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**WO 01/42365 A1**

(54) Title: ROOM TEMPERATURE CURABLE SILICONE SEALANT

(57) Abstract: A one part room, temperature vulcanizable silicone sealant composition containing a moisture curable polyorganosiloxane polymer exhibits, when cured, a tensile modulus at 50% elongation of from about 30 pounds per square inch to about 100 pounds per square inch and exhibits a reduced tendency to stain substrates in contact with the cured.

## ROOM TEMPERATURE CURABLE SILICONE SEALANT

### FIELD OF THE INVENTION

The invention relates to one part room temperature vulcanizable ("RTV") silicone sealants, more particularly to one part RTV silicone sealants that exhibit a reduced tendency to stain porous substrates.

### BRIEF DESCRIPTION OF THE RELATED ART

5 Silicone compositions which cure to produce elastomers are widely used as sealants and caulks in building and construction applications. Known silicone sealant compositions may stain substrates to which they are applied, particularly porous substrates, such as for example, marble, concrete, granite, sandstone, and limestone. Furthermore, the exposed surfaces of cured sealants tend to attract dirt, dust, grime and other forms of pollution.

10 Many attempts have been made to alleviate the staining and dirt pick-up problems. For example, Mikami et al (US 5,432,218 ) discloses a room temperature curable polysiloxane with paintability and improved resistance to stain due to a component containing an unsaturated fatty acid, such as soy oil fatty acids, linseed oil fatty acids, and tung oil fatty acids. Similarly, a combination of a drying  
15 oil and zinc oxide which increases the longevity of the drying oil has been claimed as the responsible component for lengthening the nonstain and dirt pickup effects of a two part silicone polymer sealant (US 5,733,960). Kinami et. al. (US 5,326,816) discloses organopolysiloxane sealants that exhibit reduced staining.

### SUMMARY OF THE INVENTION

20 In a first embodiment, the present invention is directed to a one part, temperature vulcanizable silicone sealant composition comprising a moisture curable polyorganosiloxane polymer and a filler wherein the sealant composition, when cured, exhibits a tensile modulus at 50% elongation of from about 30 pounds per

square inch to about 100 pounds per square inch and exhibits a reduced tendency to stain substrates in contact with the cured sealant.

In a second embodiment, the present invention is directed to a silicone sealant, comprising:

- 5           (a) a moisture curable organopolysiloxane component, comprising a mixture or reaction product of:
- (i) an organopolysiloxane polymer comprising, on average, from greater than 1 to less than 2 reactive sites per molecule, wherein greater than about 90 parts by weight per 100 parts  
10           by weight of organopolysiloxane polymer has at least one reactive site per molecule, and
- (ii) a polyfunctional organosilicon compound comprising one or hydrolyzable groups per molecule and at least one functional group that is capable of reacting with the reactive sites of the  
15           organopolysiloxane polymer,
- (b) a condensation cure catalyst, and
- (c) a filler.

20           In a third embodiment, the present invention is directed to a silicone sealant comprises a moisture curable organopolysiloxane component, comprising a mixture or reaction product of:

- (i) a mixture of one or more linear organopolysiloxane polymers having one hydrolyzable silyl end group and one non-hydrolyzable silyl end group per molecule and a linear organopolysiloxane polymer having two hydrolyzable silyl end groups per molecule, wherein the mixture  
25           comprises, on average, from greater than 1 to less than 2 hydrolyzable silyl end group per molecule, and

- (ii) a polyfunctional organosilicon compound comprising two or more hydrolyzable groups per molecule.

The composition of the present invention, when cured, exhibits a reduced tendency to stain or bleed into substrates and a reduced tendency to pick-up dirt on the surface of the sealant.

#### DETAILED DESCRIPTION OF THE INVENTION

In a preferred embodiment the composition of the present invention contains, based on 100 parts by weight ("pbw"), of the composition, no more than 10 pbw more preferably, no more than 5 pbw, still more preferably no more than 2 pbw non-curable plasticizers. Most preferably, the composition of the present invention contains no or substantially no conventional non-curable plasticizers. Non-curable plasticizers are compounds that are useful to reduce the tensile modulus of the cured sealant composition and that are substantially chemically inert components of the sealant composition, i.e., that have no functional groups that are capable of reacting with the moisture curable organopolysiloxane polymer under moisture cure conditions. Suitable non-curable plasticizers include, for example, polyorganosiloxane plasticizers, such as, for example, trimethylsilyl-terminated polydimethylsiloxane polymers, and organic plasticizer compounds, such as, for example, dioctyl phthalate.

In a preferred embodiment, the sealant of the present invention, when cured, exhibits a tensile modulus at 50% elongation, determined according to ASTM D412, of from about 30 pounds per square inch ("psi") to about 100 psi, more preferably, from about 45 pounds per square inch ("psi") to about 65 psi, and still more preferably from about 45 psi to about 55 psi.

In a preferred embodiment, the silicone sealant of the present invention comprises, based on 100 parts by weight of the sealant composition, from 20 pbw to 90 pbw, more preferably from 30 pbw to 75 pbw, even more preferably from 40

pbw to 60 pbw, of the moisture curable organopolysiloxane polymer, from 0.1 pbw to 10 pbw, more preferably from 1 pbw to 7 pbw, even more preferably from 3 pbw to 5 pbw, of the catalyst and from 1 pbw to 80 pbw, more preferably from 2 pbw to 78 pbw, even more preferably from 3 pbw to 65 pbw, of the filler.

5           The organopolysiloxane polymer may be any organopolysiloxane polymer having, on average, from greater than 1 to less than 2, more preferably from 1.1 to 1.9 and even more preferably from 1.3 to 1.7, reactive sites per molecule. In a preferred embodiment, based on 100 pbw of the organopolysiloxane polymer, greater than or equal to about 95 pbw, more preferably greater than or equal to  
10           about 98 pbw, even more preferably greater than or equal to about 99 pbw and most preferably, substantially all, of the organopolysiloxane polymer has at least one reactive site per molecule. Suitable reactive sites are silicon-bonded substituents, such as for example, hydrogen atoms, alkenyl groups and hydrolyzable groups which are reactive with the primary functional groups of the polyfunctional  
15           organosilicon component of the present invention, as further described below, under selected reaction conditions or under processing conditions anticipated during compounding of the composition of the present invention or under moisture cure conditions. Suitable hydrolyzable groups, include, for example, hydroxy, alkoxy, oximo, amino, aminoxy and acyloxy groups.

20           In a first preferred embodiment, the organopolysiloxane polymer comprises a mixture of an organopolysiloxane polymer having two reactive sites per molecule and an organopolysiloxane polymer having one reactive site per molecule. In a second preferred embodiment, the organopolysiloxane consists essentially of a mixture of an organopolysiloxane polymer having two reactive sites per molecule  
25           and an organopolysiloxane polymer having one reactive site per molecule. In a third preferred embodiment, the organopolysiloxane polymer consists of a mixture of an organopolysiloxane polymer having two reactive sites per molecule and an organopolysiloxane polymer having one reactive site per molecule.

In a first preferred embodiment, the organopolysiloxane mixture comprises one or more linear organopolysiloxane polymers having two reactive sites per molecule and one or more linear organopolysiloxane polymers having one reactive site per molecule. In a second preferred embodiment, the organopolysiloxane mixture consists essentially of one or more linear organopolysiloxane polymers having two reactive sites per molecule and one or more linear organopolysiloxane polymers having one reactive site per molecule. In a third preferred embodiment, the organopolysiloxane mixture consists of one or more linear organopolysiloxane polymers having two reactive sites per molecule and one or more linear organopolysiloxane polymers having one reactive site per molecule.

In the case of mixtures of linear organopolysiloxane polymers having two reactive sites per molecule and one or more linear organopolysiloxane polymers having one reactive site per molecule, the relative amount of reactive sites can be expressed in an alternative way, that is, it is preferred that from 50% to 99%, more preferably from 60% to 95%, still more preferably from 70% to 90% of the terminal silicon atoms of the linear organopolysiloxane polymers are substituted with reactive substituent groups, such as, for example, a hydrolyzable group, and from 1% to 50%, more preferably from 20 to 40%, still more preferably from 10% to 30% of the of the linear organopolysiloxane polymers are substituted with non-reactive substituent groups, such as for example, alkyl groups.

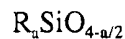
Suitable organopolysiloxane polymers are made by conventional polymerization techniques, wherein the relative amount of reactants are controlled to provide an organopolysiloxane polymer having a selected amount of reactive sites per molecule.

In a preferred embodiment, a silicon bonded hydroxy, that is, silanol, functional organopolysiloxane polymer is made by a base catalyzed equilibration/chain extension polymerization reaction of a cyclic polysiloxane, such as, for example, octamethylcyclotetrasiloxane, and a trialkyl-stopped

polydialkylsiloxane polymer, such as, for example, trimethyl-stopped polydimethylsiloxane, wherein a stoichiometric amount of water is added to the reaction mixture to arrive at a selected average silanol content. The product of the polymerization reaction is then neutralized with phosphoric acid.

5 In a preferred embodiment, the organopolysiloxane polymer exhibits a viscosity of from 5,000 to 500,000 centiPoise (“cp”), preferably from 20,000 to 150,000 cp, and more preferably from 40,000 to 80,000 cp, at 25 °C.

In a preferred embodiment, the organopolysiloxane polymer comprises a mixture of two or more silicone polymers or copolymers having structural units according to structural formula (I):



wherein each R is independently H, hydroxyl or a monovalent hydrocarbon radical hydroxyl, wherein  $0 \leq a \leq 4$ , provided that at least one R group per molecule of the organopolysiloxane polymer is H, hydroxyl or alkenyl and, on average, more than 1 and less than 2 R groups per molecule of the organopolysiloxane polymer are each H, hydroxyl or alkenyl.

Suitable monovalent hydrocarbon radicals include monovalent acyclic hydrocarbon radicals, monovalent alicyclic hydrocarbon radicals and monovalent aromatic hydrocarbon radicals.

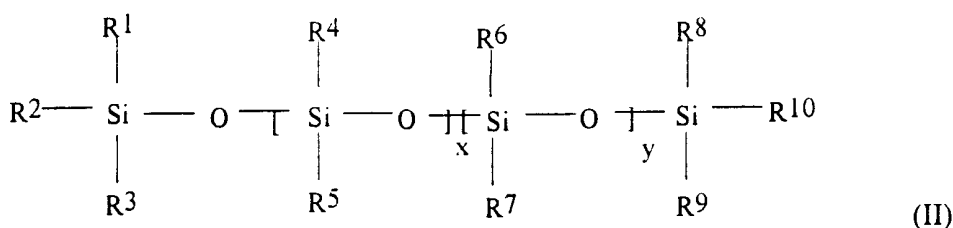
20 As used herein, the terminology “monovalent acyclic hydrocarbon radical” means a monovalent straight chain or branched hydrocarbon radical, preferably containing from 1 to 20 carbon atoms per radical, which may be saturated or unsaturated and which may, optionally, be substituted, for example with one or more halo groups. Suitable monovalent acyclic hydrocarbon radicals include, for example, alkyl radicals, such as, for example, methyl, ethyl, sec-butyl, tert-butyl, 25 octyl, dodecyl, stearyl and eicosyl, haloalkyl, such as trifluoropropyl, alkenyl

radicals, such as, for example, ethenyl and propenyl, and alkynyl radicals, such as, for example, propynyl and butynyl.

As used herein, the terminology “alicyclic hydrocarbon radical” means a radical containing one or more saturated hydrocarbon rings, preferably containing from 6 to 10 carbon atoms per ring, per radical which may optionally be substituted on one or more of the rings with one or more alkyl groups, each preferably containing from 2 to 6 carbon atoms per group and which, in the case of two or more rings, may be fused rings. Suitable monovalent alicyclic hydrocarbon radicals include, for example, cyclohexyl and cyclooctyl.

As used herein, the terminology “monocyclic aromatic hydrocarbon radical” means a hydrocarbon radical containing one aromatic ring per radical, which may optionally be substituted on the aromatic ring with one or more alkyl groups, each preferably containing from 2 to 6 carbon atoms per group. Suitable monovalent aromatic hydrocarbon radicals include, for example, phenyl, tolyl, xylyl, 2,4,6-trimethylphenyl and naphthyl.

In a highly preferred embodiment, the organopolysiloxane polymer comprises a mixture of two or more linear polymers or copolymers of the structural formula (II):



wherein:

each R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> is independently H, hydroxyl or a monovalent hydrocarbon radical, provided that at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> per molecule is H,

hydroxyl or alkenyl and, on average based on all molecules of the mixture, more than 1 and less than 2 of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> per molecule are each H, hydroxyl or alkenyl, and

5 m is selected to provide a polymer that exhibits a viscosity of from 5,000 to 500,000 cp at 25 °C.

In a preferred embodiment, each R<sup>1</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> is independently (C<sub>1</sub>-C<sub>8</sub>)alkyl, fluoroalkyl or phenyl and each R<sup>2</sup> and R<sup>10</sup> is hydroxyl, (C<sub>1</sub>-C<sub>8</sub>)alkyl, fluoroalkyl or phenyl.

10 In a preferred embodiment, each R<sup>1</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> is independently (C<sub>1</sub>-C<sub>8</sub>)alkyl, fluoroalkyl or phenyl and each R<sup>2</sup> and R<sup>10</sup> is H, alkenyl, (C<sub>1</sub>-C<sub>8</sub>)alkyl, fluoroalkyl or phenyl.

Suitable polyfunctional organosilicon compounds are those that contain a primary functional group such, as for example, an H, alkoxy or alkenyl group, that capable of reacting with the reactive sites of the organopolysiloxane polymer under  
15 selected reaction conditions or under processing conditions anticipated during compounding of the composition of the present invention or under moisture cure conditions, and that contain one or more secondary functional groups per molecule, preferably hydrolyzable groups, such as, for example, alkoxy, oximo, amino, aminoxy or acyloxy groups, each of which is reactive under room temperature  
20 vulcanization conditions to thereby allow moisture curing of the sealant composition. The polyfunctional organosilicon compounds can be silanes of partially hydrolyzed products of silanes.

Suitable polyfunctional organosilicon compound include, for example, vinyltrimethoxysilane, tetramethoxysilane, methyltriethoxysilane, tetraethoxysilane,  
25 methyltrimethoxysilane, methylphenyldiethoxysilane, 3,3,3-trifluoropropyltrimethoxysilane, methyl(tri(methylethylketoximo)silane,

ethyl(tri(N,N-diethylamino)silane, methyltri(N-methylacetamido)silane, n-propylorthosilicate and ethylpolysilicate.

In a preferred embodiment, the polyfunctional organosilicon compound is one according to the structural formula (III):



wherein:

each  $R^{11}$  is independently H, alkoxy, alkenyl, oximo, amino, aminoxy, acyloxy or a monovalent hydrocarbon radical, provided that at least one  $R^{11}$  is H, alkoxy or alkenyl and that at least one other  $R^{11}$  is alkoxy, oximo, amino, aminoxy or acyloxy.

In a first preferred embodiment, at least three  $R^{11}$  substituents are each alkoxy, more preferably  $(C_1-C_8)$ alkoxy, even more preferably, methoxy or ethoxy, and the remaining  $R^{11}$  substituent, if any, is  $(C_1-C_8)$ alkyl,  $(C_2-C_8)$ alkenyl, aryl or fluoroalkyl. Preferred polyfunctional organosilicon compounds include, for example, vinyltrimethoxysilane, tetramethoxysilane, methyltriethoxysilane, tetraethoxysilane, methyltrimethoxysilane. Most preferably, polyfunctional organosilicon compound comprises methyltrimethoxysilane.

In a second preferred embodiment, one  $R^{11}$  is H or alkenyl, at least two  $R^{11}$  substituents are each alkoxy, more preferably  $(C_1-C_8)$ alkoxy, even more preferably, methoxy or ethoxy, and the remaining  $R^{11}$  substituent, if any, is  $(C_1-C_8)$ alkyl, aryl or fluoroalkyl. Preferred polyfunctional organosilicon compounds include, for example, vinyltrimethoxysilane, vinyltriethoxysilane .

In a preferred embodiment, the moisture curable organopolysiloxane polymer is made by reaction of 100 pbw of a functional organopolysiloxane polymer with from about 1.0 to about 30 pbw, more preferably from about 2.0 to

about 15 pbw, and most preferably from about 3.0 to about 10 pbw of the polyfunctional organosilicon compound.

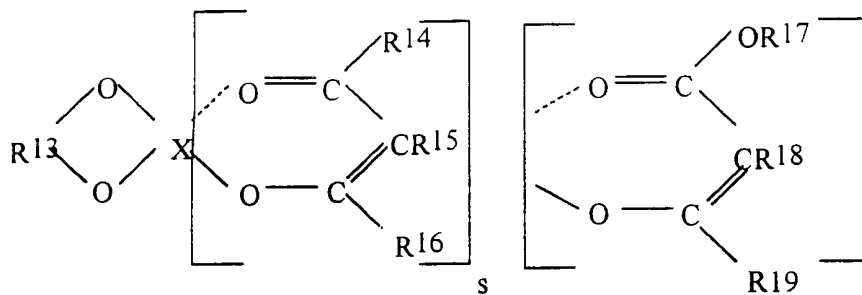
In a preferred embodiment, a suitable moisture curable organopolysiloxane polymer is formed during compounding of the composition of the present invention by an in situ condensation reaction of a silanol, that is, silicon bonded hydroxy, organopolysiloxane polymer with a polyfunctional organosilicon compound having alkoxy primary functional groups.

Alternatively, a suitable moisture curable organopolysiloxane polymer is formed by reacting the organopolysiloxane polymer with the polyfunctional organosilicon compound prior to addition to the composition of the present invention. In a first embodiment, the moisture curable organopolysiloxane polymer is formed by a condensation reaction of a hydroxy functional organopolysiloxane polymer with a polyfunctional organosilicon compound having alkoxy primary functional groups in the presence of a condensation cure catalyst, such as for example a condensation cure catalyst as described in more detail below. In a second embodiment, the moisture curable organopolysiloxane polymer is formed by an addition reaction of (i) an alkenyl functional organopolysiloxane polymer with a polyfunctional organosilicon compound having hydride primary functional groups or (ii) a hydride functional organopolysiloxane polymer with a polyfunctional organosilicon compound having alkenyl primary functional groups under hydrosilylation conditions in the presence of a suitable hydrosilylation catalyst, such as, for example a platinum or rhodium-containing hydrosilylation catalyst.

The condensation cure catalyst of the composition of the present invention are those that, in the presence of moisture, catalyze the room temperature crosslinking of the crosslinkable organopolysiloxane polymer. Suitable condensation cure catalysts include, for example, dialkyltin carboxylates, such as, for example, dibutyl tin dilaurate, dibutyl tin diacetate, and tin-2-ethylhexanoate, alkyl titanates, such as for example, tetrabutyl tin titanate, tetra-n-propyl titanate,

and organosiloxy titanium compounds. Various other condensation catalysts are known in the art.

In a preferred embodiment, the condensation cure catalyst comprises a compound according to structural formula (IV):



wherein:

X is titanium, lead, tin, zirconium, antimony, iron, cadmium, barium, manganese, zinc, chromium, cobalt, nickel, aluminum, gallium or germanium;

10

$R^{13}$  is a divalent, optionally substituted, hydrocarbon radical;

$R^{14}$ ,  $R^{16}$  and  $R^{19}$  are each independently a monovalent hydrocarbon radical;

$R^{15}$  and  $R^{18}$  are each independently H or a monovalent hydrocarbon radical;

$R^{17}$  is a monovalent hydrocarbon radical, amino, ether, or a polyether group of the formula  $(C_qH_{2q}O)_vR^{20}$ .

15

$R^{20}$  is a monovalent hydrocarbon radical;

q and v are each integers, wherein  $2 \leq q \leq 4$  and  $1 \leq v \leq 20$ ; and

s and t are each numbers, wherein  $0.7 \leq s \leq 1.3$ ; and  $0.8 \leq t \leq 1.2$ .

In a preferred embodiment, X is titanium.

In a preferred embodiment, s and t are each 1.

In a highly preferred embodiment, R<sup>13</sup> is a divalent hydrocarbon radical of 2 to 20 carbon atoms, more preferably 2-10 carbon atoms, per group, optionally substituted with halo, cyano, nitro, carboxyl, carboxy ester, acyl halohydrocarbon or hydrocarbon substituent groups of up to 8 carbon atoms per group.

In preferred embodiment, X is titanium, R<sup>13</sup> is propyl, R<sup>15</sup> and R<sup>18</sup> are each H, R<sup>14</sup> R<sup>16</sup> and R<sup>19</sup> are each methyl and R<sup>17</sup> is ethyl.

The preparation of compounds according to structural formula (III) is described in U.S. Patent Nos. 3,689,454 and 3,779,986.

In a preferred embodiment, the composition of the present invention comprises from 0.1 to 10 pbw, preferably from 1 to 7 pbw, and most preferably from 3 to 5 pbw of the condensation cure catalyst.

The filler component of the composition of the present invention comprises a reinforcing filler, a semi-reinforcing filler, a non-reinforcing filler or a mixture thereof.

In a preferred embodiment, the filler of the present invention comprises a reinforcing filler. Suitable reinforcing fillers include, for example, fumed silica, surface-treated, for example, hydrophobicized, fumed silica, carbon black, titanium dioxide, ferric oxide, aluminum oxide, as well as other metal oxides and are commercially available from a number of sources. In a preferred embodiment, the reinforcing filler comprises fumed silica.

In a preferred embodiment, the silicone sealant of the present invention comprises, based on 100 parts by weight of the sealant composition, from 1 pbw to 10 pbw, more preferably from 2 pbw to 8 pbw, even more preferably from 3 pbw to 5 pbw, of a reinforcing filler.

The filler may, optionally, comprise a semi-reinforcing or non-reinforcing filler. Suitable semi-reinforcing or non-reinforcing fillers include, for example, quartz, precipitated silica, hydrophobicized precipitated silica, calcium carbonate and are commercially available from a number of sources. In a preferred  
5 embodiment, the semi-reinforcing or non-reinforcing filler comprises calcium carbonate.

In a preferred embodiment, the silicone sealant of the present invention comprises, based on 100 parts by weight of the sealant composition, from 0 pbw to 70 pbw, more preferably from 30 pbw to 60 pbw, even more preferably from 40  
10 pbw to 60 pbw, of a semi-reinforcing or non-reinforcing filler.

The composition of the present invention may, optionally, further comprise a hydrocarbon fluid to adjust the viscosity of the composition. The hydrocarbon fluid may be any (C<sub>5</sub>-C<sub>24</sub>)hydrocarbon fluid, including aliphatic, alicyclic and aromatic (C<sub>5</sub>-C<sub>24</sub>)hydrocarbon fluids, such as for example, heptane, eicosane, cyclohexane,  
15 cyclooctane, benzene and toluene or a mixture of such fluids. In a preferred embodiment, the hydrocarbon fluid comprises one or more linear or branched (C<sub>5</sub>-C<sub>24</sub>)alkanes, more preferably one or more linear (C<sub>10</sub>-C<sub>18</sub>)alkanes. Suitable hydrocarbon fluids include, for example, heptane, hexane, octane, nonane, decane, undecane, dodecane, heptadecane, octadecane, eicosane. In a preferred  
20 embodiment, the composition of the present invention comprises from 1 pbw to 40 pbw, more preferably from 2 pbw to 20 pbw, even more preferably from 3 pbw to 10 pbw, of the hydrocarbon fluid.

The silicone sealant composition of the present invention may, optionally, further comprise other known components, such as, for example, dyes, pigments  
25 anti-oxidants, UV stabilizers, adhesion-enhancing agents, thermal stabilizing agents, biocides, non-silicone polymers, can be used in this composition, as long as they do not interfere with the non staining, dirt pickup or other properties of the silicone sealant composition.

The composition of the present invention is made by combining and mixing the components of the composition. The mixing may be conducted as a batch process or as a continuous process and any convenient mixing apparatus, such as for example, a planetary mixer, may be used to mix the components. In a preferred embodiment, the composition of the present invention is made by continuously  
5 compounding the composition in an extruder, preferably a twin screw extruder.

The composition of the present invention is used by exposing the composition to ambient moisture and allowing the composition to cure. Preferably, the composition is maintained in moisture-impervious packaging up until the time of  
10 use. In a preferred embodiment, the composition is used to seal a gap between a first substrate and a second substrate, wherein the second substrate is spaced apart from the first substrate to form a gap, by applying an amount of the composition effective to bridge the gap and allowing the composition to cure in place to form an elastomeric seal between the substrates.

15 An assembly, comprising a first substrate, a second substrate, spaced apart from the first substrate, and a cured silicone sealant composition of the present invention disposed between the first and second substrates and bonded to each of the substrates, wherein the assembly exhibits an improved resistance to staining and dirt pick up.

20 In a preferred embodiment, at least one of the first and second substrates is a porous substrate, such as, for example, a marble, concrete, granite, sandstone, or limestone substrate.

#### Example 1 and Comparative Examples C1 - C6

25 The composition of Example 1 was made by combining, based on 100 pbw total sealant composition, the following components in a Werner-Pfleiderer twin screw extruder:

- 5 (a) 44.4 pbw of an organopolysiloxane polymer (a hydroxy-terminated dimethylsiloxane polymer containing, based on the total weight of endgroups, 18.6 wt% trimethylsilyl endgroups and 81.4 wt % dimethylsilanol endgroups (about 1.63 silicone-bonded hydroxy groups per molecule) groups and exhibiting a viscosity of a 54,000 centiPoise);
- (b) 5.0 pbw of a reinforcing filler (octamethylcyclotetrasiloxane-treated fumed silica);
- 10 (c) 43.0 pbw of a non-reinforcing filler (stearic acid treated calcium carbonate filler, Hi-Pflex 100 from Specialty Minerals Inc),
- (d) 5.0 pbw of a mixture of linear, aliphatic (C<sub>12</sub>-C<sub>15</sub>) hydrocarbons (Conosol D-200, Conoco) ; and
- (e) 2.60 pbw of a liquid blend consisting, based on total weight of the blend, of:
- 15 (i) 57 wt% of a polyfunctional silicon compound (methyltrimethoxysilane),
- (ii) 11 wt% of an adhesion promoter (tris-[3-(trimethoxysilyl)propyl] isocyanurate), and
- 20 (iii) 32 wt% of a curing catalyst (1,3-propanedioxytitanium (ethylacetoacetate-acetylacetonate).

The organopolysiloxane polymer, fumed silica and calcium carbonate were continuously fed into barrel 1 of the extruder. The hydrocarbon fluid and liquid blend were added further downstream. A vacuum was applied at barrel 12. The extruder processing temperature was maintained at 75°C from barrel 1 to barrel 11. 25 Barrels 12-14 were cooled such that the RTV sealant exited the extruder at between 25-35°C.

After standing for 4 days at room temperature, the sealant composition of Example 1 was tested for a variety of rheological and cured physical properties. The ASTM test methods used and test results are listed in TABLE I below.

TABLE I

Property	ASTM Test Method	Ex 1
Specific Gravity	C97	1.36
Application Rate (g/min)	C1183	279
Tack Free Time (hr)	C679	6
1/8 inch cure through time (hr)	--	24
Boeing Flow (in)	D2202	0.10
Properties for 7 Day RT Cured Sheet		
Durometer, Shore A	C661	24
Tensile Strength (psi)	D412	251
Elongation (%)	D412	649
Modulus @ 50% elongation (psi)	D412	56
Peel Adhesion after 14 day cure (ppi/%cohesive failure)	C794	
- on concrete		32/50
- on polished granite		37/100
- on marble		32/100
- on anodized aluminum		28/100
- on glass		29/100
- on Duranar™ coated aluminum		34/100
- on polyacrylate		27/100
- on polycarbonate		30/100

#### Stain Testing

The compositions of Example 1 and Comparative Examples C1 - C6 below were subjected to stain testing according to ASTM C-1248 and according to an extended stain test wherein H-specimens were placed outdoors at a 75° angle, facing upward for an extended period of time.

Ex#	Sealant	Approximate Modulus @ 50% elongation (psi)
C1	Silicone sealant containing polyorganosiloxane plasticizer (trimethylsilyl-terminated polydimethylsiloxane)	56
C2	Silicone sealant containing polyorganosiloxane plasticizer (trimethylsilyl-terminated polydimethylsiloxane)	50
C3	Silicone Sealant (Dow Corning 790)	25
C4	Silicone Sealant (Dow Corning 795)	65
C5	Siliconized polyether sealant containing organic plasticizer (dioctyl phthalate)	35
C6	Siliconized polyether sealant containing organic plasticizer (dioctyl phthalate)	25

TABLE II below shows the stain and dirt pickup properties for the composition of Example 1 and the compositions of Comparative Examples C1- C6.

The following notation is used in the TABLE II: No Staining Detected (+++), Stain Barely Detected (++) , Very Little Stain (+), Stain Noticeable (-), Stain Very Apparent (--), Unacceptable Stain (---).

TABLE II

Ex #	ASTM C-1248 Results	Extended Stain Test Results			
		Initial	1 Month	2 Month	4 Month
1	no stain	+++	+++	+++	+++
C1	significant stain	+++	-	-	--
C2	significant stain	+++	-	-	---
C3	significant stain	+++	++	+	+
C4	significant stain	+++	++	+	+
C5	significant stain	+++	-	-	--
C6	significant stain	+++	++	+	+

The composition of the present invention exhibits a reduced tendency to stain or bleed into substrates and a reduced tendency to pick-up dirt on the surface of the sealant. Sealant compositions that exhibit tensile modulus of less than or equal to 100 psi typically include non-curable plasticizers to adjust the tensile modulus of such compositions. However, the non-curable plasticizers tend to promote staining, bleeding and dirt pick-up. The sealant composition of the present invention exhibits a tensile modulus of less than or equal to 100 psi and, compared to conventional compositions which contain non-curable plasticizers, exhibits a reduced tendency to stain or bleed into substrates and a reduced tendency to pick-up dirt on the surface of the sealant.

Since the composition of the present invention contains only a small to negligible amount of organopolysiloxane polymer lacking reactive sites, the cured sealant composition contains only a small to negligible amount of free organopolysiloxane polymer, that is, substantially all of the organopolysiloxane polymer becomes chemically bound into a crosslinked organopolysiloxane network of cured sealant composition. The use of a selected amount organopolysiloxane polymer having one reactive site per molecule allows control of the crosslink density of the network and tensile modulus of the cured sealant, without requiring the use of the non-curable plasticizers. The cured sealant composition contains substantially no free non-curable plasticizers or organopolysiloxane polymer species that can then bleed from the sealant and into the substrate and stain the substrate. It is believed that the substantial absence of non-curable plasticizers and free organopolysiloxane polymer species increases the surface tension of exposed surfaces of the cured sealant composition and thereby reduces its affinity for dirt, grime, carbon and other pollutants.

## CLAIMS

1. A one part room, temperature vulcanizable silicone sealant composition, comprising a moisture curable polyorganosiloxane polymer and a filler wherein the sealant composition, when cured, exhibits a tensile modulus at 50% elongation of from about 30 pounds per square inch to about 100 pounds per square inch and exhibits a reduced tendency to stain substrates in contact with the cured.
2. The composition of claim 1, wherein, based on 100 parts by weight of the composition, no more than 10 parts by weight non-curable plasticizers.
3. A silicone sealant, comprising:
- (a) a moisture curable organopolysiloxane component, comprising a mixture or reaction product of:
- (i) an organopolysiloxane polymer comprising, on average, from greater than 1 to less than 2 reactive sites per molecule, wherein greater than about 90 parts by weight per 100 parts by weight of organopolysiloxane polymer has at least one reactive site per molecule, and
- (ii) a polyfunctional organosilicon compound comprising one or hydrolyzable groups per molecule and at least one functional group that is capable of reacting with the reactive sites of the organopolysiloxane polymer,
- (b) a condensation cure catalyst, and
- (c) a filler.
4. The sealant composition of claim 3, wherein the sealant composition comprises, based on 100 parts by weight of the sealant composition, from 20 parts by weight to 90 parts by weight of the moisture curable organopolysiloxane

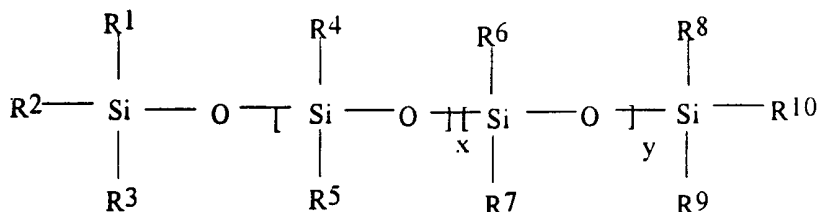
polymer, from 0.1 parts by weight to 10 parts by weight, of the catalyst and from 1 parts by weight to 80 parts by weight of the filler.

5. The composition of claim 3, wherein reactive sites of the organopolysiloxane polymer are silicon-bonded hydrogen, hydroxyl or alkenyl substituents.

5

6. The composition of claim 3, wherein the organopolysiloxane polymer exhibits a viscosity of from 5,000 to 500,000 centiPoise.

7. The composition of claim 3, wherein the organopolysiloxane polymer comprises a mixture of two or more linear polymers or copolymers of the structural formula:



wherein:

each R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> is independently H, hydroxyl or a monovalent hydrocarbon radical, provided that at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> per molecule is H, hydroxyl or alkenyl and, on average based on all molecules of the mixture, more than 1 and less than 2 of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup>, R<sup>9</sup> and R<sup>10</sup> per molecule are each H, hydroxyl or alkenyl, and

m is selected to provide a polymer that exhibits a viscosity of from 5,000 to 500,000 cp at 25 °C.

8. The composition of claim 7, wherein each R<sup>1</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> is independently (C<sub>1</sub>-C<sub>8</sub>)alkyl, fluoroalkyl or phenyl and each R<sup>2</sup> and R<sup>10</sup> is hydroxyl, (C<sub>1</sub>-C<sub>8</sub>)alkyl, fluoroalkyl or phenyl.

9. The composition of claim 7, wherein each R<sup>1</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> is independently (C<sub>1</sub>-C<sub>8</sub>)alkyl, fluoroalkyl or phenyl and each R<sup>2</sup> and R<sup>10</sup> is H, alkenyl, (C<sub>1</sub>-C<sub>8</sub>)alkyl, fluoroalkyl or phenyl.

10. The composition of claim 3 wherein organopolysiloxane polymer comprises, on average, from 1.1 to 1.9 reactive sites per molecule.

11. The composition of claim 3 wherein organopolysiloxane polymer comprises, on average, from 1.3 to 1.7 reactive sites per molecule.

5 12. The composition of claim 3, wherein the polyfunctional organosilicon compound is one according to the structural formula:



10 wherein each  $R^{11}$  is independently H, alkoxy, alkenyl, oximo, amino, aminoxy, acyloxy or a monovalent hydrocarbon radical, provided that at least one  $R^{11}$  is H, alkoxy or alkenyl and that at least one other  $R^{11}$  is alkoxy, oximo, amino, aminoxy or acyloxy.

15 13. The composition of claim 12, wherein at least three  $R^{11}$  substituents are each alkoxy, more preferably  $(C_1-C_8)$ alkoxy, even more preferably, methoxy or ethoxy, and the remaining  $R^{11}$  substituent, if any, is  $(C_1-C_8)$ alkyl,  $(C_2-C_8)$ alkenyl, aryl or fluoroalkyl.

14. The composition of claim 13, wherein the polyfunctional organosilicon compound comprises vinyltrimethoxysilane, tetramethoxysilane, methyltriethoxysilane, tetraethoxysilane, methyltrimethoxysilane or a mixture thereof.

20 15. The composition of claim 12, wherein one  $R^{11}$  is H or alkenyl, at least two  $R^{11}$  substituents are each alkoxy, more preferably  $(C_1-C_8)$ alkoxy, even more preferably, methoxy or ethoxy, and the remaining  $R^{11}$  substituent, if any, is  $(C_1-C_8)$ alkyl, aryl or fluoroalkyl.

25 16. The composition of claim 15, wherein the polyfunctional organosilicon compound comprises vinyltrimethoxysilane, vinyltriethoxysilane or a mixture thereof.

17. The composition of claim 3, wherein the filler comprises fumed silica, hydrophobicized fumed silica, carbon black, titanium dioxide, ferric oxide, aluminum oxide quartz, precipitated silica, hydrophobicized precipitated silica, calcium carbonate or a mixture thereof.

5 18. The composition of claim 3, further comprising a (C<sub>5</sub>-C<sub>24</sub>)hydrocarbon fluid.

19. The composition of claim 3, wherein the sealant composition comprises from 1 parts by weight to 40 parts by weight (C<sub>5</sub>-C<sub>24</sub>)hydrocarbon per 100 parts by weight of the sealant composition.

10 20. An assembly, comprising a first substrate, a second substrate, spaced apart from the first substrate, and a cured mass of a silicone sealant composition according to claim 3 disposed between the first and second substrates and bonded to each of the substrates.

15 21. The assembly of claim 20 wherein at least one of the first and second substrates is a porous substrate.

22. The assembly of claim 20 wherein the porous substrate is a marble, concrete, granite, sandstone, or limestone substrate.

23. A silicone sealant, comprising a moisture curable organopolysiloxane component, comprising a mixture or reaction product of:

- 5 (i) a mixture of one or more linear organopolysiloxane polymers having one hydrolyzable silyl end group and one non-hydrolyzable end group per molecule and a linear organopolysiloxane polymer having two hydrolyzable silyl end groups per molecule, wherein the mixture comprises, on average, from greater than 1 to less than 2 hydrolyzable silyl end group per molecule, and
- 10 (ii) a polyfunctional organosilicon compound comprising two or more hydrolyzable groups per molecule.

24. The sealant composition of claim 23, further comprising: (b) a condensation cure catalyst, and (c) a filler.

15 25. The sealant composition of claim 24, wherein the sealant composition comprises, based on 100 parts by weight of the sealant composition, from 20 parts by weight to 90 parts by weight of the moisture curable organopolysiloxane polymer, from 0.1 parts by weight to 10 parts by weight, of the catalyst and from 1 parts by weight to 10 parts by weight of the reinforcing filler.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/31577

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C08L83/04 C09D183/04

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)

IPC 7 C08L C09D

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 718 369 A (DOW CORNING) 26 June 1996 (1996-06-26)	3-8, 10-12, 20, 23, 24
Y	page 6, line 12 -page 9, line 1; examples ---	1-25
X	US 4 618 646 A (TAKAGO TOSHIO ET AL) 21 October 1986 (1986-10-21) abstract column 1, line 55-64; examples 1,2; tables 1,2 ---	1, 2
X	EP 0 799 860 A (DOW CORNING) 8 October 1997 (1997-10-08) page 2, line 5-22; example; table --- -/--	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

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PCT/US 00/31577

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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