxysilyl)benzene.

9. The copolymer in accordance with claim 2, wherein the poly(fluoroalkylorganosiloxane) has a glass transition temperature not exceeding about -54°C and a weight average molecular weight in a range between about 60,000 and about 190,000.

10. The copolymer in accordance with claim 9, wherein the poly(fluoroalkylorganosiloxane) comprises tris[(trifluoropropyl)methyl]cyclosiloxane.

11. A depolymerization resistant condensation curable poly(fluoroalkylorganosiloxane-polysilarylene)siloxane copolymer comprising a reaction product of bis(diorganohydroxysilyl)arylene and poly(fluoroalkylorganosiloxane).

12. A method for making a poly(fluoroalkylorganosiloxane-polysilarylene)siloxane copolymer comprising effecting reaction between bis(diorganohydroxysilyl)arylene and poly(fluoroalkylorganosiloxane).

13. The method in accordance with claim 12, wherein the reaction is conducted at a temperature in a range between about 60°C and about 150°C.

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

15. 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.

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

17. 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.

18. The method in accordance with claim 16, wherein the quencher comprises a silyl phosphate.

19. The method in accordance with claim 12, wherein the bis(diorganohydroxysilyl)arylene comprises the formula

\[ \text{HO} - \left( R_1 R_2 Si \right)_a \]

where \( Q_1 \) is a C(6-12) divalent aromatic organic radical, and \( R \) is a C(1-12) alkyl radical.

20. The method in accordance with claim 19, wherein the bis(diorganohydroxysilyl)arylene comprises 1,4-bis(dimethylhydroxysilyl)benzene.

21. The method in accordance with claim 12, wherein the poly(fluoroalkylorganosiloxane) has a glass transition temperature not exceeding about -54°C and a weight average molecular weight in a range between about 60,000 and about 190,000, comprising effecting reaction between 1,4-bis(dimethylhydroxysilyl)benzene and tris[(trifluoropropyl)methyl]cyclosiloxane in the presence of sodium fluorosilanolate and silyl phosphate at a temperature in a range between about 60°C and about 150°C.

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