

TITLE OF THE INVENTION

Organopolysiloxane Composition, Surface Treating Agent,
and Silicone Rubber Article

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BACKGROUND OF THE INVENTION

10 Field of the Invention

This invention relates to an organopolysiloxane composition capable of forming a matte, abrasion resistant coating on silicone rubber, a surface treating agent comprising the same, and a silicon rubber article having
15 such a coating on silicone rubber.

Prior Art

In general, silicone rubber materials have a glossy surface and lack a high-quality appearance. They must be
20 surface treated for matting before they can be used in applications where design features are of importance.

Most surface treating agents used for such a purpose are curable silicone compositions because they firmly adhere to rubber substrates. To give a matte finish to cured
25 coatings of silicone compositions, large amounts of inorganic powder such as silica, diatomaceous earth, calcium carbonate and alumina must be added. The inorganic powder when added in large amounts, however, adversely affects the physical properties of cured coatings and adhesion thereof
30 to rubber substrates. The cured coatings are thus substantially reduced in abrasion resistance. Also, when the curable silicone compositions have low viscosity or contain solvents, the inorganic powder tends to settle and coalesce. It is difficult to disperse the once coalesced
35 powder again.

Other than the inorganic powder, polymethylsilsesquioxane powder is also known as a matte-finishing additive as

disclosed in Japanese Patent Application Kokai (JP-A) No. 161468/1992 and Japanese Patent Publication (JP-B) No. 22189/1992. Silicone compositions having polymethylsilsesquioxane powder added thereto are improved in powder dispersibility, but expensive, and form cured coatings whose abrasion resistance is unacceptable in applications where coatings are subject to repetitive friction. Another drawback is that polymethylsilsesquioxane will sediment when a solvent is used.

SUMMARY OF THE INVENTION

An object of the invention is to provide an organopolysiloxane composition capable of forming on a silicone rubber surface a cured coating which imparts a matte finish, an expedient design appearance and abrasion resistance.

Another object of the invention is to provide a surface treating agent which is effectively applicable to silicone rubber. A further object of the invention is to provide a silicone rubber article having a coating of the organopolysiloxane composition on silicone rubber.

We have found that by adding a polycarbonate resin powder having a mean particle size of up to 50 μm to an addition reaction curing type organopolysiloxane composition comprising an organopolysiloxane having at least two alkenyl groups each attached to a silicon atom in a molecule of the following average compositional formula:



wherein R^1 is a substituted or unsubstituted monovalent hydrocarbon group free of an aliphatic unsaturated bond, R^2 is an alkenyl group, letters a and b are positive numbers satisfying $1.6 \leq a \leq 2.0$, $0.001 \leq b \leq 0.5$, and $1.9 \leq a + b \leq 2.1$, an organohydrogenpolysiloxane having at least two hydrogen atoms each attached to a silicon atom in a molecule of the following average compositional formula:



wherein R^3 is a substituted or unsubstituted monovalent hydrocarbon group free of an aliphatic unsaturated bond, letters c and d are positive numbers satisfying $0.8 \leq c \leq 2$, $0.01 \leq d \leq 1$, and $0.85 \leq c + d \leq 2.5$, and a platinum catalyst, there is obtained an organopolysiloxane composition capable of forming on a silicone rubber surface an abrasion resistant cured coating which gives a matte finish and an expedient design appearance. By coating a surface of silicone rubber with the organopolysiloxane composition and curing the coating, there is obtained a silicone rubber article having a high-quality appearance. The organopolysiloxane composition is thus useful as a surface treating agent in applications where frictional forces are repetitively applied over a long term, for example, key tops and rubber contacts of business machines.

Accordingly, the present invention provides an organopolysiloxane composition comprising

(A) an organopolysiloxane of formula (1) having at least two alkenyl groups each attached to a silicon atom in a molecule,

(B) an organohydrogenpolysiloxane of formula (2) having at least two hydrogen atoms each attached to a silicon atom in a molecule, in an amount to provide 0.4 to 10 hydrogen atoms attached to a silicon atom in the organohydrogenpolysiloxane per alkenyl group in organopolysiloxane (A),

(C) 2 to 50 parts by weight per 100 parts by weight of organopolysiloxane (A) and organohydrogenpolysiloxane (B) combined of a polycarbonate resin powder having a mean particle size of up to 50 μm , and

(D) a catalytic amount of a platinum catalyst.

DETAILED DESCRIPTION OF THE INVENTION

Component (A) of the organopolysiloxane composition according to the invention is an organopolysiloxane having at least two alkenyl groups each attached to a silicon atom

in a molecule, which is of the following average compositional formula:



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wherein R^1 is a substituted or unsubstituted monovalent hydrocarbon group free of an aliphatic unsaturated bond; R^2 is an alkenyl group, letters a and b are positive numbers satisfying $1.6 \leq a \leq 2.0$, $0.001 \leq b \leq 0.5$, and $1.9 \leq a + b \leq 2.1$, preferably $1.8 \leq a \leq 2.0$, $0.002 \leq b \leq 0.1$, and $1.95 \leq a + b \leq 2.04$.

In formula (1), R^1 groups may be the same or different and selected from substituted or unsubstituted monovalent hydrocarbon groups free of an aliphatic unsaturated bond, preferably having 1 to 12 carbon atoms, especially 1 to 8 carbon atoms, for example, alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, neopentyl, hexyl, octyl, decyl, and dodecyl; cycloalkyl groups such as cyclopentyl, cyclohexyl, and cycloheptyl; aryl groups such as phenyl, tolyl, xylyl, and naphthyl; aralkyl groups such as benzyl, phenylethyl, and phenylpropyl; and substituted ones of these groups wherein all or some of the hydrogen atoms are replaced by halogen atoms such as fluorine, bromine and chlorine or cyano groups, such as chloromethyl, chloropropyl, bromoethyl, trifluoropropyl, and cyanoethyl. It is preferred from the standpoints of chemical stability and ease of synthesis that all R^1 groups are methyl although some of the methyl groups may be replaced by phenyl or trifluoropropyl groups if necessary to provide desired properties. R^2 groups may be the same or different and selected from alkenyl groups preferably having 2 to 8 carbon atoms, especially 2 to 4 carbon atoms, for example, vinyl, allyl, propenyl, isopropenyl, butenyl and pentenyl groups. Among these, vinyl and allyl groups are preferred, and vinyl is most

preferred from the standpoints of chemical stability and ease of synthesis.

It is noted that at least two alkenyl groups contained in a molecule may be attached to silicon atoms at molecular chain ends and/or midway the molecular chain. It is preferred from the standpoints of a curing rate and cured properties that alkenyl groups be attached to silicon atoms at both ends of the molecular chain.

The organopolysiloxane preferably has a viscosity of at least 100 centistokes at 25°C, more preferably 400 to 500,000 centistokes at 25°C. With a viscosity of less than 100 centistokes, a cured coating would be brittle and fail to follow deformation of the underlying substrate. With a viscosity of more than 500,000 centistokes, an uncured composition would have a higher viscosity and be inconvenient to handle unless a large amount of solvent is used. Two or more organopolysiloxanes may be used in combination insofar as their viscosity is within the above-defined range.

Typically the organopolysiloxane has an average degree of polymerization, representative of the number of silicon atoms in a molecule, of about 150 to about 2,000.

With respect to molecular structure, the organopolysiloxane may have a linear, branched, cyclic or three-dimensional network structure. Most often, it is a linear diorganopolysiloxane having a backbone portion consisting essentially of recurring diorganosiloxane units and end-blocked with a triorganosiloxy unit.

Component (B) is an organohydrogenpolysiloxane having at least two, preferably at least three hydrogen atoms each attached to a silicon atom in a molecule. It is of the following average compositional formula:



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wherein R^3 is a substituted or unsubstituted monovalent hydrocarbon group free of an aliphatic unsaturated bond,

letters c and d are positive numbers satisfying $0.8 \leq c \leq 2$, $0.01 \leq d \leq 1$, and $0.85 \leq c + d \leq 2.5$, preferably $1 \leq c \leq 1.95$, $0.1 \leq d < 1$, and $1.3 \leq c + d \leq 2.3$.

The organohydrogenpolysiloxane serves as a crosslinking agent. In the presence of a platinum catalyst as component (D), hydrogen atoms attached to silicon atoms in the organohydrogenpolysiloxane as component (B) gives rise to addition reaction with alkenyl groups attached to silicon atoms in the organopolysiloxane as component (A), producing a cured coating of three-dimensional network structure.

In the organohydrogenpolysiloxane of formula (2), the substituents other than the hydrogen atoms attached to silicon atoms, that is, R^3 groups are exemplified by such groups having 1 to 12 carbon atoms, especially 1 to 8 carbon atoms, as mentioned for R^1 . The R^3 groups may be the same or different. It is preferred from the standpoints of chemical stability and ease of synthesis that all R^3 groups are methyl although some of the methyl groups may be replaced by phenyl or trifluoropropyl groups if necessary to provide desired properties.

The organohydrogenpolysiloxane has at least two, preferably at least three hydrogen atoms each attached to a silicon atom, that is, at least two, preferably at least three SiH groups in a molecule. The hydrogen atom may be attached to a silicon atom at the end of and/or midway a molecular chain.

The molecular structure of the organohydrogenpolysiloxane is not critical. It may have a linear structure consisting essentially of recurring divalent siloxane units ($=SiO_{2/2}$) and blocked with a monovalent siloxy unit ($=SiO_{1/2}$), a cyclic structure consisting of divalent siloxane units, a branched structure or a three-dimensional network structure (resinous one). The organohydrogenpolysiloxane may be a homopolymer consisting of at least one kind of siloxane units having a silicon-hydrogen bond (i.e., monoorganohydrogensiloxane units: $R^3(H)SiO_{2/2}$, diorganohydrogensiloxy

units: $(R^3)_2(H)SiO_{1/2}$, or hydrosiloxane units; $HSiO_{3/2}$) or a copolymer of such units with at least one of triorganosilone $((R^3)_3SiO_{1/2})$, diorganosiloxane $((R^3)_2SiO_{2/2})$, monoorganosiloxane $(R^3SiO_{3/2})$ and SiO_2 units.

5 The organohydrogenpolysiloxane may have any desired degree of polymerization. It is, however, preferred from the standpoints of compatibility with component (A) and ease of synthesis that the number of silicon atoms in a molecule be up to about 300, especially about 4 to about 150. For
10 similar reasons, the organohydrogenpolysiloxane preferably has a viscosity of up to about 500 centistokes at 25°C, especially about 0.5 to about 300 centistokes at 25°C.

 The organohydrogenpolysiloxane (B) is blended in such amounts that there are available 0.4 to 10 hydrogen atoms,
15 preferably 1 to 5 hydrogen atoms attached to a silicon atom in the organohydrogenpolysiloxane per alkenyl group attached to a silicon atom in the organopolysiloxane (A). If the number of silicon atom-attached hydrogen atoms is less than 0.4, a coating fails to provide a necessary strength because
20 of short curing. If the number of silicon atom-attached hydrogen atoms is more than 10, a coating will foam during curing and its physical properties will change with time.

 Component (C) is a polycarbonate resin powder having a mean particle size of up to 50 μm which is effective for
25 depriving a cured coating resulting from the inventive composition of gloss, reducing the tackiness of the coating, and improving the abrasion resistance of the coating.

 The polycarbonate resin powder should have a mean particle size of up to 50 μm , especially 0.3 to 40 μm . The
30 mean particle size can be measured as a weight average mean particle size by a well-known technique in the art such as a laser beam diffraction analysis and the like. A mean particle size in excess of 50 μm adversely affects the mechanical strength and abrasion resistance of a cured
35 coating. Powder with a mean particle size of less than 0.3 μm is not only difficult to prepare, but also difficult to uniformly disperse, failing to achieve its additive effect.

Preferably the polycarbonate resin powder having such a mean particle size consists of spherical or flake particles although polyhedral, profile and flat particles are also acceptable.

5 The polycarbonate resin powder is blended in an amount of 2 to 50 parts by weight, preferably 5 to 30 parts by weight per 100 parts by weight of organopolysiloxane (A) and organohydrogenpolysiloxane (B) combined. The desired advantages are not obtained with less than 2 parts of the
10 polycarbonate whereas more than 50 parts of the polycarbonate adversely affects the mechanical strength and abrasion resistance of a cured coating.

 Component (D) is a platinum catalyst which catalyzes addition reaction between organopolysiloxane (A) and organo-
15 hydrogenpolysiloxane (B). Any of well-known platinum catalysts may be used. Examples include platinum black, chloroplatinic acid, alcohol-modified chloroplatinic acid, and complexes of platinum with olefins, aldehydes, vinylsiloxanes and acetylene alcohols. The platinum
20 catalyst is used in a catalytic amount which may be suitably adjusted in accordance with a desired curing rate. Often, the platinum catalyst is used in such an amount that there is 0.1 to 1,000 parts, especially 1 to 300 parts by weight of metallic platinum per million parts by weight of
25 organopolysiloxane (A). Less than 0.1 ppm of platinum would be ineffective to catalyze, leading to short curing. More than 1,000 ppm of platinum is not economically recommended.

 The organopolysiloxane composition of the invention may be obtained by mixing predetermined amounts of the above-
30 mentioned components (A) to (D). If necessary, fillers, pigments, co-adhesive agents, reaction control agents or the like may be additionally blended. For improving slippage, nonfunctional dimethylpolysiloxanes, especially high viscosity dimethylpolysiloxanes may be added. Examples of
35 the filler include reinforcing fillers such as fumed silica and precipitated silica which may or may not have been treated to be hydrophobic, silicone resins, and organic resins, and extending fillers such as silica aerogel, ground

quartz and diatomaceous earth. These fillers may be used alone or in admixture of two or more. The silicone resin useful as the reinforcing filler is exemplified by a silicone resin consisting essentially of $R_3SiO_{1/2}$ units and
5 SiO_2 units and/or $RSiO_{3/2}$ units wherein R is selected from vinyl and monovalent hydrocarbon groups free of an aliphatic unsaturated bond as previously defined for R^1 wherein the molar ratio of $R_3SiO_{1/2}$ unit to SiO_2 unit is from 0.4/1 to 1.2/1, especially from 0.5/1 to 1/1. If desired, such a
10 silicone resin is blended in an amount of 0 to 100 parts by weight, especially 10 to 50 parts by weight per 100 parts by weight of organopolysiloxane (A).

Exemplary pigments include inorganic pigments such as carbon black, iron oxide, titanium oxide and zinc oxide.
15 The co-adhesive agents include tetraalkoxysilanes such as tetramethoxysilane and tetraethoxysilane; trialkoxysilanes such as trimethoxysilane, triethoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane, methyltrimethoxysilane, and methyltriethoxysilane; partial hydrolysates of these
20 silanes; and epoxy functional group-containing alkoxysilanes such as α -silyl esters, γ -glycidoxypropyltrimethoxysilane, γ -glycidoxypropyltriethoxysilane, and β -(3,4-epoxycyclohexyl)-ethyltrimethoxysilane. The reaction control agents include vinylsiloxane, acetylene alcohols, ethynyl group-containing
25 silanes or siloxanes, and triallyl isocyanurate. Where the vinyl group-containing silicone resin and/or vinylsiloxane is blended as the additive, there should be available 0.4 to 10 hydrogen atoms directly attached to a silicon atom per unsaturated bond of alkenyl group attached to a silicon atom
30 in the entire composition.

UV absorbers may also be added to the composition of the invention. For example, carbon black and benzotriazole may be blended as the UV absorber. The amount of these optional components added may be conventional insofar as the
35 object of the invention is not impaired.

The composition of the invention is readily prepared by uniformly mixing the above-mentioned components. Since reaction between components (A) and (B) quickly proceeds in the presence of component (D), the composition should preferably be stored as a two-part package before use. For example, one part contains a portion of component (A) and components (C) and (D) whereas the other part contains the remainder of component (A) and component (B). On use, predetermined amounts of these two parts are mixed by a suitable technique. Where acetylene alcohols, ethynyl group-containing silanes or siloxanes are used as the reaction control agents, the composition can be stored as a one-part package.

The composition of the invention may be used for the treatment of various silicone rubber substrates by the method described below. The organopolysiloxane composition of the invention as such or after diluted with an organic solvent into a solution can be applied to a surface of silicone rubber substrate by known techniques such as dipping, spraying, brush coating, knife coating, roll coating, and screen printing. The organic solvents used herein include n-hexane, n-heptane, cyclohexane, industrial gasoline, petroleum naphtha, isoparaffin, benzene, toluene, xylene, isopropyl alcohol, butyl alcohol, cyclohexanone, methyl ethyl ketone, low molecular weight siloxanes, cyclic siloxanes, and mixtures thereof. Among these solvents, industrial gasoline, petroleum naphtha, isoparaffin, toluene, xylene, and low molecular weight siloxanes are preferably used alone or in admixture with one or two of isopropyl alcohol, methyl ethyl ketone and cyclohexanone. The amount of the organic solvent used may be properly selected in accordance with the viscosity of the composition. Where the composition is diluted with the organic solvent, the coating is dried to remove the solvent and then heat cured at a temperature of 60 to 200°C for about 30 seconds to about 120 minutes, obtaining a coated silicone rubber article.

The organopolysiloxane composition of the invention, when it is applied to a surface of various silicone rubber substrates, is effective for rendering the silicone rubber surface matte and imparting design features thereto. In addition, the inventive composition forms a cured coating having improved abrasion resistance as compared with treatment with prior art organopolysiloxane compositions. Therefore, the inventive composition is an adequate surface treating agent capable of forming a coating which is fully durable against abrasion. The organopolysiloxane composition is thus useful as a surface treating agent in applications where frictional forces are repetitively applied over a long term, for example, key tops and rubber contacts of office equipment.

EXAMPLE

Examples of the present invention are given below by way of illustration and not by way of limitation. All parts are by weight.

Examples 1 and 2

An organopolysiloxane composition was prepared by mixing

350 parts of a linear dimethylpolysiloxane end-blocked with a trivinylsilyl group and having a viscosity of 100,000 centistokes at 25°C,

300 parts of a 50% by weight xylene solution of a methylvinylpolysiloxane resin consisting of $(\text{CH}_3)_3\text{SiO}_{1/2}$, $(\text{CH}_2=\text{CH})(\text{CH}_3)_2\text{SiO}_{1/2}$, and SiO_2 units, the sum of $(\text{CH}_3)_3\text{SiO}_{1/2}$ and $(\text{CH}_2=\text{CH})(\text{CH}_3)_2\text{SiO}_{1/2}$ units to the SiO_2 units being 0.8/1, the resin having a vinyl value of 0.08 mol/100 g,

70 parts of flake polycarbonate (PC) resin powder having a mean particle size of 25 μm ,

0.9 part of an n-octyl alcohol solution of chloroplatinic acid (metallic platinum concentration 2% by weight),

0.3 part of 3-methyl-1-butyn-3-ol, and
20 parts of an organohydrogenpolysiloxane of the
average formula: $(\text{CH}_3)_3\text{SiO}[(\text{CH}_3)\text{HSiO}]_{38}\text{Si}(\text{CH}_3)_3$
in a planetary mixer until the mixture became homogeneous.

5 Xylene, 500 parts, was added to the composition, obtaining a
xylene solution of the organopolysiloxane composition
(Example 1).

A portion of the xylene solution of the organopoly-
siloxane composition was transferred to another container
10 where it was allowed to stand for 30 days at room
temperature (25°C). The aged solution was agitated to find
that the polycarbonate resin flakes could be readily
dispersed uniformly in the solution again.

A xylene solution of organopolysiloxane composition was
15 prepared as in Example 1 except that 35 parts of the flake
polycarbonate resin powder was blended (Example 2).

The solutions of organopolysiloxane composition
prepared in Examples 1 and 2 were knife coated onto silicone
rubber plates, which had been vulcanized and cured, to a
20 thickness of 10 μm , air dried for 5 minutes, and heat cured
at 180°C for 300 seconds. There were obtained non-tacky,
tough cured coatings.

Comparative Examples 1 and 2

25 A cured coating was formed as in Example 1 except that
the polycarbonate resin powder was omitted (Comparative
Example 1).

A cured coating was formed as in Example 1 except that
70 parts of polymethylsilsesquioxane (PMS) spherical powder
30 having a mean particle size 1.2 μm was used instead of the
polycarbonate resin powder (Comparative Example 2).

The cured coatings were measured for gloss and abrasion
resistance by the following tests. The results are shown in
Table 1.

Glossiness

Using a glossmeter IG-310 manufactured by Horiba Mfg. K.K., the coating was measured for glossiness at an incident angle of 60° and an acceptance angle of 60°.

5 Abrasion resistance

An abrasion test was carried out under the following conditions.

	Tester	reciprocating abrasion tester
	Friction pad	sand-laden eraser rubber
10		(SH502 by Lion K.K.)
	Load	500 grams
	Stroke	25 mm
	Cycle	700 cycles/min.

Abrasion resistance was determined by inspecting the
15 cured coating every 70 cycles, and counting the number of
abrasion cycles repeated until the cured coating was peeled
from the substrate or the cured coating itself was worn out
to expose the substrate. The count reported in Table 1
means that abrasion of the substrate started subsequent to
20 that count because the substrate was already abraded at the
next inspection.

Table 1

	<u>E1</u>	<u>E2</u>	<u>CE1</u>	<u>CE2</u>
25 PC resin powder, pbw*	20	10	0	20 (PMS)
Glossiness	0	3	52	19
Abrasion resistance, count	1050	840	140	350

* per 100 parts of organopolysiloxane (A)

30 As is evident from Table 1, organopolysiloxane
compositions of the invention form cured coatings which
render the surface of silicone rubber matte and are improved
in abrasion resistance over prior art organopolysiloxane
compositions.

35 While this invention has been described with respect to
a preferred embodiment, it will be understood by those
skilled in the art that various changes and modifications

may be made without departing from the spirit and scope of the invention.



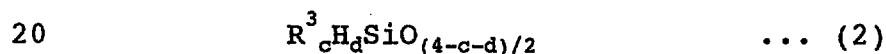
CLAIMS:

1. An organopolysiloxane composition comprising
(A) an organopolysiloxane having at least two alkenyl
5 groups each attached to a silicon atom in a molecule,
represented by the following average compositional formula:



- 10 wherein R^1 is a substituted or unsubstituted monovalent
hydrocarbon group free of an aliphatic unsaturated bond, R^2
is an alkenyl group, letters a and b are positive numbers
satisfying $1.6 \leq a \leq 2.0$, $0.001 \leq b \leq 0.5$, and $1.9 \leq a + b \leq$
2.1,

- 15 (B) an organohydrogenpolysiloxane having at least two
hydrogen atoms each attached to a silicon atom in a
molecule, represented by the following average compositional
formula:



- wherein R^3 is a substituted or unsubstituted monovalent
hydrocarbon group free of an aliphatic unsaturated bond,
letters c and d are positive numbers satisfying $0.8 \leq c \leq 2$,
25 $0.01 \leq d \leq 1$, and $0.85 \leq c + d \leq 2.5$, in an amount to
provide 0.4 to 10 hydrogen atoms attached to a silicon atom
in said organohydrogenpolysiloxane per alkenyl group in said
organopolysiloxane (A),

- (C) 2 to 50 parts by weight per 100 parts by weight of
30 said organopolysiloxane (A) and said organohydrogen-
polysiloxane (B) combined of a polycarbonate resin powder
having a mean particle size of up to 50 μm , and

- (D) a catalytic amount of a platinum catalyst.

- 35 2. A surface treating agent comprising the organopoly-
siloxane composition of claim 1.



3. A silicone rubber article having on a surface of silicone rubber a coating which is obtained by curing the organopolysiloxane composition of claim 1.