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(54) **Title**: SILICONE RUBBER COMPOSITION

(57) **Abstract**: A composition capable of forming a cured product having an excellent compression set property even after exposure to air over an extended period is provided. The composition contains (A) a polyorganopolysiloxane having at least two alkenyl groups to be bonded to silicon atoms in one molecule and a viscosity of 10 to 1,000,000 mPa·s at 25°C, (B) an organohydrogenpolysiloxane having at least two hydrogen atoms to be bonded to silicon atoms in one molecule, (C) silica having a BET specific surface area of 50 m^2/g or more, (D) a sulfur-containing inorganic filler including an inorganic filler mixture obtained by mixing a sulfur-containing compound with an inorganic filler, an inorganic filler reactant obtained by reacting a sulfur-containing compound with an inorganic filler, or the like, and (E) an addition reaction catalyst, and the composition has a viscosity of 50,000 to 5,000,000 mPa·S at 25°C and a shear rate of 0.9 s^{-1}.

DESCRIPTION

SILICONE RUBBER COMPOSITION

TECHNICAL FIELD

[0001]

The present invention relates to an addition-curable liquid silicone rubber composition capable of forming a cured product that is formed only by primary curing and has an excellent compression set property even after exposure to air over an extended period.

BACKGROUND ART

[0002]

Silicone rubber has excellent heat resistance, cold resistance, electrical insulation, and weatherability, and good environmental safety. For this reason, the silicone rubber is widely used for various applications including automotive parts such as a connector seal and a spark plug boot, electrical and electronic parts such as a roller for a copying machine and a packing for a microwave oven, architectural parts such as a sealant, a nipple for a baby bottle, and tools for diving.

In particular, liquid silicone rubber can be applied to automation by injection molding, mass production by molding for a short time, and molding unnecessary for post-processing of a molded product without formation of a burr. Therefore, in recent years, the demand of liquid silicone rubber has rapidly increased and in particular, the demand for application of automotive water-proof seal has increased. Further, a material in which the amount of low molecular weight cyclic siloxane in silicone rubber is decreased in advance and a secondary thermal curing process can be omitted has been increasingly required. However, when the secondary thermal curing process is omitted, there is a problem in which compression set as an important property of silicone rubber is not sufficient. This problem has become more serious. Therefore, silicone rubber having good compression set without the secondary thermal

curing process has been required.

[0003]

Regarding this matter, Patent Literature 1 describes a silicone rubber composition that has low compression set immediately after molding while excellent tear strength and shore A hardness are maintained by adding precipitated silica as a reinforcing filler and using a low compression set additive.

[0004]

Patent Literature 2 describes a liquid silicone rubber composition used for injection molding that has high strength and low compression set by adding precipitated silica as a reinforcing filler and a certain amount of siloxane having an alkenyl group in a state of raw rubber.

CITATION LIST

PATENT LITERATURE

[0005]

Patent Literature 1: Japanese Patent Application Laid-Open No. 2002-114909

Patent Literature 2: Japanese Patent Application Laid-Open No. 2009-221295

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0006]

In the inventions described in the documents (Patent Literatures 1 and 2), the strength and good compression set of silicone cured product are achieved, but the documents do not specifically describe whether such a good compression set property is obtained over an extended period. Further, the documents do not specifically describe whether such a good compression set property is obtained only by primary curing. Therefore, a problem in which compression set obtained only by primary curing is not sufficient cannot be solved.

[0007]

The present invention has been made in view of the circumstances, and an object of the present invention is to provide a composition capable of forming a cured product having an excellent compression set property even after exposure to air over an extended period. Another object of the present invention is to provide an addition-curable liquid silicone rubber composition capable of holding an excellent compression set property over an extended period without a secondary thermal curing process.

SOLUTION TO PROBLEM

[0008]

The present inventor has intensively studied, and as a result, has found that when a compound obtained by reacting a sulfur-containing compound with a filler or a filler surface-treated with a sulfur-containing compound is mixed in an addition-curable silicone rubber composition, the problem can be solved. The present invention has been completed on the basis of the knowledges.

[0009]

Specifically, a silicone rubber composition of the present invention contains (A) 100 parts by mass of polyorganopolysiloxane having at least two alkenyl groups to be bonded to silicon atoms in one molecule and a viscosity of 10 to 1,000,000 mPa·s at 25°C, (B) an organohydrogenpolysiloxane having at least two hydrogen atoms to be bonded to silicon atoms in one molecule in an amount corresponding to a ratio of the number of silicon atom-bonded hydrogen atoms to the number of the alkenyl groups in the component (A) of 0.5 to 10.0, (C) 5 to 70 parts by mass of silica having a specific surface area measured by a BET method of 50 m^2/g or more, (D) 0.001 to 5.0 parts by mass of a sulfur-containing inorganic filler including an inorganic filler mixture obtained by mixing a sulfur-containing compound with an inorganic filler, an inorganic filler reactant obtained by

reacting a sulfur-containing compound with an inorganic filler, or an inorganic filler surface-treated with a sulfur-containing compound, and (E) a catalytic amount of an addition reaction catalyst. The silicone rubber composition has a viscosity of 50,000 to 5,000,000 mPa·s at 25°C and a shear rate of 0.9 s^{-1}.

All measurements of viscosity were made with the apparatus Physica MCR301 of Anton Paar GmbH, Germany at a shear rate of 0.9s^{-1}.

[0010]

In the silicone rubber composition, the sulfur-containing compound used as the component (D) is preferably a thiocyanato group-containing compound, and more preferably a thiocyanato group-containing alkoxysilane compound.

[0011]

In the silicone rubber composition, the silica (C) is preferably wet silica.

ADVANTAGEOUS EFFECTS OF INVENTION

[0012]

According to the silicone rubber composition of the present invention, when a compound obtained by reacting a sulfur-containing compound with a filler or a filler surface-treated with a sulfur-containing compound is mixed, a cured product having an excellent compression set property even after exposure to air over an extended period can be obtained. Even when a secondary thermal curing process is not performed, such an excellent compression set property can be held over an extended period.

DESCRIPTION OF EMBODIMENTS

[0013]

Hereinafter, the silicone rubber composition according to the present invention will be described in detail.

[0014]

(Component (A))

The component (A) is a polyorganopolysiloxane having at least two alkenyl groups to be bonded to silicon atoms in one molecule and a viscosity of 10 to 1,000,000 mPa·s at 25°C. The component (A) is liquid at room temperature (23°C ± 15°C, hereinafter as the same). Herein, the number of the alkenyl groups to be bonded to silicon atoms in one molecule is preferably 2 to 50, and more preferably 2 to 20. The number of carbon atoms in each alkenyl group is preferably 2 to 8, more preferably 2 to 6, and further preferably 2. Therefore, it is more preferable that the alkenyl groups be a vinyl group.

[0015]

The component (A) usually has an average composition formula of the following formula (1):

$$R^1_aSiO_{(4-a)/2} \quad (1).$$

In the formula (1), R^1s are the same or different substituted or unsbustituted monovalent hydrocarbon groups having 1 to 10 carbon atoms, and a is 1.5 to 2.8.

The number of carbon atoms in R^1 is preferably 1 to 8. Further, a is preferably 1.8 to 2.5, and more preferably 1.95 to 2.05.

[0016]

Examples of the unsubstituted monovalent hydrocarbon group among the monovalent hydrocarbon groups represented by R^1 may include an alkyl group such as a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, a tert-butyl group, a pentyl group, a neopentyl group, a hexyl group, a cyclohexyl group, an octyl group, a nonyl group, and a decyl group, an aryl group such as a phenyl group, a tolyl group, a xylyl group, and a naphthyl group, an aralkyl group such as a benzyl group, a phenylethyl group, and a phenylpropyl group, and an alkenyl group such as a vinyl group, an allyl group, a propenyl group, an isopropenyl group, a butenyl group, a hexenyl group, a cyclohexenyl group, and an octenyl group.

Examples of the substituted monovalent hydrocarbon group may include a group in which a part or all of the hydrogen atoms of the above-described unsubstituted monovalent hydrocarbon group is substituted with a halogen atom such as a fluorine atom, a bromine atom, and a chloride atom, a cyano group, and the like. Specific examples thereof may include a chloromethyl group, a chloropropyl group, a bromoethyl group, a trifluoropropyl group, and a cyanoethyl group. It is preferable that 90% or more of the monovalent hydrocarbon group represented by R^1 be a methyl group, and it is more preferable that the monovalent hydrocarbon group represented by R^1 except for an alkenyl group be all a methyl group.

[0017]

The component (A) may be one kind or a mixture of two or more kinds. The content of alkenyl groups in the component (A) is usually 1.0×10^{-6} to 5.0×10^{-4} mol/g, and preferably 1.0×10^{-5} to 2.0×10^{-4} mol/g. When the content of alkenyl groups is less than the above-described range, the rubber hardness is too low, and the resulting composition may be gel. When the content of alkenyl groups is more than the range, the crosslink density is too high, and the resulting composition may be a rubber having high hardness. The alkenyl groups may be bonded to a silicon atom at the terminal, at the middle, or at the terminal and middle of the molecular chain. In order to impart an excellent mechanical property to a cured composition, it is preferable that the alkenyl groups be positioned at least at the terminal of the molecular chain.

[0018]

The component (A) basically has a linear structure in which both terminals of the molecular chain are capped with a triorganosiloxy group and the main chain includes a repeating unit of diorganosiloxane. The component (A) may have a partially branched structure or a cyclic structure. Herein, "partially" means 33% by mass or less of the component (A).

[0019]

The viscosity at 25°C of the component (A) is preferably

10 to 500,000 mPa·s, and more preferably 100 to 250,000 mPa·s. When the viscosity of the component (A) is 100 to 250,000 mPa·s, high fluidity is imparted to the silicone rubber composition before curing, and an excellent mechanical property is imparted to the silicone rubber composition after curing. Therefore, this range is particularly preferred.

[0020]

(Component (B))

The component (B) is an organohydrogenpolysiloxane having at least two hydrogen atoms to be bonded to silicon atoms in one molecule. The component (B) is a component for curing the composition of the present invention into a rubber elastic body or a gel by reacting the hydrogen atoms to be bonded to silicon atoms in the component (B) with the alkenyl groups in the component (A).

The component (B) is an organohydrogenpolysiloxane having at least 2, preferably 3 or more, more preferably 3 to 200, further preferably 3 to 100, or particularly preferably 4 to 50 hydrogen atoms (SiH groups) to be bonded to silicon atoms in one molecule. The component (B) is one kind of organohydrogenpolysiloxane or a mixture of two or more kinds thereof. The component (B) acts as a curing agent for cross-linking and curing the composition by hydrosilylation reaction of the SiH groups in the molecule with alkenyl groups bonded to silicon atoms in the component (B) and the component (A).

[0021]

The component (B) usually has an average composition formula of the following formula (2):

$$R^3_cH_dSiO_{(4-c-d)/2} \quad (2).$$

In the formula (2), R^3s are the same or different substituted or unsbustituted monovalent hydrocarbon groups having 1 to 10 carbon atoms, c is 0.7 to 2.1, d is 0.001 to 1.0, and (c + d) is a positive number satisfying 0.8 to 3.0.

It is preferable that R^3 in the formula (2) have 1 to 8 carbon atoms, c be 0.8 to 2.0, d be 0.001 to 1.0, and (c + d) be 1.0 to 2.5.

[0022]

Examples of R^3 may include the same groups as those exemplified in R^1 in the formula (1). It is preferable that R^3 be a monovalent hydrocarbon group having no aliphatic unsaturated group among the monovalent hydrocarbon groups exemplified in R^1.

[0023]

The component (B) may have any molecular structure such as linear, cyclic, branched, and three-dimensional network. In this case, the number (or polymerization degree) of silicon atoms in one molecule is usually 2 to 300, preferably 3 to 200, and more preferably 4 to 150. When the number of silicon atoms in one molecule falls within the above-described range, the viscosity of the silicone composition falls within a range suitable for injection molding. Therefore, this range is preferred. The hydrogen atoms to be bonded to silicon atoms may be positioned at the terminal, at the middle, or at the terminal and middle of the molecular chain.

[0024]

Examples of the component (B) may include 1,1,3,3-tetramethyldisiloxane, 1,3,5,7-tetramethylcyclotetrasiloxane, a methylhydrogensiloxane cyclic polymer, a methylhydrogensiloxane-dimethylsiloxane cyclic copolymer, tris(dimethylhydrogensiloxy)methylsilane, tris(dimethylhydrogensiloxy)phenylsilane, a methylhydrogenpolysiloxane having both molecular terminals capped with trimethylsiloxy groups, a dimethylsiloxane-methylhydrogensiloxane copolymer having both molecular terminals capped with trimethylsiloxy groups, a dimethylpolysiloxane having both molecular terminals capped with dimethylhydrogensiloxy groups, a dimethylsiloxane-methylhydrogensiloxane copolymer having both molecular terminals capped with dimethylhydrogensiloxy groups, a methylhydrogensiloxane-methylphenylsiloxane copolymer having both molecular terminals capped with trimethylsiloxy groups, a methylhydrogensiloxane-methylphenylsiloxane-dimethylsiloxane

copolymer having both molecular terminals capped with trimethylsiloxy groups, a copolymer composed of a $(CH_3)_2HSiO_{1/2}$ unit and a $SiO_{4/2}$ unit, and a copolymer composed of a $(CH_3)_2HSiO_{1/2}$ unit, a $SiO_{4/2}$ unit, and a $(C_6H_5)_3SiO_{1/2}$ unit.

Among these, it is preferable that the component (B) be a polymethylhydrogensiloxane containing a $(CH_3)HSiO_{2/2}$ unit, a polymethylhydrogensiloxane containing a $(CH_3)_2SiO_{2/2}$ unit, or a polymethylphenylhydrogensiloxane containing a $(CH_3)(C_6H_5)SiO_{2/2}$ unit.

[0025]

The amount of the component (B) to be mixed is usually 0.2 to 20 parts by mass, and preferably 0.5 to 10 parts by mass, relative to 100 parts by mass of the component (A).

In the present invention, the ratio of the number of silicon atom-bonded hydrogen atoms (SiH groups) in the component (B) to the number of alkenyl groups in the component (A) is 0.5 to 10.0, and particularly preferably 0.8 to 5.0. When this ratio is less than the above-described range, cross-linking is insufficient, and a sticky rubber may be obtained. When this ratio is more than the range, bubbling appears in a molded product, and the molded product is difficult to be separated from a mold. The physical properties, particularly heat resistance after curing may be largely changed.

[0026]

(Component (C))

The silica of the component (C) imparts sufficient strength to silicone rubber. As the silica of the component (C), for example, fumed silica (dry silica) or wet silica is used. In particular, wet silica is preferred since it has an excellent compression set property.

The silica of the component (C) has a specific surface area measured by a BET method of 50 m^2/g or more, preferably 100 to 500 m^2/g, and more preferably 150 to 300 m^2/g. When the specific surface area of the component (C) is less than 50 m^2/g, sufficient strength may not be achieved.

Although the silica of the component (C) may be used as

it is, it is preferable to use silica that is treated in advance with a hydrophobizing surface treatment agent, or silica that is surface-treated by addition of surface treatment agent during mixing with the component (A). As the surface treatment agent, a known surface treatment agent such as alkylalkoxysilane, alkylchlorosilane, alkylsilazane, a silane-coupling agent, a titanate-based treatment agent, and a fatty acid ester is used. One kind of the surface treatment agent may be used alone or two or more kinds thereof may be used simultaneously or separately.

[0027]

The amount of the component (C) to be mixed is 5 to 70 parts by mass, and preferably 15 to 50 parts by mass, relative to 100 parts by mass of the component (A). When the amount is less than 5 parts by mass, sufficient rubber strength may not be achieved. When the amount is more than 70 parts by mass, compression set may be increased.

[0028]

It is preferable that the silica of the component (C) be wet silica since the wet silica has an excellent compression set property.

[0029]

(Component (D))

The component (D) is a sulfur-containing inorganic filler including an inorganic filler mixture obtained by mixing a sulfur-containing compound with an inorganic filler, an inorganic filler reactant obtained by reacting a sulfur-containing compound with an inorganic filler, or an inorganic filler surface-treated with a sulfur-containing compound.

The reason why the component (D) contains a sulfur-containing compound or is a reactant of sulfur-containing compound will be described below.

In order to impart an excellent compression set property even after exposure to air over an extended period to cured silicone rubber, it is necessary that an additional cross-linking reaction caused by an addition reaction catalyst with

heat history after curing be suppressed. Therefore, when the composition contains a component having an action that does not affect a cross-linking reaction during primary curing and suppresses a cross-linking reaction in secondary curing or in heat history after the curing, the object is achieved. The sulfur-containing compound has this action.

The sulfur-containing compound used for preparation of the component (D) is not limited to particular kinds, but it may be a generally used compound. Examples thereof may include an organic sulfur compound such as thiol (mercaptan, alkylthiol, arylthiol, mercaptoheterocycle, mercaptoimidazole, and mercaptobenzimidazole), ketene acetal, thioacetal, sulfane (thioether), disulfane (dithioether), polysulfane, thioamide, thiourea, thiuram (thiuram monosulfide, thiuram disulfide, thiuram polysufide, bisthiocarbamoyl monosulfane, bisthiocarbamoyl disulfane, and bisthiocarbamoyl polysufane), a thiuronium salt, thiocarbamate, dithiocarbamate, and Zn salt, Fe salt, Ni salt, Co salt, and Cu salt thereof, thiocyanate, and isothiocyanate; a thiocarbonyl compound such as thioaldehyde, thioketone, thiolactone, and thiocarboxylic acid; and a thiaheterocyclic compound such as thiophene, 1,2-dithiol, 1,3-dithiol, 1,2-dithiol-thione, 1,3-dithiol-thione, thiazole, mercaptothiazole, mercaptothiadizole, benzo-dithiol, benzo-dithiol-thione, benzothiazole, mercaptobenzothiazole, phenothiazole, and thanthrene. Among these, a thiol group-containing compound (mercapto group-containing compound) and a thiocyanato group-containing compound are preferred, and a thiocyanato group-containing alkoxysilane compound is more preferred since availability is good and the compression set property is improved.

[0030]

It is preferable that the component (D) have an action that does not suppress an addition reaction during primary curing and suppresses the reaction in subsequent heat history. It is not preferable that the component (D) be present in such a state that the component is likely to be released in the

silicone rubber composition. In order to activate a releasing or suppression effect only at a point when the subsequent heat history is imparted, it is considered that the component (D) is mixed or reacted with the inorganic filler, or the inorganic filler is present in the silicone rubber composition in a state of inorganic filler surface-treated with the component (D). Thus, a desired action is achieved.

Therefore, it is necessary that the sulfur-containing compound be chemically bonded to the surface of the inorganic filler or bonded to the surface of the inorganic filler by a chemical bond like a hydrogen bond. The surface of the inorganic filler is often covered with a polar chemical group, particularly a hydroxyl group. In order to produce such a bond, it is necessary that the sulfur-containing compound has a chemical structure having a function of the bond.

The chemical bond is not limited, and preferably has an alkoxysilyl group. It is the most preferable that the sulfur-containing compound used as the component (D) be a sulfur-containing alkoxysilane.

[0031]

The structure and molecular weight of sulfur-containing alkoxy compound that is preferably used as the component (D) and the kind and induction amount of the alkoxy group are not limited. Examples thereof may include a sulfur-containing alkoxysilane including mercaptoalkyl-alkyl-alkoxysilane having an average composition formula of the following formula (4), bis(trialkoxysilyl-alkyl)mono-, di-, and polysulfane having an average composition formula of the following formula (5), and thiocyanatoalkyl trialkoxysilane having an average composition formula of the following formula (6):

$(R^5O)_{3-m}R^6{}_nSi-R^7-SH$ (4),

$[(R^8O)_3Si-R^9-]_2-S_n$ (5), and

$(R^{10}O)_3Si-R^{11}-SCN$ (6).

[0032]

R^5 is a substituted or unsbustituted aliphatic saturated monovalent hydrocarbon group having 1 to 10 carbon atoms, and

preferably 1 to 6 carbon atoms. As R^5, for example, an alkyl group is used. A methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, or a cycloalkyl group is preferably used. A cyclopentyl group, a cyclohexyl group, or a cycloheptyl group is more preferably used.

R^6 is a substituted or unsbustituted aliphatic saturated monovalent hydrocarbon group having 1 to 10 carbon atoms, and preferably 1 to 6 carbon atoms. As R^6, for example, an alkyl group is used. A methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, a cycloalkyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, an aryl group, an alkaryl group, a phenyl group, a tolyl group, a xylyl group, a mesityl group, or a benzyl group is preferably used.

As R^7, for example, a substituted or unsbustituted aliphatic saturated divalent hydrocarbon group having 1 to 10 carbon atoms, and preferably 1 to 6 carbon atoms is used. For example, R^7 is an alkylene group, preferably a methylene group, an ethylene group, a propylene group, a butylene group, a hexylene group, or a phenylene group, and more preferably a propylene group.

R^8 and R^{10} are the same as the groups of R^5. R^9 and R^{11} are the same as the groups of R^7.

m is 0 to 3, and preferably 0.5 to 2.5. n is 1 to 10, and preferably 2 or 4.

[0033]

The component (D) may be each of the sulfur-containing alkoxysilanes, a mixture of a mixture of the sulfur-containing alkoxysilanes with the inorganic filler, or a compound in which an inorganic filler is surface-treated with each of the sulfur-containing alkoxysilanes. It is more preferable that the sulfur-containing alkoxysilane be thiocyanatoalkyl trialkoxysilane.

[0034]

Examples of the inorganic filler that is mixed or reacted with the sulfur-containing compound or surface-treated with

the sulfur-containing alkoxysilane may include silicon-containing fillers including silicon dioxide such as dry silica and wet silica, quartz powder, diatomaceous earth, calcium silicate, zirconium silicate, and zeolite, metal oxide such as iron oxide, zinc oxide, titanium dioxide, and aluminum oxide, and metal carbonate such as calcium carbonate, magnesium carbonate, and zinc carbonate.
As the inorganic filler, silicon dioxide is preferably used, and wet silica is more preferably used.

[0035]

The amount of the component (D) to be mixed is 0.001 to 5.0 parts by mass, and preferably 0.01 to 2.0 parts by mass, relative to 100 parts by mass of the component (A).

A higher effect of decreasing the compression set property only by primary curing can be obtained in the case of the inorganic filler surface-treated with the sulfur-containing alkoxysilane than in the case of the mixture or reactant of the sulfur-containing compound with the inorganic filler. The compression set at high temperature for an extended period is considered as follows. The sulfur-containing compound that is reacted with the surface of the filler and bonded to the surface is gradually released from the surface of the filler and suppresses a cross-linking reaction due to the heat history of the addition-curable silicone rubber, and as a result, the effect of decreasing the compression set can be held over an expended period of time.

[0036]

(Component (E))

The addition reaction catalyst of the component (E) is a hydrosilylation reaction catalyst. Examples of the hydrosilylation reaction catalyst may include a platinum catalyst such as platinum black, platinic chloride, chloroplatinic acid, a reactant of chloroplatinic acid with monohydric alcohol, a complex composed of chloroplatinic acid and olefin, and platinum bisacetoacetate, a palladium catalyst, and a rhodium catalyst. Among these hydrosilylation reaction

catalysts, platinum and a platinum-based compound are preferred.

The amount of the addition reaction catalyst to be mixed can be a so-called catalytic amount. The amount is usually 0.1 to 1,000 ppm, and particularly about 1 to about 500 ppm in terms of mass of platinum group metal relative to the total amount of the components (A) and (B).

[0037]

As another optional component, if necessary, a filler such as quartz powder, diatomaceous earth, calcium carbonate, and aluminum oxide, a conductive filler such as carbon black, conductive zinc oxide, and metal powder, a hydrosilylation reaction controlling agent such as a nitrogen-containing compound, an acetylene compound, a phosphorus compound, a nitrile compound, carboxylate, a tin compound, a mercury compound, and a sulfur compound, a heat-resistant agent such as iron oxide, titanium oxide, and cerium oxide, an internal mold release agent such as dimethyl silicone oil, alkoxysilane that serves as an adhesiveness-imparting agent, thixotropic property-imparting agent, or an adhesion improver, a phenyl-modified silicone oil for imparting self-lubricating property to a cured silicone rubber, or the like, may be added.

[0038]

The addition curable silicone rubber composition of the present invention can be obtained by uniformly mixing the components (A) to (E) and the optional component(s) at normal temperature. Further, the composition can be obtained preferably by thermally treating the components (A) and (C) at 100 to 200°C for 1 to 15 hours by a planetary mixer, a kneader, or the like, followed by mixing with the components (B), (D), and (E), and the optional component(s).

[0039]

As a method for molding and curing the silicone rubber composition of the present invention, a conventional method can be adopted. As the molding method, a liquid injection molding method is suitably adopted. As a curing condition

(primary curing), a heating condition including at 100 to 200°C for 5 seconds to 30 minutes, and preferably at 120 to 200°C for about 10 seconds to about 15 minutes may be adopted. Further, a good compression set property can be obtained only by primary curing, but if necessary, secondary curing (post curing) may be performed. In this case, post curing can be performed under a condition including at 150 to 220°C, and particularly at 180 to 200°C, for about 0.5 to about 12 hours, and particularly for about 1 to about 6 hours.

[0040]

The silicone rubber composition of the present invention has a viscosity of 50,000 to 5,000,000 mPa·s at 25°C and a shear rate of 0.9 s^{-1}.

EXAMPLES

[0041]

Hereinafter, the present invention will be specifically described with reference to Examples and Comparative Examples, but the present invention is not limited to the following Examples. In Examples, part(s) represents part(s) by mass.

[0042]

<Hardness Test Method>

A test was carried out in accordance with JIS K 6249 (Testing methods for uncured and cured silicone rubber).

[0043]

<Compressive Set Measurement Method>

A test was carried out using a small specimen (diameter: 13.0 mm, thickness: 6.3 mm) at a compression of 25% in accordance with JIS K 6249 (Testing methods for uncured and cured silicone rubber). The compression set was measured at 150°C and 180°C.

[0044]

<Example 1>

100 parts of polydimethylsiloxane having both terminals each capped with a dimethylvinylsilyl group and a viscosity of 20,000 mPa·s at 25°C (component (A)), 36 parts of wet silica

having a specific surface area of 200 m^2/g (component (C)), 10 parts of hexamethyldisilazane, and 3 parts of ion-exchanged water were mixed with stirring at normal temperature for 1 hour. The mixture was heated to 150°C, and further mixed under heating for 2 hours to obtain a base compound.

The base compound was cooled to normal temperature. To 100 parts of the base compound, 2.5 parts of polymethylhydrogensiloxane having a $(CH_3)HSiO_{2/2}$ unit and a $(CH_3)_2SiO_{2/2}$ unit at a ratio of 33/67 and a viscosity of 150 mPa·s at 25°C (component (B)), 0.2 parts of silica filler surface-treated with thiocyanatopropyltriethoxysilane (component (D)), 0.2 parts of platinum catalyst (Pt concentration: 1% by mass) (component (E)), and 0.1 parts of acetylene alcohol as an additive for controlling a curing rate were each added, and the mixture was uniformly mixed, to prepare a silicone rubber composition according to the present invention.

The silicone rubber composition was press-cured at 170°C for 5 minutes to obtain a silicone rubber cured product.

The hardness and compression set of the cured product were measured in accordance with JIS K 6249. The results are shown in Table 1.

[0045]

<Example 2>

100 parts of polydimethylsiloxane having both terminals each capped with a dimethylvinylsilyl group and a viscosity of 20,000 mPa·s at 25°C (component (A)), 36 parts of fumed silica having a specific surface area of 200 m^2/g (component (C)), 10 parts of hexamethyldisilazane, and 3 parts of ion-exchanged water were mixed with stirring at normal temperature for 1 hour. The mixture was heated to 150°C, and further mixed under heating for 2 hours to obtain a base compound.

The base compound was cooled to normal temperature. To 100 parts of the base compound, 2.5 parts of polymethylhydrogensiloxane having a $(CH_3)HSiO_{2/2}$ unit and a $(CH_3)_2SiO_{2/2}$ unit at a ratio of 33/67 and a viscosity of 150

mPa·s at 25°C (component (B)), 0.2 parts of silica filler surface-treated with thiocyanatopropyltriethoxysilane (component (D)), 0.2 parts of platinum catalyst (Pt concentration: 1% by mass) (component (E)), and 0.1 parts of acetylene alcohol as an additive for controlling a curing rate were each added, and the mixture was uniformly mixed, to prepare a silicone rubber composition according to the present invention.

The silicone rubber composition was press-cured at 170°C for 5 minutes to obtain a silicone rubber cured product.

The hardness and compression set of the cured product were measured in accordance with JIS K 6249. The results are shown in Table 1.

[0046]

<Comparative Example 1>

A silicone rubber composition was prepared in the same manner as in Example 1 except that the silica filler surface-treated with thiocyanatopropyltriethoxysilane (component (D)) was not added. The silicone rubber composition was press-cured at 170°C for 5 minutes to obtain a silicone rubber cured product. The hardness and compression set of the cured product were measured in accordance with JIS K 6249. The results are shown in Table 1.

[0047]

<Comparative Example 2>

A silicone rubber composition was prepared in the same manner as in Example 1 except that the silica filler surface-treated with thiocyanatopropyltriethoxysilane (component (D)) was not added in Example 2. The silicone rubber composition was press-cured at 170°C for 5 minutes to obtain a silicone rubber cured product. The hardness and compression set of the cured product were measured in accordance with JIS K 6249. The results are shown in Table 1.

[0048]

[Table 1]

		Examle 1	Example 2	Comparative Examle 1	Comparative Example 2
HARDNESS (DUROMETER A)		53	53	52	52
COMPRESSION SET (%) 150°C	70 hours	13	11	23	43
	250 hours	17	17	28	57
	500 hours	20	23	31	59
	750 hours	22	33	34	61
	1000 hours	24	49	36	62
	1500 hours	27	-	39	-
COMPRESSION SET (%) 180°C	24 hours	12	9	30	48
	70 hours	17	16	38	60
	250 hours	23	42	41	63

Industrial Applicability

[0049]

The addition-curable liquid silicone rubber composition of the present invention forms a cured product having the excellent compression set property even after exposure to air over an extended period. Even when a secondary thermal curing process is not performed, the excellent compression set property can be held over an extended period. The composition is a material suitable for seal parts requiring heat resistance over an extended period, including, for example, automotive seal parts such as an automotive connector water-proof seal part, and seal parts for electrical and electronic apparatus.

CLAIMS

1. A silicone rubber composition comprising:

(A) 100 parts by mass of polyorganopolysiloxane having at least two alkenyl groups to be bonded to silicon atoms in one molecule and a viscosity of 10 to 1,000,000 mPa·s at 25°C;

(B) an organohydrogenpolysiloxane having at least two hydrogen atoms to be bonded to silicon atoms in one molecule in an amount corresponding to a ratio of a number of silicon atom-bonded hydrogen atoms to a number of the alkenyl groups in the component (A) of 0.5 to 10.0;

(C) 5 to 70 parts by mass of silica having a specific surface area measured by a BET method of 50 m^2/g or more;

(D) 0.001 to 5.0 parts by mass of a sulfur-containing inorganic filler including any one selected from the group consisting of an inorganic filler mixture obtained by mixing a sulfur-containing compound with an inorganic filler, an inorganic filler reactant obtained by reacting a sulfur-containing compound with an inorganic filler, and an inorganic filler surface-treated with a sulfur-containing compound; and

(E) a catalytic amount of an addition reaction catalyst, wherein

the silicone rubber composition has a viscosity of 50,000 to 5,000,000 mPa·s at 25°C and a shear rate of 0.9 s^{-1}.

2. The silicone rubber composition according to claim 1, wherein the sulfur-containing compound used as the component (D) is a thiocyanato group-containing compound.

3. The silicone rubber composition according to claim 1, wherein the sulfur-containing compound used as the component (D) is a thiocyanato group-containing alkoxysilane compound.

4. The silicone rubber composition according to any one of claims 1 to 3, wherein the silica (C) is wet silica.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/057325

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K9/06 C08G77/12 C08G77/20 C08L83/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08K C08L C08G C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 977 249 A (KOVAR INGOMAR [DE] ET AL) 2 November 1999 (1999-11-02) column 1, line 60 - column 2, line 19 column 4, lines 4-21 column 5, lines 7-48 column 6, lines 6-26 examples 1,2 claims 1,9,10,11 -----	1-4
X	US 5 998 548 A (BRENNENSTUHL WERNER [DE] ET AL) 7 December 1999 (1999-12-07) column 2, lines 11-41 column 3, line 39 - column 4, line 7 column 5, lines 18-31 column 6, lines 4-19 ----- -/--	1-4

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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

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

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 569 688 A (MEGURIYA NORIYUKI [JP] ET AL) 29 October 1996 (1996-10-29) column 2, lines 35-48 column 3, lines 30-42 column 4, lines 26-29 column 5, lines 3-29 examples 1-6 -----	1-4

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/057325

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