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(54) Title: ONE-PART CURABLE SILICONE COMPOSITION

(57) Abstract: The present invention relates to a one-part curable silicone composition comprising: (A) an organopolysiloxane having at least two silicon-bonded alkenyl groups per molecule; (B) an organohydrogenpolysiloxane having at least two silicon-bonded hydrogen atoms per molecule; (C) a platinum group metal base hydrosilylation catalyst; (D) an hydrosilylation reaction inhibitor; and (E) an acrylic and/or methacrylic compound. The one-part curable silicone composition exhibits good store stability and can cure at relatively low temperatures to form a cured product with good adhesion to various substrates.



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## **DESCRIPTION**

### **ONE-PART CURABLE SILICONE COMPOSITION**

#### Cross-Reference to Related Applications

5   **[0001]** This application claims priority to and all advantages of U.S. Pat. Appl. No. 62/587226 filed on 16 November 2017, the content of which is hereby incorporated by reference.

#### Technical Field

10   **[0002]** The present invention relates to a one-part curable silicone composition that can cure at relatively low temperatures to form a cured product with good adhesion to various substrates.

#### Background Art

15   **[0003]** Hydrosilylation-curable silicone compositions form cured products having excellent characteristics such as weather resistance and heat resistance, and they cure particularly quickly by heating, without producing by-products at the time of curing, so such compositions are used as adhesives, sealing agents, or coating agents for electric/electronic devices.

20   **[0004]** Examples of such curable silicone compositions include a curable silicone composition comprising: an organopolysiloxane having at least two silicon-bonded alkenyl groups per molecule, an organohydrogenpolysiloxane having at least two silicon-bonded hydrogen atoms per molecule, a hydrosilylation reaction catalyst, an allyl ester compound, a nitril compound, and an adhesion prompter (see Patent Document 1); a curable silicone composition comprising: an organopolysiloxane having at least two alkenyl groups per molecule, an organopolysiloxane having at least two silicon-bonded hydrogen atoms per molecule, a hydrosilylation reaction catalyst, and an acid anhydride having a silicon-bonded alkoxy group (see Patent Document 2); and a curable silicone composition comprising: an organopolysiloxane having at least two alkenyl groups per molecule, an organopolysiloxane resin comprising  $R_3SiO_{1/2}$  units and  $SiO_{4/2}$  units, wherein each R is independently an aliphatic unsaturation-free  $C_1$ - $C_{10}$  monovalent hydrocarbon group or  $C_2$ - $C_6$  alkenyl group, in a molar ratio  $R_3SiO_{1/2} / SiO_{4/2}$  of 0.6 to 1.0, an organohydrogenpolysiloxane having at least three silicon-bonded hydrogen atoms per molecule, and a platinum group metal base catalyst (see Patent Document 3).

30   **[0005]** Such curable silicone compositions are provided in two components that are divided into an organopolysiloxane having silicon-bonded hydrogen atoms and a hydrosilylation reaction catalyst in order to ensure storage stability. The two components must be uniformly mixed for use. Consequently, the inherent performance would not be adequately demonstrated if the mixture ratio of the two components should vary or if the two components are not adequately mixed.

[0006] While, in general, such curable silicone compositions cure at high temperatures such as 100 °C or more to sufficiently cure to form a cured product with good adhesion to substrates. So, the curable silicone composition cannot cure sufficiently at low temperatures such as 80 °C or below, and even if they cure, the cured products cannot adhere sufficiently to the substrates.

[0007] Therefore, even if the curable silicone composition described in each of Patent Documents 1 to 3 would be one-part, it was difficult to be consistent with good storage stability in a form of one-part and good adhesion of the cured products to various substrates.

#### Prior Art Documents

##### Patent Documents

Patent Document 1: Japanese Patent Application Publication No. 2009-221312 A

Patent Document 3: United States Patent Application Publication No. 2012/0309921 A1

Patent Document 3: United States Patent Application Publication No. 2016/0053148 A1

#### Summary of Invention

##### Technical Problem

[0008] An object of the present invention is to provide an one-part curable silicone composition which exhibits good storage stability, and by curing at relatively low temperatures, forms a cured product exhibiting good adhesion to various substrates.

##### Solution to Problem

[0009] The one-part curable silicone composition of the present invention comprises:

- (A) an organopolysiloxane having at least two silicon-bonded alkenyl groups per molecule;
- (B) an organohydrogenpolysiloxane having at least two silicon-bonded hydrogen atoms per molecule, in which a content of silicon-bonded hydrogen atoms is at least 1 mass% of this component, in an amount such that a content of silicon-bonded hydrogen atoms in this component is from 0.1 to 10 moles per 1 mole of silicon-bonded alkenyl groups in component (A);
- (C) a platinum group metal base hydrosilylation catalyst, in an amount of from 1 to 200 ppm of the platinum group metal in this component in terms of mass units with respect to the present composition;
- (D) a hydrosilylation reaction inhibitor, in an amount of from 0.1 to 1 mass% of the present composition; and
- (E) an acrylic and/or methacrylic compound, in an amount of from 0.1 to 5 mass% of the present composition.

[0010] Component (A) is preferably

- (A-1) a straight-chain organopolysiloxane having at least two silicon-bonded alkenyl

groups per molecule;

(A-2) an organopolysiloxane resin composed of a  $R^1_3SiO_{1/2}$  unit and  $SiO_{4/2}$  unit, with a molar ratio ( $R^1_3SiO_{1/2}$  unit) / ( $SiO_{4/2}$  unit) of 0.6 to 1.7, wherein each  $R^1$  represents a monovalent hydrocarbon group with 1 to 12 carbon atoms, however, at least two  $R^1$  per molecule are alkenyl groups with 2 to 12 carbon atoms; or a mixture of components (A-1) and (A-2), and is more preferably the mixture of components (A-1) and (A-2), wherein a content of component (A-1) is at least 10 mass% of the mixture of components (A-1) and (A-2).

[0011] Component (D) preferably comprises an acetylenic alcohol and an unsaturated carboxylic ester.

[0012] Component (E) is preferably 3-methacryoxypropyl trimethoxysilane, 3-methacryoxypropyl triethoxysilane, or methyl methacrylate.

[0013] The one-part curable silicone composition of the present invention is preferably an adhesive, a sealing agent, or a coating agent for an electric/electronic device.

#### Effects of Invention

[0014] The one-part curable silicone composition according to the present invention, exhibits good storage stability, and by curing at relatively low temperatures, can form a cured product exhibiting good adhesion to various substrates.

#### Detailed Description of the Invention

##### [0015] <One-part curable silicone composition>

The one-part curable silicone composition according to the present invention comprises the above components (A) to (E). Such one-part curable silicone composition exhibits good storage stability, and by curing at low temperature such as 80 °C or below, can form a cured product exhibiting good adhesion to substrates contacted during curing. Each of the components will be described in detail below.

[0016] Component (A) is an organopolysiloxane having at least two silicon-bonded alkenyl groups per molecule. Examples of the alkenyl groups include alkenyl groups having from 2 to 12 carbon atoms such as vinyl groups, allyl groups, butenyl groups, pentenyl groups, hexenyl groups, heptenyl groups, octenyl groups, nonenyl groups, decenyl groups, undecenyl groups, and dodecenyl groups, among which vinyl groups are preferable. In addition, examples of groups bonding to silicon atoms other than alkenyl groups in component (A) include alkyl groups having from 1 to 12 carbon atoms such as methyl groups, ethyl groups, propyl groups, isopropyl groups, butyl groups, isobutyl groups, tert-butyl groups, pentyl groups, neopentyl groups, hexyl groups, cyclohexyl groups, heptyl groups, octyl groups, nonyl groups, decyl groups, undecyl groups, and dodecyl groups; aryl groups having

from 6 to 20 carbon atoms such as phenyl groups, tolyl groups, xylyl groups, and naphthyl groups; aralkyl groups having from 7 to 20 carbon atoms such as benzyl groups, phenethyl groups, and phenylpropyl groups; and groups in which some or all of the hydrogen atoms of these groups are substituted with halogen atoms such as fluorine atoms, chlorine atoms, or bromine atoms. Furthermore, the silicon atoms in component (A) may have small amounts of hydroxyl groups or alkoxy groups such as methoxy groups or ethoxy groups within a range that does not impair the object of the present invention.

**[0017]** Examples of the molecular structure of component (A) include a straight-chain structure, a partially branched straight-chain structure, a branched-chain structure, a cyclic structure, and a three-dimensional reticular structure. Component (A) may be one type of organopolysiloxane having these molecular structures or may be a mixture of two or more types of organopolysiloxanes having these molecular structures.

**[0018]** Such component (A) is preferably (A-1) a straight-chain organopolysiloxane; (A-2) an organopolysiloxane resin; or a mixture of components (A-1) and (A-2).

**[0019]** Examples of such component (A-1) include dimethylpolysiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, dimethylsiloxane-methylvinylsiloxane copolymers capped at both molecular terminals with dimethylvinylsiloxy groups, dimethylsiloxane-methylphenylsiloxane copolymers capped at both molecular terminals with dimethylvinylsiloxy groups, methylphenylpolysiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, dimethylsiloxane-methylvinylsiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, dimethylsiloxane-methylvinylsiloxane-methylphenylsiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, a mixture of dimethylpolysiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, and dimethylpolysiloxane capped at one molecular terminal with dimethylvinylsiloxy group and at another molecular terminal with dimethylhydroxysiloxy group, a mixture of dimethylpolysiloxanes capped at both molecular terminals with dimethylvinylsiloxy groups, and dimethylpolysiloxane capped at both molecular terminals with dimethylhydroxysiloxy group, and mixtures of two or more types thereof.

**[0020]** Component (A-2) is an organopolysiloxane resin composed of a  $R^1_3SiO_{1/2}$  unit and  $SiO_{4/2}$  unit. In the formula, each  $R^1$  represents a monovalent hydrocarbon group with 1 to 12 carbon atoms. The monovalent hydrocarbon groups are exemplified by methyl groups, ethyl groups, propyl groups, or similar alkyl group; vinyl groups, allyl groups, butenyl groups, pentenyl groups, hexenyl groups, or similar alkenyl groups; phenyl groups, tolyl groups, xylyl groups, or similar aryl groups; benzyl groups, phenethyl groups, or similar aralkyl groups; and 3-chloropropyl groups, 3,3,3-trifluoropropyl groups, or similar halogenated alkyl groups.

However, at least two  $R^1$  per molecule are alkenyl groups. Component (A-2) may have residual silanol groups which arise from the hydrolysis of reactive silanes that are used to prepare component (A-2).

**[0021]** The molar ratio of  $R^1_3SiO_{1/2}$  units to  $SiO_{4/2}$  units in component (A-2) falls within the range of 0.6 to 1.7, preferably within the range of 0.6 to 1.5. This is because when the molar ratio is greater than or equal to the lower limit of the aforementioned range, solubility of this component to other components is improved, and when the molar ratio is less than or equal to the upper limit of the aforementioned range, mechanical properties of the cured product are improved.

**[0022]** When a mixture of component (A-1) and component (A-2) is used as component (A), the content of component (A-1) is preferably at least 10 mass% or at least 40 mass% of the total amount of components (A-1) and (A-2) in that handleability of the obtained composition is good. In addition, the content of component (A-1) is preferably at most 90 mass% of the total amount of components (A-1) and (A-2) in that mechanical properties of the cured product are good.

**[0023]** Component (B) is an organohydrogenpolysiloxane having at least two silicon-bonded hydrogen atoms per molecule, in which a content of silicon-bonded hydrogen atoms is at least 1 mass% of this component. This is because when the content of silicon-bonded hydrogen atoms is greater than or equal to the lower limit of the aforementioned range, curability of the present composition is improved. Examples of groups bonding to silicon atoms other than hydrogen groups in component (B) include alkyl groups having from 1 to 12 carbon atoms such as methyl groups, ethyl groups, propyl groups, isopropyl groups, butyl groups, isobutyl groups, tert-butyl groups, pentyl groups, neopentyl groups, hexyl groups, cyclohexyl groups, heptyl groups, octyl groups, nonyl groups, decyl groups, undecyl groups, and dodecyl groups; aryl groups having from 6 to 20 carbon atoms such as phenyl groups, tolyl groups, xylyl groups, and naphthyl groups; aralkyl groups having from 7 to 20 carbon atoms such as benzyl groups, phenethyl groups, and phenylpropyl groups; and groups in which some or all of the hydrogen atoms of these groups are substituted with halogen atoms such as fluorine atoms, chlorine atoms, or bromine atoms. Furthermore, the silicon atoms in component (B) may have small amounts of hydroxyl groups or alkoxy groups such as methoxy groups or ethoxy groups within a range that does not impair the object of the present invention.

**[0024]** Examples of the molecular structure of component (B) include straight-chain, partially branched straight-chain, branched chain, cyclic, and three-dimensional reticular structures, and the molecular structure is preferably a partially branched straight-chain, branched chain,

or three-dimensional reticular structure.

**[0025]** Examples of such component (B) include methylhydrogenpolysiloxanes capped at both molecular terminals with trimethylsiloxy groups, dimethylsiloxane-methylhydrogensiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, dimethylpolysiloxanes capped at both molecular terminals with dimethylhydrogensiloxy groups, dimethylsiloxane-methylhydrogensiloxane copolymers capped at both molecular terminals with dimethylhydrogensiloxy groups, methylhydrogensiloxane-diphenylsiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, methylhydrogensiloxane-diphenylsiloxane-dimethylsiloxane copolymers capped at both molecular terminals with trimethylsiloxy groups, copolymers consisting of  $(\text{CH}_3)_2\text{HSiO}_{1/2}$  units and  $\text{SiO}_{4/2}$  units, copolymers consisting of  $(\text{CH}_3)_2\text{HSiO}_{1/2}$  units,  $\text{SiO}_{4/2}$  units, and  $(\text{C}_6\text{H}_5)\text{SiO}_{3/2}$  units, and mixtures of two or more types thereof.

**[0026]** The content of component (B) is an amount such that the content of silicon-bonded hydrogen atoms in this component is from 0.1 to 10 moles and preferably from 0.5 to 5 moles per 1 mole of silicon-bonded alkenyl groups in component (A). This is because when the content of component (B) is less than or equal to the upper limit of the aforementioned range, mechanical properties of the cured product are good, whereas when the content of component (B) is greater than or equal to the lower limit of the aforementioned range, curability of the composition is good.

**[0027]** Component (C) is a platinum group metal base hydrosilylation catalyst used to accelerate the curing of the present composition. Examples of component (C) include platinum group element catalysts and platinum group element compound catalysts, and specific examples include platinum-based catalysts, rhodium-based catalysts, palladium-based catalysts, and combinations of at least two types thereof. In particular, platinum-based catalysts are preferable in that the curing of the present composition can be dramatically accelerated. Examples of these platinum-based catalysts include finely powdered platinum; platinum black; chloroplatinic acid, alcohol-modified chloroplatinic acid; chloroplatinic acid/diolefin complexes; platinum/olefin complexes; platinum/carbonyl complexes such as platinum bis(acetoacetate), and platinum bis(acetylacetonate); chloroplatinic acid/alkenylsiloxane complexes such as chloroplatinic acid/divinyltetramethyl disiloxane complexes, and chloroplatinic acid/tetravinyl tetramethyl cyclotetrasiloxane complexes; platinum/alkenylsiloxane complexes such as platinum/divinyltetramethyl disiloxane complexes, and platinum/tetravinyl tetramethyl cyclotetrasiloxane complexes; complexes of chloroplatinic acid and acetylene alcohols; and mixtures of two or more types thereof. In particular, platinum-alkenylsiloxane complexes are preferable in that the curing of the present

composition can be accelerated.

**[0028]** Examples of the alkenylsiloxane used in the platinum-alkenylsiloxane complex include 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, alkenylsiloxane oligomers in which some of methyl groups of these alkenylsiloxanes are substituted with ethyl groups, phenyl groups, or the like, and alkenylsiloxane oligomers in which vinyl groups of these alkenylsiloxanes are substituted with allyl groups, hexenyl groups, or the like. In particular, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane is preferable in that the stability of the platinum-alkenylsiloxane complex that is produced is good.

**[0029]** In order to improve the stability of the platinum-alkenylsiloxane complexes, it is preferable to dissolve these platinum-alkenylsiloxane complexes in an alkenylsiloxane oligomer such as 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, 1,3-diallyl-1,1,3,3-tetramethyldisiloxane, 1,3-divinyl-1,3-dimethyl-1,3-diphenyldisiloxane, 1,3-divinyl-1,1,3,3-tetraphenyldisiloxane, or 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane or an organosiloxane oligomer such as a dimethylsiloxane oligomer, and it is particularly preferable to dissolve the complexes in an alkenylsiloxane oligomer.

**[0030]** The content of component (C) is in an amount of from 1 to 200 ppm of the platinum group metal in this component in terms of mass units with respect to this composition. Specifically, the content is preferably an amount such that the content of platinum group metal in component (C) is in the range of from 0.01 to 150 ppm, in the range of from 0.01 to 100 ppm, or in the range of from 0.1 to 100 ppm in terms of mass units with respect to the present composition. This is because when the content of component (C) is greater than or equal to the lower limit of the aforementioned range, curability of the composition is good, whereas when the content of component (C) is less than or equal to the upper limit of the aforementioned range, coloration of the cured product is suppressed.

**[0031]** Component (D) is a hydrosilylation reaction inhibitor in order to prolong the usable time at ambient temperature and to improve storage stability. Examples of component (D) include acetylenic alcohols such as 1-ethynyl-cyclohexan-1-ol, 2-methyl-3-butyn-2-ol, 2-phenyl-3-butyn-2-ol, 2-ethynyl-isopropan-2-ol, 2-ethynyl-butan-2-ol, and 3,5-dimethyl-1-hexyn-3-ol; silylated acetylenic alcohols such as trimethyl (3,5-dimethyl-1-hexyn-3-oxy) silane, dimethyl bis(3-methyl-1-butyn-oxy) silane, methylvinyl bis(3-methyl-1-butyn-3-oxy) silane, and ((1,1-dimethyl-2-propynyl)oxy)trimethylsilane; unsaturated carboxylic esters such as diallyl maleate, dimethyl maleate, diethyl fumarate, diallyl fumarate, and bis(2-methoxy-1-methylethyl) maleate, mono-octylmaleate, mono-isooctylmaleate, mono-allyl maleate, mono-methyl maleate, mono-ethyl fumarate, mono-allyl fumarate, and 2-methoxy-1-methylethylmaleate; ene-yne compounds such as 2-isobutyl-1-buten-3-yne, 3,5-dimethyl-

3-hexen-1-yne, 3-methyl-3-penten-1-yne, 3-methyl-3-hexen-1-yne, 1-ethynyl cyclohexene, 3-ethyl-3-buten-1-yne, and 3-phenyl-3-buten-1-yne; and mixtures of two or more types thereof. In particular, a mixture of an acetylenic alcohol and an unsaturated carboxylic ester is preferable in order to prevent the cured product from developing surface wrinkle.

5 **[0032]** The content of component (D) is in an amount of from 0.1 to 1000 ppm in this component in terms of mass units with respect to this composition. Specifically, the content is preferably an amount of from 1 to 1000 ppm or an amount of from 10 to 500 ppm in this component in terms of mass units with respect to the present composition. This is because when the content of component (D) is greater than or equal to the lower limit of the  
10 aforementioned range, storage stability of the present composition is good, whereas when the content of component (D) is less than or equal to the upper limit of the aforementioned range, curability of the present composition at low temperatures is good.

**[0033]** Component (E) is an acrylic and/or methacrylic compound in order to improve adhesion to various substrates with which the composition makes contact during curing at  
15 low temperatures. Examples of such component (E) include a silane compound containing an acrylic and/or methacrylic group such as 3-methacyloxypropyl trimethoxysilane, 3-methacyloxypropyl methyldimethoxysilane, 3-methacyloxypropyl triethoxysilane; and an acrylic and/or methacrylic monomer such as methyl acrylate, ethyl acrylate, methyl methacrylate. In particular, 3-methacyloxypropyl trimethoxysilane, 3-methacyloxypropyl  
20 triethoxysilane, and methyl methacrylate is preferable in that the adhesive to various engineered plastics is good.

**[0034]** The content of component (E) is in an amount of from 0.1 to 5 mass% of the present composition, preferably in the range of from 0.1 to 3 mass% or in the range of from 0.5 to 3 mass% of the present composition. This is because when the content of component (E) is  
25 greater than or equal to the lower limit of the aforementioned range, adhesion of the cured product is good, whereas when the content of component (E) is less than or equal to the upper limit of the aforementioned range, curability of the present composition at low temperatures is good.

**[0035]** Typical additives include but are not limited to filler, pigments, dyes, flame retardants, and heat and/or ultraviolet light stabilizers to enhance physical properties of the cured  
30 product.

**[0036]** The one-part curable silicone compositions of this invention can be prepared by combining all of ingredients at ambient temperature. Any of the mixing techniques and devices described in the prior art can be used for this purpose. The particular device used  
35 will be determined by the viscosity of the ingredients and the final curable composition. Cooling of the ingredients during mixing may be desirable to avoid premature curing.

**[0037]** The one-part curable silicone composition of the present invention is particularly useful as adhesives, sealing agents, or coating agents for electric/electronic devices which are sensitive to heating.

#### Examples

5 **[0038]** The one-part curable silicone composition of the present invention will now be described using Practical and Comparative Examples. In the formula, Me and Vi represent methyl group and vinyl group respectively. Note that the viscosity is the value obtained at 25°C. The characteristics of the one-part curable silicone composition are evaluated as follows.

10 **[0039]** <Viscosity>

Viscosity is measured using a rotational viscometer such as a Brookfield synchro-lectric viscometer or a Wells-Brookfield 52 cone/plate viscometer. Since virtually all materials measured are non-Newtonian in nature, no correlation should be expected between, results obtained using different spindles (cones) or speeds. The results are generally reported in centipoise. The viscosity was measured at 0.5 and 5.0 rpm for 2 minutes. This method is based on ASTM D 4287 for cone/plate.

**[0040]** <Cure condition>

A cure condition for the low temperature curable silicone adhesive is basically applied by using 80°C for 1 hour in an oven.

20 **[0041]** <DSC T<sub>c</sub>>

Differential scanning calorimetry (DSC) is a technique for studying the thermal behavior of materials as they undergo physical and chemical changes during heating, cooling or in an isothermal mode. The results are reported on the form of an annotated thermogram with features identified by the analyst. With DSC instruments the amount of heat flow or enthalpy change associated with the transition can be measured via calibration with accept, different sources.

**[0042]** <Hardness of the cured product>

A cured product with 6 mm thickness was obtained by curing the 80°C of low-temperature-curable silicone composition for 1 hour in the oven. Then, hardness of the cured product was measured by using Shore A hardness according to ASTM D 2240 "Standard Test Method for Rubber Property - Durometer Hardness".

**[0043]** <MDR>

The rheological properties and curing characteristics of vulcanizing elastomeric materials are determined using a Monsanto moving die rheometer. The torque required to oscillate the lower die through a small arc is measured. the displaced, torque, s', increases as the elastomer vulcanizes and is automatically plotted and/or calculated via preset computerized

conditions as pound-inch versus time. The curve is a function of the test temperature and the characteristic of the cured and uncured elastomer, plasticity, scorch time, durometer, cure rate and modulus. The instrument is also capable of measuring non-displaced torque, s" (loss modulus) and calculating tan delta (ratio of s"/s'). Temperature setting for the MDR

5 measurement was applied in 80°C for 1 hour and observation of curing curve was checked by time. This method is based on ASTM D 5289-92.

**[0044] <Pot life>**

Pot life is described as the time necessary for a system to double in viscosity after catalyzation. This is considered to be the normal useable working time. The test is designed  
10 for any material that will cure at room temperature on which a, viscosity measurement may be made. A 'pass/fail' result may be reported if a minimum time is specified. Cure rate is described as the time necessary to reach the specified viscosity. Pot life index may be reported by dividing the final specified, viscosity by the original. Other reporting modes may be specified. For the pot life measurement, Brookfield viscometer was used with 52 cone  
15 plate. This procedure is based on ASTM D 1824.

**[0045] <Surface wrinkle>**

Surface wrinkles are checked with visible wrinkle on the cured adhesive samples and a cure condition for the low temperature curable silicone adhesive is basically applied by using 80°C for 1 hour in an oven.

20 **[0046] <Lap shear strength>**

The adhesion characteristic of primers, adhesives and/or sealants is determined by measuring the amount of pull required to separate, by shear, a double laminate. The results are reported in pounds per square inch, unless otherwise, specified. The amount of adhesive or cohesive failure is estimated by examination of the exposed surface of the substrates.

25 This procedure is based on ASTM D 816. Lap shear test specimen is prepared by using Al plate and sample is cured at 80°C for 1 hour in an oven.

**[0047] <Adhesion failure mode-cohesive failure>**

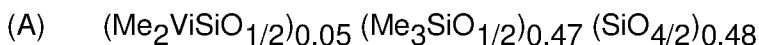
The adhesion of a non-curing or low strength material to a substrate is determined by preparing a sandwich of the material between two pieces of substrate, manually pulling the  
30 substrate apart, and visually estimating the area of cohesive failure. Three configurations may be used to prepare the sandwich. The average of three separate sandwiches is reported to the nearest 5%. The standard substrate may be specified. 100% cohesive failure indicates good adhesion of the material. The percent cohesive failure may be estimated and reported.

**[0048]** <Practical Examples 1 to 11 and Comparative Example 1>

The following components were uniformly mixed according to the compositions (parts by mass) shown in Tables 1 to 3 to prepare the one-part curable silicone compositions of Practical Examples 1 to 11 and Comparative Example 1. In the formulae, Vi represents a vinyl group, and Me represents a methyl group. Moreover, in Tables 1 to 3, "SiH/Vi" represents the total moles of silicon-bonded hydrogen atoms in component (B) per 1 mole of total vinyl groups in component (A) in the one-part curable silicone composition.

**[0049]** The following components were used as component (A).

Component (a-1): a mixture having 0.56 mass% of vinyl groups content and consisting of 74 mass % of a dimethylpolysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups having a viscosity of 40,000 mPa•s and having 0.09 mass% of vinyl group content, and 26 mass % of an organopolysiloxane resin having 1.89 mass% of vinyl groups content and represented by the average unit formula:



Component (a-2): a dimethylpolysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups having a viscosity of 10,000 mPa•s and having 0.14 mass% of vinyl groups content.

Component (a-3): a dimethylpolysiloxane capped at both molecular terminals with dimethylvinylsiloxy groups having a viscosity of 2,000 mPa•s and having 0.23 mass% of vinyl groups content.

**[0050]** The following component was used as component (B).

Component (b-1): a methylhydrogenpolysiloxane capped at both molecular terminals with trimethylsiloxy groups, having a viscosity of 20 mPa•s and having 1.56 mass% of silicon-bonded hydrogen atoms content.

**[0051]** The following component was used as component (C).

Component (c-1): 1,3-divinyl-1,1,3,3-tetramethyl disiloxane solution of a 1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex of platinum (platinum metal content = approximately 8,800 ppm)

**[0052]** The following components were used as component (D).

Component (d-1): 1-ethynyl cyclohexan-1-ol

Component (d-2): bis (2-methoxy-1-methylethyl) maleate

**[0053]** The following components were used as component (E).

Component (e-1): 3-methacryloxypropyl trimethoxysilane

Component (e-2): methyl methacrylate

Component (e-3): hydroxypropyl acrylate

Component (e-4): 2-hydroxyethyl methacrylate

Component (e-5): glycidyl methacrylate

Component (e-6): 3-glycidoxypopyl trimethoxysilane

**[0054]** The following component was used as an arbitrary component.

Component (f-1): carbon black powder (This carbon black powder was added as a master batch consisting of 50 mass% of this carbon black powder and 50 mass% of component (a-3) above.)

**[0055]** [Table 1]

| Item \ Category                                             |                             |       | Practical Examples |              |             |             |             | Comp.        |
|-------------------------------------------------------------|-----------------------------|-------|--------------------|--------------|-------------|-------------|-------------|--------------|
|                                                             |                             |       | 1                  | 2            | 3           | 4           | 5           | Exam. 1      |
| One-part curable<br>silicone composition<br>(parts by mass) | (A)                         | (a-1) | 71.52              | 69.83        | 70.48       | 70.48       | 70.67       | 72.66        |
|                                                             |                             | (a-2) | 20.00              | 20.00        | 20.00       | 20.00       | 20.00       | 20.00        |
|                                                             |                             | (a-3) | 0.25               | 0.25         | 0.25        | 0.25        | 0.25        | 0.25         |
|                                                             | (B)                         | (b-1) | 2.93               | 4.62         | 3.97        | 3.97        | 3.78        | 1.79         |
|                                                             | (C)                         | (c-1) | 1.70               | 1.70         | 1.70        | 1.70        | 1.70        | 1.70         |
|                                                             | (D)                         | (d-1) | 0.15               | 0.15         | 0.15        | 0.15        | 0.15        | 0.15         |
|                                                             |                             | (d-2) | 0.20               | 0.20         | 0.20        | 0.20        | 0.20        | 0.20         |
|                                                             | (E)                         | (e-1) | 3.00               | -            | -           | -           | -           | -            |
|                                                             |                             | (e-2) | -                  | 3.00         | -           | -           | -           | -            |
|                                                             |                             | (e-3) | -                  | -            | 3.00        | -           | -           | -            |
|                                                             |                             | (e-4) | -                  | -            | -           | 3.00        | -           | -            |
|                                                             |                             | (e-5) | -                  | -            | -           | -           | 3.00        | -            |
|                                                             |                             | (e-6) | -                  | -            |             |             |             | 3.00         |
|                                                             | (f-1)                       |       | 0.25               | 0.25         | 0.25        | 0.25        | 0.25        | 0.25         |
| SiH/Vi                                                      |                             |       | 2.9                | 4.6          | 3.9         | 3.9         | 3.7         | 1.7          |
| Cure Condition                                              |                             |       | Y                  | Y            | Y           | Y           | Y           | Y            |
| DSC Tc (°C)                                                 |                             |       | 83.0               | 79.4         | 78.2        | 77.6        | 76.2        | 86.7         |
| Hardness of the<br>cured product                            |                             |       | 43                 | 45           | 40          | 40          | 45          | 44           |
| Adhesion<br>Properties                                      | Lap Shear<br>Strength (Psi) |       | 585.06             | 660.38       | 332.37      | 357.71      | 528.10      | 473.42       |
|                                                             | Adhesion<br>Failure Mode    |       | C.F.<br>100%       | C.F.<br>100% | C.F.<br>60% | C.F.<br>20% | C.F.<br>40% | A.F.<br>100% |

[0056] [Table 2]

| Category<br>Item                                            |                             |       | Practical Examples |        |        |        |
|-------------------------------------------------------------|-----------------------------|-------|--------------------|--------|--------|--------|
|                                                             |                             |       | 6                  | 7      | 8      | 9      |
| One-part curable<br>silicone composition<br>(parts by mass) | (A)                         | (a-1) | 74.89              | 72.39  | 70.57  | 67.62  |
|                                                             |                             | (a-2) | 20.00              | 20.00  | 20.00  | 20.00  |
|                                                             |                             | (a-3) | 0.25               | 0.25   | 0.25   | 0.25   |
|                                                             | (B)                         | (b-1) | 1.56               | 2.06   | 3.88   | 4.83   |
|                                                             | (C)                         | (c-1) | 1.70               | 1.70   | 1.70   | 1.70   |
|                                                             | (D)                         | (d-1) | 0.15               | 0.15   | 0.15   | 0.15   |
|                                                             |                             | (d-2) | 0.20               | 0.20   | 0.20   | 0.20   |
|                                                             | (E)                         | (e-1) | 1.00               | 3.00   | 3.00   | 5.00   |
|                                                             | (f-1)                       |       | 0.25               | 0.25   | 0.25   | 0.25   |
| SiH/Vi                                                      |                             |       | 1.5                | 2.0    | 3.8    | 5.0    |
| Viscosity<br>(mPa•s)                                        | 0.5 rpm / 3 min.            |       | 34,930             | 33,340 | 30,160 | 26,990 |
|                                                             | 5 rpm / 3 min.              |       | 33,660             | 30,960 | 28,260 | 24,450 |
| Pot life<br>(viscosity after 6 hrs.)                        | 0.5 rpm / 3 min.            |       | 44,450             | 39,690 | 41,280 | 39,690 |
|                                                             | 5 rpm / 3 min.              |       | 41,590             | 36,670 | 39,210 | 36,510 |
| Cure Condition                                              |                             |       | Y                  | Y      | Y      | Y      |
| DSC Tc (°C)                                                 |                             |       | 85.8               | 82.7   | 78.9   | 76.5   |
| Curing properties<br>(min.)                                 | ts-1                        |       | 2.98               | 2.51   | 1.21   | 1.09   |
|                                                             | t10                         |       | 2.83               | 2.45   | 1.23   | 1.11   |
|                                                             | t50                         |       | 3.95               | 3.53   | 1.45   | 1.28   |
|                                                             | t90                         |       | 9.14               | 9.07   | 3.93   | 2.73   |
| Hardness of the<br>cured product                            |                             |       | 25                 | 29     | 47     | 48     |
| Adhesion<br>Properties                                      | Lap Shear<br>Strength (Psi) |       | 452.81             | 461.59 | 676.36 | 648.87 |
|                                                             | Adhesion                    |       | C.F.               | C.F.   | C.F.   | C.F.   |
|                                                             | Failure Mode                |       | 100%               | 100%   | 100%   | 100%   |

**[0057]** [Table 3]

| Category<br>Item                                            |                             |       | Practical Examples |              |              |
|-------------------------------------------------------------|-----------------------------|-------|--------------------|--------------|--------------|
|                                                             |                             |       | 10                 | 11           | 12           |
| One-part curable<br>silicone composition<br>(parts by mass) | (A)                         | (a-1) | 71.50              | 71.25        | 71.52        |
|                                                             |                             | (a-2) | 20.00              | 20.00        | 20.00        |
|                                                             |                             | (a-3) | 0.25               | 0.25         | 0.25         |
|                                                             | (B)                         | (b-1) | 3.00               | 3.05         | 2.93         |
|                                                             | (C)                         | (c-1) | 1.70               | 1.70         | 1.70         |
|                                                             | (D)                         | (d-1) | 0.30               | 0.30         | 0.15         |
|                                                             |                             | (d-2) | -                  | 0.20         | 0.20         |
|                                                             | (E)                         | (e-1) | 1.00               | 3.00         | 3.00         |
|                                                             | (f-1)                       |       | 0.25               | 0.25         | 0.25         |
| SiH/Vi                                                      |                             |       | 2.9                | 3.0          | 2.9          |
| Viscosity<br>(mPa•s)                                        | 0.5 rpm / 3 min.            |       | 27,540             | 26,450       | 27,000       |
|                                                             | 5 rpm / 3 min.              |       | 25,560             | 23,540       | 25,560       |
| Pot life<br>(time for x2 viscosity)                         |                             |       | > 8 hrs.           | > 24 hrs.    | > 15 hrs.    |
| Cure Condition                                              |                             |       | Y                  | Y            | Y            |
| DSC Tc (°C)                                                 |                             |       | 85.6               | 95.6         | 83.0         |
| Hardness of the<br>cured product                            |                             |       | 47                 | 45           | 45           |
| Surface wrinkle                                             |                             |       | Observed           | Non          | Non          |
| Adhesion<br>Properties                                      | Lap Shear<br>Strength (Psi) |       | 591.20             | 574.30       | 585.06       |
|                                                             | Adhesion<br>Failure Mode    |       | C.F.<br>100%       | C.F.<br>100% | C.F.<br>100% |

**[0058]** <Practical Example 13>

The one-part curable silicone composition prepared in Practical Example 8 was cured on  
5 substrates shown in Table 4 by heating 80 °C for 30 min., and adhesion properties were  
evaluated as follows.

**[0059]** <Adhesion Properties>

The pull-off adhesion testing can be one of the alternating adhesion test method. The test  
method describes as below. The procedure of pull-off adhesion test is following. Firstly, the  
10 prepared Teflon zig was placed on metal substrate and secondly, potting adhesive material

was filled in Teflon hole which has 6 mm diameters and then cured adhesive material in the oven at 80°C for 1 hour. Thirdly, Teflon zig was removed from the substrate and then pull-off test was carried out by manual measurements. It was determined that a degree of adhesion performance if cohesive failure onto substrates (glass, Al, EMC, PCB, PET) was perfectly observed or not.

**[0060]** [Table 4]

| Substrates \ Adhesion Properties | Force (N/mm <sup>2</sup> ) | Adhesion Failure Mode |
|----------------------------------|----------------------------|-----------------------|
| *Glass                           | 0.83                       | C.F. 100%             |
| *Al                              | 0.85                       | C.F. 100%             |
| *EMC                             | 0.82                       | C.F. 100%             |
| *PCB                             | 0.91                       | C.F. 100%             |
| *PET                             | 0.80                       | C.F. 100%             |

#### Industrial Applicability

**[0061]** The one-part curable silicone composition of the present invention has outstanding storage stability, does not require mixture prior to use, and cures at relatively low temperatures and forms a cured product that exhibits good adhesion to various substrates contacted during curing. Consequently, it is ideal as an adhesive, coating agent or a sealing agent for an electric/electronic device.

**[0062]** Many modifications and other embodiments of the invention will come to mind to one skilled in the art to which this invention pertains, having the benefit of the teachings presented in the foregoing description. Accordingly, it is to be understood that the invention is not to be limited to the specific embodiments disclosed and that modifications and other embodiments are intended to be included within the scope of the appended claims.

**CLAIMS**

What is claimed is:

1. A one-part curable silicone composition comprising:

(A) an organopolysiloxane having at least two silicon-bonded alkenyl groups per molecule;

(B) an organohydrogenpolysiloxane having at least two silicon-bonded hydrogen atoms per molecule, in which a content of silicon-bonded hydrogen atoms is at least 1 mass% of this component, in an amount such that a content of silicon-bonded hydrogen atoms in this component is from 0.1 to 10 moles per 1 mole of silicon-bonded alkenyl groups in component (A);

(C) a platinum group metal base hydrosilylation catalyst, in an amount of from 1 to 200 ppm of the platinum group metal in this component in terms of mass units with respect to the composition;

(D) a hydrosilylation reaction inhibitor, in an amount of from 0.1 to 1 mass% of the composition; and

(E) an acrylic and/or methacrylic compound, in an amount of from 0.1 to 5 mass% of the composition.

2. The one-part curable silicone composition according to Claim 1, wherein component (A) is:

(A-1) a straight-chain organopolysiloxane having at least two silicon-bonded alkenyl groups per molecule;

(A-2) an organopolysiloxane resin composed of a  $R^1_3SiO_{1/2}$  unit and  $SiO_{4/2}$  unit, with a molar ratio ( $R^1_3SiO_{1/2}$  unit) / ( $SiO_{4/2}$  unit) of 0.6 to 1.7, wherein each  $R^1$  represents a monovalent hydrocarbon group with 1 to 12 carbon atoms, however, at least two  $R^1$  per molecule are alkenyl groups with 2 to 12 carbon atoms; or a mixture of components (A-1) and (A-2).

3. The one-part curable silicone composition according to Claim 2, wherein component (A) is the mixture of components (A-1) and (A-2), wherein a content of component (A-1) is at least 10 mass% of the mixture of components (A-1) and (A-2).

4. The one-part curable silicone composition according to any one of Claims 1 to 3, wherein component (D) comprises an acetylenic alcohol and an unsaturated carboxylic ester.

5. The one-part curable silicone composition according to any one of Claims 1 to 4, wherein component (E) is 3-methacryoxypropyl trimethoxysilane, 3-methacryoxypropyl triethoxysilane, or methyl methacrylate.

6. The one-part curable silicone composition according to any one of Claims 1 to 5, wherein the composition is an adhesive, a sealing agent, or a coating agent for an electric/electronic device.

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/US2018/061287****A. CLASSIFICATION OF SUBJECT MATTER****C08G 77/20(2006.01)i, C08G 77/12(2006.01)i, C08G 77/08(2006.01)i, C08K 5/05(2006.01)i, C08K 5/101(2006.01)i, C08K 5/5415(2006.01)i, C08G 77/48(2006.01)i, C09D 183/04(2006.01)i, C09J 183/04(2006.01)i, C09K 3/10(2006.01)i**

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)

C08G 77/20; C08L 83/04; C09D 183/04; C09D 7/12; C09J 133/14; C09J 183/06; H01L 21/30; H01L 33/00; H01L 33/40; H01L 33/56; C08G 77/12; C08G 77/08; C08K 5/05; C08K 5/101; C08K 5/5415; C08G 77/48; C09J 183/04; C09K 3/10

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) &amp; Keywords: curable, dimethylpolysiloxane, dimethylvinyl, Pt catalyst, methacryl, acryl, maleate, cyclohexanol

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                         | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | US 2015-0376481 A1 (DOW CORNING CORPORATION) 31 December 2015<br>See paragraphs [0039]-[0064], [0104], [0105], [0152]-[0158]; claims 1-12. | 1,2,4                 |
| Y         |                                                                                                                                            | 3                     |
| Y         | US 2016-0280938 A1 (DOW CORNING TORAY CO., LTD.) 29 September 2016<br>See paragraphs [0057], [0058]; table 2.                              | 3                     |
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| A         | US 2009-0146175 A1 (BAHADUR MANEESH et al.) 11 June 2009<br>See the whole document.                                                        | 1-4                   |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

11 April 2019 (11.04.2019)

Date of mailing of the international search report

**11 April 2019 (11.04.2019)**

Name and mailing address of the ISA/KR

International Application Division

Korean Intellectual Property Office

189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea

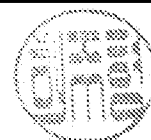


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# INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/US2018/061287**

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3. ☒ Claims Nos.: 5,6  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/US2018/061287**

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

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