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(54) MERCAPTOSILOXANE ELASTOMER AND METHOD OF PREPARATION

(71) We, DOW CORNING CORPORATION of Midland, Michigan, United States of America, a corporation organised under the laws of the State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to silicone elastomer forming compositions containing sulphur, methods of preparing the elastomers and to the elastomers formed by the process.

Compositions containing mercaptoorgano functional siloxanes and aliphatically unsaturated organosiloxanes have been described in the prior art. For example, U.S. Patent No. 3,816,282 suggests silicone rubber compositions which cure at room temperature in the presence of electromagnetic and particulate radiation. The compositions exposed to the radiation for curing comprise an organopolysiloxane having a viscosity of 100 to 100,000 centipoise at 25°C., from 0.1 to 2.0 mole percent of the organic groups as silicon-bonded vinyl radicals and from 1.98 to 2.05 organic groups per silicon atom, an organopolysiloxane fluid having the formula $R^{3}a\ [HS(CH_{2c}]_{b}Sio^{\frac{4-a-b}{2}}$ where R^{3} is an alkyl or aryl group of up to 18 carbon atoms, *c* is from 1 to 25, *a* is from 0.088 to 2.08, *b* is from 0.009 to 0.97 and *a* +*b* is from 2.019 to 2.16 and the number of mercapto siloxane units equal or exceed the number of non mercapto siloxane units, and from 0.025% to 1% by weight of the composition of a free radical source which includes certain organic peroxides.

German Offenlegungsschrift No 2,008,426 suggests five different possibilities of making three dimensionally cross-linked silicone polymers, these reaction proceeding in the presence of radical reaction initiators at a temperature of 30 to 110° or by UV light initiation.

British Patent Specification No. 1,409,223 discloses and claims a composition; curable upon exposure to ultravoilet light, which comprises,

(A) a siloxane consisting essentially of from 0.5 to 100 mole percent of vinyl containing siloxane units of the general formula

$$(CH_2=CH)\ R_nSiO_{\frac{3-n}{2}}$$

wherein R is a monovalent hydrocarbon or monovalent halogenated hydrocarbon radical containing 1 - 30 carbon atoms and *n* has a value from 0 to 2, any other siloxane units present being any non-vinyl containing siloxane units having the general formula.

$$R=_{m}Si0_{\frac{4-m}{2}}$$

wherein R' is a monovalent hydrocarbon other than $CH_2=CH$- or a non-vinyl containing monovalent halogenated hydrocarbon radical containing 1 - 30 carbon atoms and *m* has a value from 0 to 3,

(B) a siloxane containing at least one silicon bonded hydrogen atom,

the ratio of silicon bonded vinyl groups in (A) to the silicon bonded hydrogen atoms in (B) being in the range of 1:100 to 100:1, temperature, as well as with heat, with organic peroxide alone. For example, U.S. Specification No. 3,816,282 requires specific mercapto-containing siloxanes and radiation for curing the composition, German Offenlegungsschrift No. 2,008,426 places strict limitations on the type of alkenyl siloxanes and mercapto siloxanes which can be combined to provide a three dimensional crosslinked siloxane and finally British Patent Specification 1,409,233 requires the presence of a photo-sensitizer and ultraviolet light to cure the compositions. Thus, it was unexpected that polydiorganosiloxanes having a high vinyl content and a class of mercaptoorganopolysiloxanes could be cured to an elastomer with organic peroxide at both room temperature and by heating.

Accordingly the present invention provides a composition curable to an elastomer comprising a material prepared by mixing (A) a vinyl containing polydiorganosiloxane having a viscosity of at least 0.3 Pa.s at 25°C. and comprising a combination of two triorganosiloxy units selected from trimethylsiloxy units, dimethylvinylsiloxy units and methylphenylvinylsiloxy units, from 70 to 85 mol percent dimethylsiloxane units and from 15 to 30 mol percent methlvinylsiloxane units, wherein the total number of dimethysiloxane units and methylvinylsiloxane units equals 100 mol percent, (B) a mercaptoorganopolysiloxane comprising a combination of two trimethylsiloxy units, at least 92 mol percent dimethylsiloxane units and at least two (mercaptoalkyl) methylsiloxane units per molecule up to 8 mol percent (mercaptoalkyl) methylsiloxane units, wherein the total number of dimethylsiloxane units and (mercaptoalkyl) methylsiloxane units equals 100 mol percent, the mercaptoalkyl groups having from 1 to 4 inclusive carbon atoms, and the mercaptoorganopolysiloxane having a molecular weight of at least 1,000, (A) and (B) being combined in a weight ratio sufficient to provide a molar ratio of moles of -SH group in (B) per mole of vinyl radical in (A) of from 1:1 to 10:1, (C) an organic peroxide in an amount of from 1.4 to 5.5 parts by weight based on 100 parts by weight of the combined weight of (A) and (B), and (D) a filler in an amount of from 0 to 100 parts by weight per 100 parts by weight of the combined weight of (A) and (B).

Reference is made to our copending application No. 7173/77 (Serial No. 1575212) which discloses and claims compositions curable to an elastomer which are similar to the compositions of the present invention.

The present invention also provides a method of preparing an elastomer by mixing the polydiorganosiloxane the mercaptoorganopolysiloxane, the organic peroxide and optionally the filler at a temperature below 50°C and curing at a temperature above 20°C. These compositions can be used as sealants and moulded articles.

The compositions of the present invention are prepared by mixing the ingredients (A), (B), (C) and (D). The resulting mixtures undergo some reaction as soon as they are mixed, but have a reasonable pot life to be useful. Inasmuch as, crosslinking reaction begins upon mixing, the combination of (A), (B), (C) and (D) should not be prepared too far in advance of the time cure is desired. Thus, one should determine the pot life by using small samples for each composition prior to compounding large batches of the compositions defined herein. The pot life can range from a few hours up to several weeks at room temperature. For purposes of storage, the compositions of this invention are two component or two package compositions. One can combine (A) and (C), and optionally (D) a filler for one package and (B) as a second package or one can combine part of (A), all of (C) and part of (D) in one package and in a second package combine the remainder of (A) and the remainder of (D) and all of (B). Various combinations can be used for purposes of storage, but it is cautioned that the combination of (B) and (C) may result in gelation of that mixture on storage.

Preferably, (A), (B), (C) and (D) are mixed at a temperature below 50°C. so that one does not activate the organic peroxide prematurally and cause gelation of curing during the mixing procedure.

After (A), (B), (C) and (D) are mixed, the composition will cure at room temperature, above 20°C. Compositions are best cured in the presence of oxygen gas, such as air.

The type of mixing procedure is not critical so long as it does not generate excessive heating. For high viscosity composition, such as those containing gums or high filler loadings, a two-roll mill can be used for mixing but is preferably a cooled mill, such as an internal water cooled type mill. Also the composition can be combined and mixed by using a multi-feed extruder wherein two or more components can be fed into a mixer and the composition is extruded from the apparatus. The resulting extruded article can be then left to cure at room temperature or it can be heated to accelerate the cure.

The polydiorganosiloxane (A) is a vinyl containing siloxane polymer consisting of a trimethylsiloxy terminated copolymer of from 70 to 85 mol percent dimethylsiloxane units and from 15 to 30 mol percent methylvinylsiloxane units. The polydiorganosiloxane has a viscosity of at least 0.3 pascal.second (Pa.s) at 25°C. and included fluids and gums. The flowable polydiorganosiloxanes are particularly suitable for making sealants and the gum consistency polydiorganosiloxanes are particularly useful for making extrudable articles. These polydiorganosiloxanes are known in the art.

The mercaptoorganopolysiloxane (B) comprises a trimethylsiloxy terminated siloxane copolymer containing at least two (mercaptoalkyl) methylsiloxane units per molecule and up to 8 mol percent (mercaptoalkyl) methylsiloxane units and at least 92 mol percent dimethylsiloxane units. Examples of the mercaptoalkyl groups are gamma-mercaptopropyl, beta-mercaptoethyl, delta-mercaptobutyl, alpha-mercaptoethyl and mercaptomethyl. The mercaptoorganopolysiloxane has a molecular weight greater than 1000 preferably greater than 10,000. The mercaptoorganopolysiloxanes are known in the art as evidenced by the prior art cited herein.

The organic peroxide (C) can be any of the conventional organic peroxides, such as 2,4-dicholorbezoyl peroxide, tertiary-butyl perbenzoate, benzoyl peroxide, di-tertiary-butyl peroxide, tertiary-butyl peroctoate, dicumyl peroxide and 2,5-bis (tertiary-butylperoxy)-2,5-dimethylhexane.

Filler (D) is preferably used in the compositions of this invention, but is not required. The fillers can be both treated and untreated reinforcing fillers, such as fume silica and fume silica having triorganosiloxy groups, such as trimethylsiloxy groups on the surface, carbon black or precipitated silica, and extending fillers such as crushed or ground quartz, diatomaceous earth, and calcium carbonate.

The compositions of the present invention are made by mixing (A) and (B) in weight ratios sufficient to provide a molar ratio of moles of -SH group in (B) per mole of vinyl in (A) of from 1:1 to 10:1, preferably 1.5:1 to 5:1. The organic peroxide of (C) is present in an amount of from 1.4 to 5.5 parts by weight per 100 parts by weight of the combined weight of (A) and (B). The compositions can preferably contain a filler in an amount of up to 100 parts by weight per 100 parts by weight of the combined weight of (A) and (B). Particularly, useful compositions are those which contain from 40 to 90 by weight of percent (A) and 10 to 60 by weight of percent (B). Particularly, useful compositions are those which contain from 40 to 90 by weight of percent (A) and 10 to 60 by weight of percent (B).

The compositions of this invention cure to elastomers either at room temperature or with heating, such as hot air vulcanization. The resulting elastomer has a dry or non-tacky surface and has good adhesion to substrates against which the compositions are cured. Air inhibition which is observed with conventional non-mercapto-containing peroxide cured silicone rubber composition is not observed and the inhibition by various materials such as sulphur and phosphorus in the platinum catalyzed compositions containing aliphatic unsaturated siloxanes and SiH containing siloxanes, is not observed.

The following example illustrates the invention.

Example

An elastomer was prepared by mixing 98.7 g. of a trimethylsiloxy terminated siloxane copolymer having (gammamercaptopropyl) methylsiloxane units and dimethylsiloxane units with 0.228 by percent weight -SH group and a molecular weight of 65,500, 1.27 g of a trimethylsiloxy terminated polydiorganosiloxane having dimethylsiloxane units and methylvinylsiloxane units with 7.26 percent by weight vinyl radicals and a viscosity of 21.2 Pa.s at 25°C. 30.0 g of a fume silica filler having the surface modified with trimethylsiloxy units and 7.5 g of a peroxide mixture comprising 50 by percent weight 2,4-dichlorobenzoyl peroxide and 50 by percent weight of a trimethylsiloxy endblocked polydimethylsiloxane. The composition cured to an elastomer with a tack free surface in 18 hours at room temperature, in 15 minutes at 175°C when press cured in the absence of air, and in 3 minutes at 150°C. in the presence of oxygen gas (air).

WHAT WE CLAIM IS:-

1. A composition curable to an elastomer comprising a material prepared by mixing
(A) a vinyl containing polydiorganosiloxane having a viscosity of at least 0.3 Pa.s at 25°C and comprising a combination of two triorganosiloxy units selected from trimethylsiloxy units, dimethylvinylsiloxy units and methylphenylvinylsiloxy units, from 70 to 85 mol percent dimethylsiloxane units and from 15 to 30 mol percent methylvinylsiloxane units, wherein the total number of dimethylsiloxane units and methylvinylsiloxane units equals 100 mol percent,
(B) a mercaptoorganopolysiloxane comprising a combination of two trimethylsiloxy units, at least 92 mol percent dimethylsiloxane units and at least two (mercaptoalkyl)methylsiloxane units per molecule up to 8 mol percent (mercaptoalkyl)-methylsiloxane units, wherein the total number of dimethysiloxane units and (mercaptoalkyl)methylsiloxane units equals 100 mol percent, the mercaptoalkyl groups contain from 1 to 4 inclusive carbon atoms, and the mercaptoorganopolysiloxane has a molecular weight of at least 1,000,
(A) and (B) being combined in a weight ratio sufficient to provide a molar ratio of moles of -SH group in (B) per mole of vinyl radical in (A) of from 1:1 to 10:1,
(C) from 1.4 to 5.5 parts by weight of an organic peroxide based on 100 parts by weight of the combined weight of (A) and (B), and
(D) from 0 to 100 parts by weight of a filler per 100 parts by weight of the combined weight of

(A) and (B).

2. A method of preparing an elastomer which comprises (I) mixing
(A) a vinyl containing polydiorganosiloxane as defined in claim 1.
(B) a mercaptoorganopolysiloxane as defined in claim 1.
(C) an organic peroxide as defined in claim 1.
(D) a filler as defined in claim 1, at a temperature below 50°C and
(II) curing the resulting mixture of (I) above 20°C.

3. A method as claimed in claim 2 substantially as herein described with reference to the Example.

4. An elastomer whenever prepared by a process as claimed in claim 2 or claim 3.

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