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(54) Title: ONE-PART ROOM TEMPERATURE VULCANIZING COMPOSITIONS WITH IMPROVED OIL RESISTANCE AND ADHESION

(57) Abstract

A diorganopolysiloxane polymer, an M-stopped fluid, a silica filler, a calcium carbonate filler, and gammaaminopropyl triethoxysilane cures at room temperature in the presence of a tin catalyst and a cross-linking agent to form an RTV elastomer having good adhesion and retainable tensile strength in the presence of hot engine oil.

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"ONE-PART ROOM TEMPERATURE VULCANIZING COMPOSITIONS WITH IMPROVED OIL RESISTANCE AND ADHESION"

BACKGROUND OF THE INVENTION

The present invention relates to one-part room temperature vulcanizing (RTV) silicone rubber compositions which are suitable for formed in place gasket (FIPG) applications. More particularly, the invention relates to RTV rubber compositions having good resistance to hot engine oil and good adhesion to metal parts and which are especially adapted for automotive applications. The materials also have improved retention of tensile strength in adverse environments.

RTV rubber compositions are known in the art. Such compositions are known for their ability to resist change at elevated temperatures and exposure to adverse conditions over extended periods of time. In general, materials are needed which have the outstanding properties such as good tensile strength and also retain such properties after prolonged exposure to chemical agents known to reduce or diminish their performance. In particular applications, such as gasketing applications in automobile engines, good adhesion at room temperature, tensile strength, fast curing and oil resistance are essential.

Efforts have been made in the past to produce RTV silicone elastomer compositions having increased strength and adhesion.

U.S. Patent No. 4,514,529 to Beers et al. discloses a low modulus one component RTV silicone elastomer composition having oil resistance and high elongation. The silicone elastomer is formed of a silanol terminated diorganosiloxane base polymer, a tin catalyst, an oxime cross-linking agent and low moisture fillers including stearic acid treated calcium

carbonate. The material is useful as a gasket sealant as well as an FIPG in an automobile engine. According to Beers et al., column 6, lines 12-18, the compositions containing stearic acid treated $CaCO_3$ have a modulus value at 50% of 75 psi or less; at 75% the modulus is 70 psi or less; and at 100% the modulus is 110 psi with 90 psi being preferred.

Lucas et al., U.S. Patent No. 4,523,353 discloses adhesion promoters for one component RTV silicone compositions. Exemplary materials include a variety of diverse substances including gamma-aminopropyl triethoxysilane (GAP). The materials are useful in alkoxy functional RTV materials. Ketoxime materials are not discussed.

Although one-part RTV compositions having reasonably good tensile strength and oil resistance are known in the art, it is desirable to provide improved RTV compositions having improved tensile strength, fast cure rates and good room temperature adhesion and which retain strength in the presence of hot engine oil.

It is therefore an object of the present invention to provide one-part RTV rubber composition having good room temperature adhesion and improved tensile strength properties which are retained in the presence of oil.

SUMMARY OF THE INVENTION

The present invention is based upon the discovery that a combination of a diorganopolysiloxane polymer, an M-stopped fluid, a silica filler, a calcium carbonate filler, and gamma-aminopropyl triethoxysilane will cure at room temperature in the presence of a catalyst and a cross-linking agent to form an RTV elastomer having good room temperature adhesion and

improved and retainable tensile strength in the presence of hot engine oil.

In a particular embodiment, the invention comprises (A) a base composition including (A1) 100 parts by weight of a diorganopolysiloxane polymer having a viscosity ranging from about 600 to about 300,000 cps at 25°C; (A2) from about 3 to about 25 parts by weight based upon (A1) of a silica filler; (A3) up to about 80 parts by weight based upon (A1) of an M-stopped fluid having a viscosity ranging from about 50 to about 10,000 cps at 25°C; and (A4) up to about 200 parts by weight based upon (A1) of a calcium carbonate filler preferably treated with 1% weight stearic acid. In addition, the RTV composition also includes (B) a catalyst solution comprising (B1) up to about 0.5 parts by weight based upon (A) of a tin based catalyst; (B2) from about 2 to about 15 parts by weight based upon (A) of a cross-linking agent comprising (a) a methyltris(methylethylketoximo)silane or (b) a vinyltris(methylethylketoximo)silane or mixtures of (a) and (b); and (B3) from about 0.1 to about 4 parts by weight based upon (A) of a gamma-aminopropyl trimethoxysilane adhesion promoter.

The RTV compositions of the invention have improved room temperature adhesion properties and importantly retain tensile strength in the presence of hot oil.

DETAILED DESCRIPTION OF THE INVENTION:

The present invention is directed to an RTV curable silicone composition having good adhesion properties and improved tensile strength which is retained in the presence of hot oil. The composition contains (A) a base composition formed of (A1) a

diorganopolysiloxane polymer having a viscosity ranging from about 600 to about 300,000 cps at 25°C; (A2) a silica filler; (A3) an M-stopped fluid; and (A4) a calcium carbonate filler. The base composition (A) is mixed with (B) a catalyst solution including (B1) a tin based catalyst; (B2) a methyl or vinyltris(methylethylketoximo)silane cross-linking agent; and (B3) a gamma-aminopropyl triethoxysilane adhesion promoter.

In accordance with the invention, (A1) is a silanol terminated diorganopolysiloxane having a viscosity ranging from about 600 to about 300,000, preferably from about 2,000 to 200,000 and more preferably from about 3,000 to about 150,000 cps at 25°C. (A1) has the formula:

$$HOR_2SiO(R_2SiO)_xSiR_2OH$$

where R is independently selected from monovalent hydrocarbon radicals, free of aliphatic unsaturation containing from 1 to about 8 carbon atoms and x varies so that (A1) has a viscosity ranging from about 600 to about 300,000 cps at 25°C. In the examples below, x is selected so that (A1a) has a viscosity of about 15,000 cps at 25°C and (A1b) has a viscosity of about 30,000 cps at 25°C.

(A2) comprises from about 3 to about 25, preferably from about 3 to about 20 and more preferably from about 5 to about 15 parts by weight based upon (A1) of a reinforcing filler such as fumed silica (SiO_2). The filler preferably has a surface area of between 100 and 300 m^2/gm, more preferably, the surface area is about 200 m^2/gm in the untreated state. The

filler may be treated with various agents so as to prevent the composition from structuring, for example, cyclopolysiloxanes as disclosed in U.S. Patent No. 2,938,009 to Lucas and silazanes as disclosed in U.S. Patent No. 3,635,743 to Smith, or both. The cyclopolysiloxanes may be, for example, a octamethylcyclotetrasiloxane (D4) present in an amount of about 15 to 20 weight percent of the filler. In the examples below, (A2) is a D4 treated fumed silica treated as in Lucas above having a surface area in the untreated state of about 200 m^2/gm.

(A3) is a processing aid or plasticizer in the form of an MDM fluid. In particular, (A3) is a trimethylsilyl stopped siloxane fluid having a viscosity ranging from about 50 to about 10,000, preferably 50 to 3,000 and more preferably 50 to 1,000 cps at 25°C. In the examples below, the M-stopped fluid is a polymer having the form:

$$R_3Si(OSiR_2)_xOSiR_3$$

where each R is CH_3 and x is selected so that the viscosity is about 100 cps at 25°C.

In the present invention, the processing aid may be present in an amount of up to 80 parts by weight, based upon (A1), preferably up to about 60 parts by weight based upon (A1) and more preferably up to about 40 parts by weight based upon (A1).

(A4) is a calcium carbonate ($CaCO_3$) filler which may be present in an amount up to about 200 parts by weight based upon (A1), preferably from about 50 to about 150 parts by weight based upon (A1) and more preferably about 50 to about 125 parts by weight based

upon (A1). In the examples below, the calcium carbonate filler is treated with stearic acid in an amount of about 1% by weight based upon the filler.

(B1) is a tin based catalyst which may be present in an amount of up to about 0.50 parts by weight based upon 100 parts of the base composition (A). Preferably, the catalyst is present in an amount from about 0.01 to about 0.4 parts by weight based upon (A), and more preferably is present in an amount ranging from about 0.05 to about 0.30 parts based upon (A).

(B2) is a cross-linking agent which may comprise alkyl- or alkenyl- or vinyl-tris(dialkyl- or dialkenyl- or alkylalkenyl-ketoximo)silane. Preferably, (B2) comprises (a) a methyltris(methylethylketoximo)silane or (b) a vinyltris(methylethylketoximo)silane or mixtures of (a) and (b). The cross-linking agent is present in an amount from about 2 to about 15 parts by weight based upon 100 parts of the base composition (A), preferably from 2 to about 10 parts by weight based upon (A), and more preferably from about 3 to about 7 parts by weight based upon (A).

(B3) is gamma-aminopropyl triethoxysilane (GAP) adhesion promoter present in an amount from about 0.1 to about 4 parts by weight based upon 100 parts of the base composition (A). Preferably the GAP is present in an amount from about 0.2 to about 2 parts by weight based upon (A) and more preferably is present in an amount ranging from about 0.3 to about 1.5 parts by weight based upon (A).

The following examples demonstrate the effect of the present invention. Examples 1 and 2 describe the preparation and testing of sealants which do not contain calcium carbonate but do contain GAP. Examples

3-5 describe the preparation and testing of sealants according to the present invention which contain both calcium carbonate and GAP. Examples 6 and 7 have no calcium carbonate or GAP. In Example 7, a tetrakis(methylethylketoximo)silane is substituted for the GAP.

Example 1

An extruder was set up to combine the following ingredients in the following proportions:

(A) base composition:

(A1a) silanol polymer (approximately 15,000 cps at 25°C) $HOR_2SiO(R_2SiO)_xSiR_2OH$ - 100 parts by weight;

(A2) D4 treated fumed silica, 200 m^2/gm in the untreated state - 13 parts by weight based upon A1;

(A3) M-stopped fluid (plasticizer) - 5 parts by weight based upon (A1).

The above materials were added to the extruder to constitute the base composition.

(B) Catalyst solution - 4.85 parts by weight based upon 100 parts (A) is added to the base composition in the following proportions:

(B1) (a) methyltris(methylethylketoximo)silane (MOS) - 3 parts by weight based upon 100 parts of the base composition;

(B1) (b) vinyltris(methylethylketoximo)silane (VOS) - 1 part by weight based upon 100 parts of the base composition (A);

(B2) gamma-aminopropyl triethoxysilane - 0.75 parts by weight based upon 100 parts of the base composition (A); and

(B3) dibutyltindilaurate (DBTDL)-0.1 parts by weight based upon 100 parts by weight of the base composition (A).

The sealant was tested and the results are listed on Table 1-A, Example 1. As can be seen from the Table, when cured for 7 days at 75°F and 50% Relative Humidity (R.H.), the material had a tensile strength of 293 psi. A similarly cured sheet after 7 days immersion in 5W30 engine oil at 150°C had a tensile strength of 65 psi. Thus, the sealant retained approximately 22% of its initial tensile strength.

Lap shear adhesion was also measured on both Alclad aluminum and carbon steel. On Alclad aluminum, the sealant had a shear strength of 186 psi and 5% cohesive failure with 93 mils of deflection before failure.

Example 2

An extruder was set up to combine the following ingredients in the following proportions:

MATERIAL		CONCENTRATION
(A1a)	Silanol polymer (≈15,000 cps)	100 parts
(A2)	D4 treated fumed silica	13 parts
(A3)	M-stopped fluid	0 parts

The above materials were added to the first section of the extruder to constitute the base portion of the RTV sealant. The catalyst solution described in Example 1 was added to the later section of the extruder at 4.85 parts per 100 parts of (A).

The sealant was tested and the results are listed in Table 1-A, Example 2. As can be seen from the

Table, this material, when cured for 7 days at 75°C and 50% R.H., had a tensile strength of 307 psi. A similarly cured sheet after 7 days immersion in 5W30 engine oil at 150°C had a tensile strength of 53 psi. Thus, the sealant retained only approximately 17% of its initial tensile strength.

Lap shear adhesion was also measured on both Alclad aluminum and cold rolled steel. On Alclad aluminum, the sealant gave at 154 psi and 50% cohesive failure with 78 mils of deflection before failure.

Example 3

An extruder was set up to combine the following ingredients in the following proportions:

MATERIAL		CONCENTRATION
(A1a)	Silanol polymer (≈15,000 cps)	100 parts
(A2)	D4 treated fumed silica	12 parts
(A3)	M-stopped fluid	5 parts
(A4)	Stearic acid treated Calcium Carbonate	50 parts

The above materials were added to the first section of the extruder to constitute the base portion of the RTV sealant.

The catalyst solution was added to the later section of the extruder as described in Example 1, at 4.85 parts per 100 parts of base.

The sealant was tested and the results are listed in Table 1-A (Example 3). As can be seen from the Table this material, when cured for 7 days at 75°F and 50% R.H., had a tensile strength of 302 psi. A

similarly cured sheet after 7 days immersion in 5W30 engine oil at 150°C had a tensile strength of 125 psi. Thus, the sealant retained approximately 41% of its initial tensile strength.

Lap shear adhesion was also measured on both Alclad aluminum and carbon steel. On Alclad aluminum, this sealant gave 210 psi and 25% cohesive failure with 94 mils of deflection before failure.

Example 4

An extruder was set up to combine the following ingredients in the following proportions:

MATERIAL		CONCENTRATION
(A1a)	Silanol polymer (≈15,000 cps)	100 parts
(A2)	D4 treated fumed silica	10 parts
(A3)	M-stopped fluid	5 parts
(A4)	Stearic acid treated Calcium Carbonate	100 parts

The above materials were added to the first section of the extruder to constitute the base portion of this RTV sealant.

The catalyst solution was added in the later section of the extruder as described in Example 1, at 4.85 parts per 100 parts of base.

The sealant was tested and the results are listed in Table 1-A (Example 4). As can be seen from the Table, when cured for 7 days at 75°F and 50% R.H., this material had a tensile strength of 295 psi. A similarly cured sheet after 7 days immersion in 5W30

engine oil at 150°C had a tensile strength of 195 psi. Thus, the sealant retained approximately 66% of its initial tensile strength.

Lap shear adhesion was also measured on both Alclad aluminum and carbon steel. On Alclad aluminum, the sealant gave 181 psi and 25% cohesive failure with 91 mils of deflection before failure.

Example 5

An extruder was set up to combine the following ingredients in the following proportions:

MATERIAL		CONCENTRATION
(A1a)	Silanol polymer (≈15,000 cps)	100 parts
(A2)	D4 treated fumed silica	10 parts
(A3)	M-stopped fluid	0 parts
(A4)	Stearic acid treated Calcium Carbonate	100 parts

The above materials were added to the first section of the extruder to constitute the base portion of this RTV sealant.

The catalyst solution was added in the later section of the extruder as described in Example 1, at 4.85 parts per 100 parts of base.

The sealant was tested and the results are listed in Table 1-B (Example 5). As can be seen from the Table, when cured for 7 days at 75°F and 50% R.H., this material had a tensile strength of 307 psi. A similarly cured sheet after 7 days of immersion in 5W30 engine oil at 150°C had a tensile strength of 227 psi.

Thus the sealant retained approximately 74% of its initial tensile strength.

Lap shear adhesion was also measured on both Alclad aluminum and carbon steel. On Alclad aluminum, this sealant gave 200 psi and 10% cohesive failure with 82 mils of deflection before failure.

The above examples demonstrate the improved elastomer stability after immersion in hot engine oil when calcium carbonate is used in these formulations.

Examples 6-9 are prepared in the same way as Examples 1-5 except that in Examples 8-9 the silanol polymer (A1b) having a viscosity of about 30,000 cps at 25°C is used instead of the lower viscosity (A1a). Amino functional silanes such as gamma-aminopropyl triethoxysilane are good adhesion promoters in the above systems but sealants containing this material can have poor retention of tensile strength after immersion in hot oil. Example 1 is one such sealant which has good adhesion but poor retention of physical properties after immersion in the engine oil.

Sealants which contain non-amino functional silane can have good retention of tensile strength after hot oil immersion but often do not have good adhesion. Examples 6 and 7 respectively contain no adhesion promoter and a non-amino functional adhesion promoter such as tetrakis(methylethylketoximo)silane. These materials have good retention of physical properties after immersion in hot oil retaining 78% and 57%, respectively, of their initial tensile strength. However, both have poor adhesion, 40 psi and 26 psi lap shear strength, respectively, to Alclad aluminum.

TABLE 1-A

INGREDIENTS	Example 1	Example 2	Example 3
(A1a) Silanol Polymer, 15,000 cps	100	100	100
(A1b) Silanol Polymer, 30,000 cps	--	--	--
(A2) D4 Fumed Silica	13	13	12
(A3) M-Stopped Fluid	5	0	5
(A4) $CaCo_3$ (Treated)	0	0	50
(B2a)(B2b) MOS:VOS	3:1	3:1	3:1
(B3)(GAP)	0.75	0.75	0.75
(B1)(DBTDL)	0.1	0.1	0.1
INITIAL PROPERTIES			
Application Rate (g/min @ 90 psi)	158	112	170
Extruder Rate	268	366	212
Tack Free Time (Min)	6	5	10
Skin Over Time (Min)	30	30	25
PHYSICAL PROPERTIES 7 DAY CURE			
Shore A	28	34	39
Tensile (psi)	293	307	302
Elongation (%)	323	303	281
50% Modulus (psi)	65	72	102
150% Modulus (psi)	135	151	199
5W30 OIL IMMERSION 7 DAY 150 C			
Shore A	1	0	8
Tensile (psi)	65	53	125
Elongation (%)	432	442	417
Swell (%)	52	43	47
C STEEL - C STEEL 7 DAY CURE			
Shear St. psi/coh %	186/5	154/50	210/25
Deflection (mil)	93	78	94
ALCLAD-ALCLAD AL			
Shear St. psi/coh %	316/100	264/75	300/75
Deflection (mil)	118	85	114

TABLE 1-B

INGREDIENTS	Example 4	Example 5	Example 6
(A1a) Silanol Polymer, 15,000 cps	100	100	100
(A1b) Silanol Polymer, 30,000 cps	--	--	--
(A2) D4 Fumed Silica	10	10	13
(A3) M-Stopped Fluid	5	0	5
(A4) $CaCo_3$ (Treated)	100	100	--
(B2a)(B2b) MOS:VOS	3:1	3:1	3:1
(B3)(GAP)	0.75	0.75	--
(B1)(DBTDL)	0.1	0.1	0.1
INITIAL PROPERTIES			
Application Rate (g/min @ 90 psi)	172	151	124
Extruder Rate	195	254	370
Tack Free Time (Min)	13	8	8
Skin Over Time (Min)	15	15	>60
PHYSICAL PROPERTIES 7 DAY CURE			
Shore A	47	52	29
Tensile (psi)	295	307	303
Elongation (%)	269	272	305
50% Modulus (psi)	135	155	75
150% Modulus (psi)	234	248	153
5W30 OIL IMMERSION 7 DAY 150 C			
Shore A	17	19	15
Tensile (psi)	195	227	237
Elongation (%)	363	330	296
Swell (%)	42	44	45
C STEEL - C STEEL 7 DAY CURE			
Shear St. psi/coh %	181/25	200/10	40/0
Deflection (mil)	91	82	26
ALCLAD-ALCLAD AL			
Shear St. psi/coh %	308/50	319/500	54/0
Deflection (mil)	115	112	28

TABLE 1-C

INGREDIENTS	Example 7	Example 8	Example 9
(A1a) Silanol Polymer, 15,000 cps	100	--	--
(A1b) Silanol Polymer, 30,000 cps	--	100	100
(A2) D4 Fumed Silica	13	10	10
(A3) M-Stopped Fluid	5	5.0	5.0
(A4) $CaCo_3$ (Treated)	--	100	100
(B2a)(B2b) MOS:VOS	3:1	4:0	4:0
(B3)(GAP)	*	0.75	0.0
(B1)(DBTDL)	0.1	0.1	0.1
INITIAL PROPERTIES			
Application Rate (g/min @ 90 psi)	61	0.15	0.05
Extruder Rate	789	91	131
Tack Free Time (Min)	5	20	45
Skin Over Time (Min)	25	50	>60
PHYSICAL PROPERTIES 7 DAY CURE			
Shore A	32	49	34
Tensile (psi)	330	301	242
Elongation (%)	270	293	439
50% Modulus (psi)	77	128	78
150% Modulus (psi)	173	232	101
5W30 OIL IMMERSION 7 DAY 150 C			
Shore A	17	19	15
Tensile (psi)	187	216	208
Elongation (%)	219	375	380
Swell (%)	43	31	30
C STEEL - C STEEL 7 DAY CURE			
Shear St. psi/coh %	26/0	222/15	50/0
Deflection (mil)	22	106	25
ALCLAD-ALCLAD AL			
Shear St. psi/coh %	38/0	340/75	87.5/0
Deflection (mil)	40	97	43.5

* 1.0 Tetrakis(Methylethylketoximo)silane

In the Examples above, the lap shear test comprises coating paired substrates e.g., Alclad aluminum - Alclad aluminum and carbon steel - carbon steel, with a given area (1/2" x 1") and thickness (0.02") of the sealant composition contacting the two coated areas allowing the compositions to cure, and pulling apart the substrates in a shear direction. The first number in the lap shear line is shear strength in psi, or the force required to cause the substrates to separate. The second number to the right of the slash is cohesive failure percent, or the amount of material remaining on the substrate with the highest failure (the least amount of sealant). Because of differential thermal expansion which occurs between two dissimilar engine components, Movement Capability is important. Movement Capability is tested by measuring the amount of deflection in a lap shear test specimen which occurs before the test specimen breaks i.e., the amount of movement in the lap shear specimen before failure. Deflection before failure is given in mils.

From the foregoing, it can be seen that calcium carbonate improves tensile strength after oil immersion, and GAP promotes adhesion. A formulation which has GAP but no calcium carbonate has good adhesion but poor oil resistance, see Examples 1 and 2. A composition having calcium carbonate but no GAP has poor adhesion but good oil resistance, see Example 9.

The compositions having a combination of both calcium carbonate and GAP exhibit good oil resistance and good adhesion as illustrated in Examples 3, 4, 5 and 8. Surprisingly, the combination of $CaCO_3$ and GAP also imparts faster skin-over time (SOT) and faster tack free time (TFT), as best illustrated in Examples

8 and 9. See also Examples 3-5 for relatively fast SOT and TFT.

Two important properties of a Silicone FIPG gasketing material are adhesion and retention of physical properties after oil immersion. In automotive gasketing applications, these sealants are applied in the uncured state.

Skin-Over-Time is defined as the time for the surface to develop a semi-resilient skin. Tack-Free-Time is defined as the time in which the material becomes dry to the touch. Both of these properties are important in automotive applications because they are indicators of fast cure rates. A fast cure is desirable because engines can not only be pressure tested for "blow-out" resistance but can be started (i.e., actually run) shortly after engine assembly. This speeds up production and allows early quality control testing and correction of product defects. It is desirable for the sealant to have a slight "skin" during these tests.

Inclusion of the adhesion promoter gamma-aminopropyl triethoxysilane (GAP) into a calcium carbonate filled ketoxime sealant not only decreases the Tack-Free-Time and Skin-Over-Time but also significantly increases movement capability while increasing the modulus of the cured elastomer. Examples 8 and 9 in Table 1-C list results generated on two samples of ketoxime sealant. Example 8 contains GAP. Example 9 contains no GAP. Except for this difference, the compositions are identical and were made under the same conditions. As can be seen, the GAP containing material had a shorter Tack-Free-Time and a shorter Skin-Over-Time. In addition, these high-

modulus, GAP containing materials have better movement capability than a similar system without GAP. The GAP containing material gave an average of 106 and 97 mils of deflection (the amount of movement of the test sample before failure) on steel and aluminum, respectively, whereas the material with no GAP gave an average of only 25 and 43.5 mils of deflection on steel and aluminum.

While the use of calcium carbonate is known as illustrated in the Beers et al. patent referred to above, the modulus achieved in the present invention is much improved over the Beers et al. reference. In particular, the present invention has modulus strengths with $CaCO_3$ which are higher than the modulus strengths set forth in Beers et al. For example, in the present invention, the modulus at 50% is between about 100 and 155 psi and at 150% it is between 199 and 250 psi. In Beers et al., the modulus at 50% is 75 psi or less with 50% being preferred and the modulus at 100 is 110 psi with 90 psi being preferred.

While there has been described what at present are considered to be the preferred embodiments of the present invention, it will be readily apparent to those skilled in the art that various changes may be made therein without departing from the invention and it is intended in the appended claims to cover such changes and modifications as fall within the true spirit and scope of the invention.

WHAT IS CLAIMED:

1. A one-part RTV composition comprising:

(A) a base composition including:

(A1) 100 parts by weight of a silanol terminated diorganopolysiloxane having a viscosity of about 600 to about 300,000 cps at 25°C having the form $HOR_2SiO(R_2SiO)_xSiR_2OH$;

(A2) from about 3 to about 25 parts by weight based upon (A1) of a silica filler having a surface area of about 100 to 300 m^2/gm in the untreated state;

(A3) up to about 80 parts by weight based upon (A1) of an M stopped fluid having a viscosity ranging from about 50 to about 10,000 cps at 25°C; and

(A4) up to about 200 parts by weight based upon (A1) of calcium carbonate; and

(B) a catalyst solution including:

(B1) up to about 0.5 parts by weight based upon 100 parts of the base composition (A) of a tin based catalyst;

(B2) from about 2 to about 15 parts by weight based upon 100 parts of the base composition (A) of a cross-linking agent including:

alkyl- or alkenyl- or vinyl-tris(dialkyl- or dialkenyl- or alkylalkenyl-ketoximo)silane; and

(3) from about .1 to about 4 parts by weight based upon 100 parts of the base composition (A) of gamma-aminopropyl triethxoysilane adhesion promoter.

2. The RTV composition of claim 1, with (A1) having a viscosity ranging from about 2,000 to about 200,000.

3. The RTV composition of claim 1, with (A1) having a viscosity between about 3,000 and 150,000 cps at 25°C.

4. The RTV composition of claim 1, wherein (A1) is a silanol terminated polydiorganosiloxane having the form $HOR_2SiO(SiOR_2)_xSiR_2OH$ wherein R is a monovalent hydrocarbon radical free of aliphatic unsaturation containing from about 1 to about 8 carbon atoms and x varies so that (A1) has a viscosity of about 600 to about 300,000 cps at 25°C.

5. The RTV composition of claim 1, wherein (A2) is present in an amount ranging from about 3 to about 20 parts by weight based upon (A1).

6. The RTV composition of claim 1, wherein (A2) is present in an amount ranging from about 5 to about 15 parts by weight based upon (A1).

7. The RTV composition of claim 1, wherein, (A2) has a surface area of about 200 m^2/gm in an untreated state.

8. The RTV composition of claim 1, wherein (A2) is D4 treated.

9. The RTV composition of claim 1, wherein (A2) is silazane treated.

10. The RTV composition of claim 1, wherein (A3) is present in an amount up to about 60 parts by weight based upon (A1).

11. The RTV composition of claim 1, wherein (A3) is present in an amount up to about 40 parts by weight of (A1).

12. The RTV composition of claim 1, wherein (A3) has a viscosity from about 50 to about 3,000 cps at 25°C.

13. The RTV composition of claim 1, wherein (A3) has a viscosity ranging from about 50 to about 1,000 cps at 25°C.

14. The RTV composition of claim 1, wherein (A4) is present in an amount ranging from about 50 to about 150 parts by weight based upon (A1).

15. The RTV composition of claim 1, wherein (A4) is present in an amount ranging from about 50 to about 125 parts by weight based upon (A1).

16. The RTV composition of claim 1, wherein (A4) is treated with about 1 weight percent stearic acid based upon (A4).

17. The RTV composition of claim 1, wherein (B1) is present in an amount ranging from about 0.1 to about 0.4 parts by weight based upon 100 parts of the base composition (A).

18. The RTV composition of claim 1, wherein (B1) is present in an amount ranging from about 0.05 to about 0.30 parts by weight based upon 100 parts of the base composition (A).

19. The RTV composition of claim 1, wherein (B1) is a dibutyltindialurate.

20. The RTV composition of claim 1, wherein (B2) is present in an amount ranging from about 2 to 10 parts by weight based upon 100 parts of the base composition (A).

21. The RTV composition of claim 1, wherein (B2) comprises (a) methyltris(methylethylketoximo)silane or, (b) vinyltris(methylethylketoximo)silane, or mixtures of (a) and (b).

22. The RTV composition of claim 1, wherein (B2) is present in an amount ranging from about 3 to about 7 parts by weight based upon 100 parts of the base composition.

23. The RTV composition of claim 1, wherein (B3) is present in an amount ranging from about 0.2 to about 2 parts by weight based upon 100 parts of the base composition (A).

24. The RTV composition of claim 1, wherein (B3) is present in an amount ranging from .3 to about 1.5 parts by weight based upon 100 parts of the base composition (A).

25. The RTV composition of claim 1, having a tensile strength after immersion in hot engine oil ranging from about 125 to about 230 psi.

26. The RTV composition of claim 1, having a shear strength of at least about 200 psi.

27. The RTV composition of claim 1, having 50% modulus ranging from about 100 to about 175 psi.

28. The RTV composition of claim 1, having a 150% modulus ranging from about 200 to about 300 psi.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/02625

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08L83/04

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C08L ; C08K

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
X	US,A,4 514 529 (MELVIN D. BEERS) 30 April 1985 cited in the application see claims 1-19	1-28
X	US,A,5 064 898 (MASATOSHI ARAI) 12 November 1991 see claims 1,2,4,5,7,9 see column 1, line 8 - line 20 see column 7, line 49 - line 55 see column 7, line 61 - line 63	1-28

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° Special categories of cited documents :[10]

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

"E" earlier document 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

"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.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
12 AUGUST 1993	25.08.93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	DEPIJPER R.D.C.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	US,A,4 960 847 (MASATOSHI ARAI) 2 October 1990 see claim 1 see column 2, line 63 - line 68 see column 3, line 16 - line 20 see column 4, line 62 - column 5, line 10 see column 5, line 30 - line 31 see column 8; example 9	1-28
X	EP,A,0 050 453 (TORAY SILICONE COMP. LTD.) 28 April 1982 see claims 1,3,4,5,7,8,9,10 see page 1, paragraph 1 see page 4, paragraph 4-6 see page 5, paragraph 2	1-28
A	EP,A,0 261 418 (TORAY SILICONE COMP. LTD.) 30 March 1988 see claim 1 see page 3, line 43 - line 53 see page 4, line 5 - line 49 see page 4, line 58 - page 5, line 9 see page 6; example 1; table 1	1

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9302625
SA 72221

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 12/08/93
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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