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<p>(54) Title: FUEL RESISTANT SILICONES</p>		
<p>(57) Abstract</p> <p>A silicon composition is described, which includes a room temperature condensation curing silicone polymer, a plasticizer, a crosslinker and precipitated calcium carbonate. Cured elastomeric adhesives formed from such composition have excellent fuel and oil resistance when applied to engine surfaces that are exposed to fuel and/or oil. Methods of making and using such compositions are also provided.</p>		

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FUEL RESISTANT SILICONES

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BACKGROUND OF THE INVENTION**Field Of The Invention**

The present invention is directed to fuel resistant silicones. More particularly, the present invention relates to fuel resistant condensation curing silicone compositions which are suitable for sealing applications. Methods of making and using such condensation curing silicone compositions are also provided.

Brief Description Of Related Technology

Conventional room temperature vulcanizable ("RTV") silicone compositions have excellent sealing and adhesive properties. Such compositions are used extensively in the automotive industry to seal, for example, powertrains against exposure to oil and antifreeze. Such compositions, however, are not currently used in applications where they will be exposed to fuel, such as for example gasoline or diesel fuel, because they are readily susceptible to

degradation and adhesive failure upon extended exposure to such fuels. Thus, alternative adhesive/sealant compositions have been developed for use as, e.g., sealants, fuel resistant O-rings and gaskets. Such compositions, however, although being fuel resistant to a certain extent, are not ideal because they do not have the excellent adhesive properties of RTV silicone adhesive compositions.

Various attempts have been made in the past to use compositions that can be formed into fuel resistant sealants, O-rings and/or gasketing materials. These attempts, however, are believed to have focused on only heat-curable compositions, and many of these are non-silicone containing.

For example, U.S. Patent Nos. 4,625,005 and 4,675,362 describe multi-component copolymer rubber compositions made from a cyano-substituted alkyl (meth)acrylate, an alkyl acrylate and a diene monomer. Such compositions are reported to have good heat resistance, ozone resistance, sour gasoline resistance and sour gasohol resistance. These compositions, however, tend to be difficult to work with and may provide less desirable adhesion compared to conventional RTV silicone compositions.

U.S. Patent Nos. 4,822,654 and 4,988,548 describe a vulcanizable rubber composition containing a vinylidene fluoride resin, a rubber composition and an optional blendable rubber composition. Such a composition is reported to have good gasoline and gasohol resistance, good sour gasoline and sour gasohol resistance and good heat resistance. Again, such a composition tends to be difficult to work with and may provide less desirable adhesive properties compared to conventional RTV silicone gasketing materials.

The patents discussed above are directed to cyanoacrylate- and vinyl-containing rubber compositions -- not silicone-containing compositions -- that are reported to have fuel resistance. They may not be as effective as

silicone adhesives for bonding surfaces together, do not provide true fuel resistance over time and may be difficult to handle. For example, careful control and monitoring of the manufacturing process of the multi-component systems set forth in the '005 and '362 patents is important to ensure that the desired properties are obtained. Such monitoring, while important, is inefficient and less desirable for labor and other economic reasons compared to, for example, ready-to-use compositions.

Thus, attempts have been made to develop silicone-containing compositions that are fuel resistant. For example, U.S. Patent No. 5,082,886 describes liquid injection molding silicone elastomers. These silicone elastomers are reported to have low compression and resistance to fuels and oils. Such silicone elastomers are made from vinyl-containing liquid organopolysiloxanes, hydrogen silicones, such as a silane or a polysiloxane, and various other optional additives. These silicone elastomers, however, are addition cured at elevated temperatures to impart high compression strength for compression gasketing. These elastomers can not be used with heat-sensitive systems, which are unable to tolerate elevated temperatures required to cure such compositions. Accordingly, the compositions set forth in the '886 patent would not be suitable for RTV adhesive sealant applications or for application directly on parts without the use of a mold. Thus, there is a need for adhesive silicone RTV compositions that can be used for various applications where strong adhesion and resistance to fuel are desirable properties.

SUMMARY OF THE INVENTION

The present invention provides a silicone composition that includes a room temperature condensation curing silicone polymer, a plasticizer, a crosslinker and precipitated calcium carbonate to impart fuel resistance to

the composition. The reaction product of this composition is a fuel resistant silicone adhesive.

5 The present invention also provides a method of applying a fuel resistant adhesive silicone composition to a surface that is exposed to fuel. This method includes applying to the surface an effective amount of a composition that includes (i) a room temperature condensation curing silanol terminated silicone polymer; (ii) a plasticizer; (iii) a crosslinker; and (iv) precipitated calcium
10 carbonate, to impart fuel resistance to the composition. The composition is then formed into an appropriate sealing configuration and allowed to condensation cure at room temperature.

15 In addition, the present invention provides a method of using a fuel-resistant mechanical seal. This method includes applying a seal forming amount of a composition on a surface of a mechanical part. The composition is formed from a room temperature condensation curing silanol terminated silicone polymer, a plasticizer, a
20 crosslinker and precipitated calcium carbonate, to impart fuel resistance to the composition. A seal is then formed about a surface of the mechanical part by room temperature vulcanization, wherein the seal remains competent when exposed to fuel over extended periods of time.

25 Also, the present invention provides a method of using a fuel resistant sealing composition. This method includes forming a seal between two or more surfaces by applying therebetween a composition including a room temperature condensation curing silanol terminated silicone
30 polymer, a plasticizer, a crosslinker and precipitated calcium carbonate, to impart fuel resistance to the composition. When cured, this composition forms a fuel resistant silicone elastomer.

35 The present invention also includes a silicone composition that when cured forms an oil and fuel resistant silicone adhesive. This composition includes a silanol-

terminated silicone fluid, an organic plasticizer, a crosslinker and precipitated calcium carbonate, to impart fuel resistance to the composition.

5 The present invention will be more fully understood by a reading of the section entitled "Detailed Description of the Invention".

DETAILED DESCRIPTION OF THE INVENTION

10 The present invention is directed to RTV silicones having good adhesion after immersion in fuel, such as for example, gasoline or diesel fuel.

15 A long-felt problem with conventional RTV silicones is that they cannot be used to form adhesive bonds between work pieces that are continuously exposed to fuel because they are quickly degraded and lose their sealing/adhesive properties. Surprisingly, it has been found that by adding precipitated calcium carbonate and a plasticizer to such RTV silicone compositions that these compositions are rendered fuel resistant.

20 Thus, the present invention provides a silicone composition that includes a room temperature condensation curing silicone polymer, a plasticizer, a crosslinker and an effective amount of precipitated calcium carbonate to impart fuel resistance to the composition. When cured, this composition forms a fuel resistant silicone adhesive. As used herein, "room temperature condensation curing silicone polymer" refers to conventional silicone polymers that are able to cure/vulcanize using moisture found in air at ambient temperature (approximately 25°C). Such polymers typically contain functional groups capable of reacting with moisture in the air to substantially cure the composition. Ordinarily, such room temperature condensation curing silicone polymers include, for example, polydiorganosiloxanes having terminal hydroxyl groups that are curable to an elastomer upon crosslinking. Other silicone compositions, however, can be used in the present

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invention provided they are capable of room temperature condensation curing to form the fuel resistant silicone compositions as described in more detail below.

5 Any condensation curing silicone polymer having the properties set forth above can be used in the present invention. Desirably, however, the condensation curing silicone polymers of the present invention have a viscosity of from about 1,000 Cst to about 80,000 Cst. More desirably, the viscosity of these condensation curing
10 silicone polymers range from about 2,000 Cst to about 50,000 Cst, such as from about 2,000 Cst to about 20,000 Cst.

The silicone compositions of the present invention also include a plasticizer component. Any conventional plasticizer capable of forming the present fuel resistant
15 silicone compositions can be used. In the present compositions, effective amounts of plasticizers are added to ensure the desired workability and performance of the final elastomer. Desirably, from about 10% to about 40% by weight of a selected plasticizer is incorporated into the
20 compositions of the present invention.

Moreover, the plasticizer can be a silicone plasticizer or an organic plasticizer. One example of a suitable silicone plasticizer is a triorganosilyl end blocked diorganosiloxane, although other silicone
25 plasticizers can be used provided they do not compromise the adhesive properties of the present composition and its ability to resist degradation from certain organic solvents including for example, fuel and oil.

Organic plasticizers can also be used in
30 conjunction with the present invention. Such organic plasticizers include, for example, polyalkylene glycol, poly(propylene oxides), hydroxyethylated alkyl phenol, dialkyldithiophosphonate, poly(isobutylenes), paraffinic or naphthenic oils, poly(alpha-olefins) and mixtures thereof.
35 Other organic plasticizers compatible with the formation of the present fuel resistant compositions are also

contemplated, such as for example, predominantly aliphatic liquid polymers and oils.

The silicone compositions of the present invention also include a crosslinker. As used herein, the term
5 "crosslinker" is intended to include any material that is able to covalently crosslink the present composition into a fuel resistant adhesive silicone elastomer. Suitable crosslinkers that can be used in conjunction with the present invention include, for example,
10 methyltrimethoxysilane, vinyltrimethoxysilane, methyltriethoxysilane, vinyltriethoxysilane, vinyltriethoxysilane, methyl tris-(N-methylbenzamido)silane, methyl tris-(isopropenoxy)silane, methyl tris (cyclohexylamino)silane, methyl tris-(methyl ethyl
15 ketoximino)silane, vinyl tris-(methyl ethyl ketoximino)silane, methyl tris-(methyl isobutyl ketoximino)silane, vinyl tris-(methyl isobutyl ketoximino)silane, tetrakis-(methyl ethyl ketoximino)silane, tetrakis-(methyl isobutyl ketoximino)silane, tetrakis-
20 (methyl amyl ketoximino)silane, dimethyl bis-(methyl ethylketoximino)silane, methyl vinyl bis-(methyl ethyl ketoximino)silane, methyl vinyl bis-(methyl isobutyl ketoximino)silane, methyl vinyl bis-(methyl amyl ketoximino)silane, tetrafunctional alkoxy-ketoxime silanes,
25 tetrafunctional alkoxy-ketoximino silanes, and enoxysilanes. Further, the enoxysilanes that can include, for example, tri- and tetrafunctional enoxysilanes.

The cured silicone compositions of the present invention are rendered fuel resistant by the presence of
30 effective amounts of precipitated calcium carbonate therein. As used herein, the term "effective amount" is intended to convey to one skilled in the art that the amount of precipitated calcium carbonate required to render the present silicone compositions fuel resistant will vary
35 depending upon the manufacturing processes used, the intended use of the final product, as well as the amount and

viscosity of the plasticizer used. As set forth below, effective fuel resistant silicone adhesives can be achieved using from about 1% to about 60% precipitated calcium carbonate by weight. Desirably from about 10% to about 50% precipitated calcium carbonate by weight, such as about 16% to about 43% is contemplated for use in conjunction with the present invention.

Other additional additives can be included in the present fuel resistant silicone compositions providing such additives do not adversely effect the ability of the present compositions to resist certain organic solvents, such as fuel and oil, and to maintain their adhesive properties. For example, a catalyst can be added to the present compositions to increase the rate of curing. Such a catalyst can include, for example, dibutyltin dilaurate, dibutyltin diacetate, dibutyltin dioctoate, dibutyltin maleate, dialkyl tin hexoate, dioctyltin dilaurate, iron octanoate, zinc octanoate, lead octanoate, cobalt naphthenate, tetrapropyltitanate, tetrabutyltitanate, tin dimethyl neo didecanoate, dialkyl tin carboxylates, mercaptans and titanates. Other conventional catalysts can also be incorporated into the present invention provided they do not adversely effect the fuel and/or oil resistant and adhesive properties of the final end product produced therefrom.

A reinforcing agent is another example of an additive that can be incorporated into the present compositions. Such reinforcing agents include, for example, titanium dioxide, lithopone, zinc oxides, zirconium silicate, silica aerogel, iron oxide, diatomaceous earth, calcium carbonate, fumed silica, precipitated silica, glass fibers, magnesium oxide, chromic oxide, zirconium oxide, aluminum oxide, crush cores, calcium clay, carbon, graphite, cork, cotton, synthetic fibers and mixtures thereof. Other conventional reinforcing agents can also be incorporated into the present invention provided they do not adversely

effect the fuel and/or oil resistant and adhesive properties of the final end product produced therefrom.

An adhesion promoter is another example of an additive that can be incorporated into the present compositions. Such adhesion promoters include, for example, 5 gamma-aminopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, trimethoxysilylpropyldiethylene 10 triamine, 3-glycidoxypropyltrimethoxy silane, gamma-mercaptopropyltrimethoxysilane, gamma-methacryloxypropyltrimethoxysilane. Other conventional adhesion promoters can also be incorporated into the present invention provided they do not adversely effect the fuel 15 and/or oil resistant and adhesive properties of the final end product produced therefrom.

Conventional pigments, such as for example, titanium dioxide pigment, can also be incorporated into the present invention provided they do not adversely effect the 20 fuel and/or oil resistant and adhesive properties of the final end product produced from the compositions of the present invention.

The compositions of the present invention can be formed into many different configurations and then 25 condensation cured over time under ambient conditions. Products formed in such a manner are useful in various industries where there is a need for fuel and/or oil resistant silicone-based elastomeric adhesives. For example, the present compositions can be used to seal and/or bond 30 together carburetor flanges, intake manifold flanges, as well as any surface in a 2 cycle engine which is exposed to fuel. Other conventional uses for the present compositions where there is a requirement for good adhesive properties, as well as fuel and/or oil resistance are also contemplated 35 herein.

In another embodiment of the present invention, there is provided a method of applying a fuel resistant adhesive silicone composition to a surface exposed to fuel during its intended use. This method includes applying to
5 the surface an effective amount of a composition as described previously. Briefly, this composition includes a room temperature condensation curing silanol terminated silicone polymer, a plasticizer, a crosslinker and an effective amount of precipitated calcium carbonate to impart
10 fuel resistance to the composition. The method further includes forming the composition into an appropriate sealing configuration using conventional techniques and then allowing the composition to condensation cure at room temperature.

15 As used herein, "appropriate sealing configuration" includes any commercially useful physical form used to form a seal and/or adhesive bond between at least two work surfaces that are exposed to, e.g., fuel.

In this method, the precipitated calcium carbonate
20 is present in an amount of from about 1% to about 60% by weight, and desirably from about 10% to about 50% by weight.

In yet another embodiment of the present invention, there is provided a method of using a fuel resistant mechanical seal. This method includes applying a
25 seal forming amount of a composition on a surface of a mechanical part wherein the composition is formed from a room temperature condensation curing silanol terminated silicone polymer, a plasticizer, a crosslinker and an effective amount of precipitated calcium carbonate to impart
30 fuel resistance to the composition as set forth previously.

The method further includes forming a seal about a mechanical surface by room temperature vulcanization, wherein the seal remains competent when exposed to fuel over extended periods of time.

In this method, the precipitated calcium carbonate is present in an amount of from about 1% to about 60% by weight, and desirably from about 10% to about 50% by weight.

Moreover, according to this method, a seal is
5 formed with the present composition about a surface that is exposed to fuel in a 2 cycle engine.

In still another embodiment of the present invention, there is provided a method of using a fuel resistant sealing composition. This method includes forming
10 a seal and/or an adhesive bond between two or more surfaces by applying therebetween the fuel resistant sealing member formed from the present composition as described above.

According to this method, a fuel resistant seal is formed using the present compositions between carburetor
15 flanges and/or intake manifolds, as well as any other surface exposed to fuel in a 2 cycle engine.

In still yet another embodiment of the present invention, there is provided an oil and fuel resistant adhesive silicone composition. This composition includes a
20 silanol terminated silicone fluid, an organic plasticizer, a crosslinker and precipitated calcium carbonate. When combined and cured, these reagents form elastomeric compositions that remain adhesive after exposure to oil and fuel. As set forth previously, a catalyst and other
25 optional additives can also be incorporated into this composition.

The following examples are provided to further illustrate methods of preparation of the fuel resistant silicone sealant compositions, as well as certain physical
30 properties thereof. These examples are illustrative only and are not intended to limit the scope of the invention in any way.

EXAMPLES

In these examples, uncured fuel resistant silicone adhesive compositions were prepared for evaluation, certain of which are within the scope of the present invention and others are for comparative purposes.

Table 1

**Inventive Formulations of Uncured Fuel
Resistant Silicone Adhesive Compositions**

Description*		Composition								
		1	2	3	4	5	6	7	8	9
1	6000 Cst Silanol Fluid	43.40	43.40	44.90	44.40	62.47	62.47	62.47	--	--
2	Fumed Silica (AEROSIL R-974)	10.00	10.00	7.50	5.00	--	--	--	5.34	1.00
3	PPT. CaCO ₃ (SOCAL 322)	16.00	16.00	16.00	20.00	--	--	--	--	43.0
4	TiO ₂ Pigment	1.00	1.00	1.00	1.00	1.00	1.00	1.00	2.01	2.70
5	INDOPOL L-14	25.00	--	16.00	25.00	--	--	--	--	--
6	Vinyl trioximino silane ("VOS")	4.00	4.00	4.00	4.00	4.00	--	--	3.81	4.00
7	Aminosilane	0.50	0.50	0.50	0.50	0.00	0.00	0.50	0.10	0.30
8	UL-28 Catalyst	0.10	0.10	0.10	0.10	0.03	0.03	0.03	0.10	--
9	100 Cst Silicone Plasticizer	--	25.00	--	--	--	--	--	--	--
10	80,000 Cst Silanol Fluid	--	--	--	--	--	--	--	--	36.00
11	20,000 Cst Silanol Fluid	--	--	--	--	--	--	--	38.97	--
12	Ground CaCO ₃ (OMYA FT)	--	-	--	--	--	--	--	32.41	--
13	L45/1000 Cst Plasticizer	--	--	--	--	24.00	24.00	24.00	16.00	12.00
14	TOS/VOS Crosslinker	--	--	--	--	-	4.00	4.00	--	1.00
15	Ureidopropyl trimethoxy silane	--	--	--	--	0.50	0.50	--	0.50	--

*Certain of the above referenced reagents were obtained commercially from the following suppliers:

<u>Tradename</u>	<u>Supplier</u>	<u>Description</u>
Socal 322	Solvay	precipitated CaCO ₃
Silanol Fluid	Dow Corning; GE; Bayer	silanol terminated polydimethylsiloxane
Aerosil R974	Cabot	surface treated fumed silica
TiO ₂	Dupont	titanium dioxide pigment
Fomrez UL-28 Catalyst	Witco	aminopropyltrimethoxysilane adhesion promoter
Aminosilane	Sivento; Dow Corning	aminopropyltrimethoxysilane adhesion promoter
SiliconePlast	Dow Corning; GE; Bayer	trimethylsilyl terminated polydimethylsiloxane
Indopol L-14	Amoco	polyisobutylene (polybutene) (organic plasticizer)

Table 1 reflects a summary of the different compositions evaluated. Compositions 1-4 in Table 1 are different embodiments of the present invention (Inventive Compositions). Compositions 5-7 in Table 1 are examples of RTV silicone systems that do not contain precipitated calcium carbonate (Comparative Examples). Compositions 8 and 9 are control compositions where ground calcium carbonate is substituted for precipitated calcium carbonate (Composition 8) and a high viscosity polymer is substituted for a low viscosity polymer (Example 9).

Example 1

Compositions 1 and 2 as set forth in Table 1 supra were prepared by combining items 1-4 and half of item 5 (Composition 1) or half of item 9 (Composition 2) with slow mixing for approximately 2 minutes. Once the powders were incorporated, the speed of the mixing was increased and a vacuum was applied. Mixing was continued under vacuum for approximately 3 hours at 100°C. The respective compositions were then allowed to cool to room temperature (approximately 25°C) for at least 10 minutes. Once at room temperature, the rest of item 5 (Composition 1) or item 9 (Composition 2) and item 6 were added to the composition and slowly mixed for 15 minutes under vacuum until the powders were incorporated. The mixing speed was then increased. Items 7 and 8 were then mixed in into the composition for 20 minutes

under vacuum. The uncured products were then collected under a nitrogen blanket.

Example 2

5 Compositions 3 and 4 as set forth in Table 1 supra
were prepared by combining items 1-4 with slow mixing for
approximately 2 minutes. Once the powders were
incorporated, the speed of the mixing was increased and a
vacuum was applied. Mixing was continued under vacuum for
10 approximately 3 hours at 100°C. The respective compositions
were then allowed to cool to room temperature (approximately
25°C) for at least 10 minutes. Once at room temperature,
items 5 and 6 were added to the composition and slowly mixed
for 15 minutes under vacuum until the powders were
15 incorporated. The mixing speed was then increased. Items 7
and 8 were then mixed in into the composition for 20 minutes
under vacuum. The uncured products were then collected
under a nitrogen blanket.

20 Example 3

Physical Properties

Certain physical properties of inventive
Compositions 1-4 and comparative Compositions 5-7 (prepared
substantially as described for inventive Compositions 1-4)
25 from Table 1 supra were evaluated and are set forth in
Tables 2 and 3 infra. Three sets of conventional lap shear
specimens were prepared from inventive Compositions 1-4 and
comparative Compositions 5-7, respectively, and were allowed
to cure for 7 days in approximately 50% relative humidity at
30 ambient temperature (approximately 25°C). The data in
Tables 2 and 3 represent the average values derived from
each experiment run in triplicate.

The "Control" columns represent the cured
elastomers of inventive Compositions 1-4 and comparative
35 Compositions 5-7 without exposure to gas or oil. The "Gas"
columns represent the cured elastomers of inventive

Compositions 1-4 and comparative Compositions 5-7 when immersed in gas for 24 hours at room temperature (25°C). The "Oil" columns represent the cured elastomers of inventive Compositions 1-4 when immersed in oil for 3 days at 120°C.

Table 2*

Oil and Fuel Resistant Properties

Composition	Joint Movement (inches)			Shear Strength (psi)			Cohesive Failure (%)		
	Control	Gas	Oil	Control	Gas	Oil	Control	Gas	Oil
1	0.116	0.06 1	0.031	148.28	43.44	174.16	10	30	0
2	0.176	0.08 6	0.151	194.03	53.71	64.00	30	100	0
3	0.119	0.07 2	0.179	107.90	42.52	176.92	20	50	30
4	0.117	0.06 5	0.170	99.06	34.83	164.88	10	30	90

Table 3*

Fuel Resistant Properties

Composition	Joint Movement (inches)		Shear Strength (psi)		Cohesive Failure (%)	
	Control	Gas	Control	Gas	Control	Gas
5	0.141	0	81.23	0	33.3	0
6	0.036	0	24.80	0	0	0
7	0.091	0	68.60	0	80	0

*All of the data set forth in Tables 2 and 3 represent the average value obtained in each of three tests, i.e., a Joint Movement test which is a measure of the linear displacement at break of conventional lap shear specimens; a Shear Strength test which is a measure of the force necessary to break the joint of the lap shear specimen; and a Cohesive Failure test which is a visual estimate of the failure within the adhesive as measured by the amount of the cured elastomer remaining on each of the test surfaces.

Values of 5-10 psi in the Shear Strength test are indicative of resistance to fuel and/or oil. As the data in Table 2 indicate, inventive Compositions 1-4 of the present invention are substantially above this threshold and provide excellent adhesion when exposed to fuel and/or oil.

Comparative Compositions 5-7 (Table 3), however, which do not contain precipitated calcium carbonate failed to demonstrate any measurable adhesive activity when exposed to fuel. These data suggest that the precipitated calcium carbonate found in the inventive Compositions of the present invention (Compositions 1-4 of Table 1) is important for the cured elastomer's ability to resist oil and retain adhesive capabilities.

Table 4

Oil and Fuel Resistant Properties

Composition	Shear Strength (psi)		
	Control	Gas	oil
8	73.48	0.00	62.85
9	139.37	4.87	79.20

Compositions 8 and 9 were treated as described in Example 3 supra, with certain exceptions as noted below. The data from Table 4 indicate that compositions 8 and 9 appear to have poor adhesion after immersion in gas for 24 hours at room temperature. In Composition 8, ground calcium carbonate is substituted for precipitated calcium carbonate. As the data in Table 4 indicate, ground calcium carbonate provides no fuel resistance to the cured elastomer, which failed to demonstrate any adhesive ability in the shear strength test.

In Composition 9, precipitated calcium carbonate was present, however, a 80,000 Cst polymer was substituted for the 6,000 Cst polymer of inventive compositions 1-4. The cured elastomer produced from this composition demonstrated poor fuel resistance, i.e., poor adhesive characteristics in the shear strength test. This result indicates that the viscosity of the polymer also plays a role in the ability of the present compositions to retain their adhesive character when exposed to fuel.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention and all such modifications are intended to be included within the scope of the claims.

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What Is Claimed Is:

1. A silicone composition, comprising:
 - a. a room temperature condensation curing silicone polymer;
 - b. a plasticizer;
 - c. a crosslinker; and
 - d. precipitated calcium carbonate, wherein reaction products formed from said silicone composition is resistant to fuel.

2. The silicone composition of Claim 1, further comprising a catalyst.

3. The silicone composition of Claim 2, wherein said catalyst includes dibutyltin dilaurate, dibutyltin diacetate, dibutyltin dioctoate, dibutyltin maleate, dialkyl tin hexoate, dioctyltin dilaurate, iron octanoate, zinc octanoate, lead octanoate, cobalt naphthenate, tetrapropyltitanate, tetrabutyltitanate, tin dimethyl neodidecanoate, dialkyl tin carboxylates, mercaptans and titanates.

4. The silicone composition of Claim 1, wherein said silicone polymer is a polydiorganosiloxane having terminal hydroxyl groups in an amount sufficient to form said silicone composition which is curable to an elastomer upon crosslinking.

5. The silicone composition of Claim 1, wherein said effective amount of precipitated calcium carbonate is from about 1% to about 60% by weight.

6. The silicone composition of Claim 1, wherein said effective amount of precipitated calcium carbonate is from about 10% to about 50% by weight.

7. The silicone composition of Claim 1, further comprising a reinforcing agent.

8. The silicone composition of claim 7, wherein said reinforcing agent is selected from the group consisting of titanium dioxide, lithopone, zinc oxides, zirconium silicate, silica aerogel, iron oxide, diatomaceous earth, calcium carbonate, fumed silica, precipitated silica, glass fibers, magnesium oxide, chromic oxide, zirconium oxide, aluminum oxide, crush cores, calcium clay, carbon, graphite, cork, cotton, synthetic fibers and mixtures thereof.

9. The silicone composition of Claim 1, wherein said crosslinker is selected from the group consisting of methyltrimethoxysilane, vinyltrimethoxysilane, methyltriethoxysilane, vinyltriethoxysilane, vinyltriethoxysilane, methyl tris-(N-methylbenzamido)silane, methyl tris-(isopropenoxy)silane, methyl tris (cyclohexylamino)silane, methyl tris-(methyl ethyl ketoximino)silane, vinyl tris-(methyl ethyl ketoximino)silane, methyl tris-(methyl isobutyl ketoximino)silane, vinyl tris-(methyl isobutyl ketoximino)silane, tetrakis-(methyl ethyl ketoximino)silane, tetrakis-(methyl isobutyl ketoximino)silane, tetrakis-(methyl amyl ketoximino)silane, dimethyl bis-(methyl ethylketoximino)silane, methyl vinyl bis-(methyl ethyl ketoximino)silane, methyl vinyl bis-(methyl isobutyl ketoximino)silane, methyl vinyl bis-(methyl amyl ketoximino)silane, tetrafunctional alkoxy-ketoxime silanes, tetrafunctional alkoxy-ketoximino silanes, and enoxysilanes.

10. The silicone composition of Claim 9, wherein said crosslinker comprises tri- and tetra-functional enoxysilanes.

11. The silicone composition of Claim 1, further comprising an adhesion promoter.

12. The silicone composition of Claim 11, wherein said adhesion promoter is selected from the group consisting of gamma-aminopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, trimethoxysilylpropyldiethylene triamine, 3-glycidoxypropyltrimethoxy silane, gamma-mercaptopropyltrimethoxysilane and gamma-methacryloxypropyltrimethoxysilane.

13. The silicone composition of Claim 1, further comprising a pigment.

14. The silicone composition of Claim 1, wherein said plasticizer is present in an amount of from about 10% to about 40% by weight.

15. The silicone composition of Claim 1, wherein said plasticizer is a silicone plasticizer or an organic plasticizer.

16. The silicone composition of Claim 15, wherein said silicone plasticizer is a triorganosilyl end blocked diorganopolysiloxane.

17. The silicone composition of Claim 15, wherein said organic plasticizer is selected from the group consisting of polyalkylene glycol, poly(propylene oxides), hydroxyethylated alkyl phenol, dialkyldithiophosphonate, poly(isobutylenes), paraffinic or naphthenic oils, poly(alpha-olefins) and mixtures thereof.

18. The silicone composition of Claim 15, wherein said organic plasticizer further comprises predominantly aliphatic liquid polymers and oils.

19. A fuel resistant cured elastomer formed as the reaction product of the composition of Claim 1.

20. The silicone composition of Claim 1, wherein said composition is used to form a seal about a surface exposed to fuel.

21. A method of providing a fuel resistant adhesive silicone composition to a surface exposed to fuel comprising:

- a. applying to said surface an effective amount of a composition comprising:
 - i. a room temperature condensation curing silanol terminated silicone polymer;
 - ii. a plasticizer;
 - iii. a crosslinker; and
 - iv. an effective amount of precipitated calcium carbonate to impart fuel resistance to said composition;
- b. forming said composition into an appropriate sealing configuration; and
- c. allowing said composition to condensation cure at room temperature.

22. The method of Claim 21, wherein said precipitated calcium carbonate is present in an amount from about 1% to about 60% by weight.

23. The method of Claim 21, wherein said forming step further includes forming said a seal about a surface exposed to fuel.

24. A method of using a fuel resistant mechanical seal comprising the steps of:

a. applying a seal forming amount of a composition on a surface of a mechanical part wherein said composition is formed from a room temperature condensation curing silanol terminated silicone polymer, a plasticizer, a crosslinker and an effective amount of precipitated calcium carbonate to impart fuel resistance to said composition; and

b. forming a seal about a mechanical surface by room temperature vulcanization, wherein said seal remains competent when exposed to fuel over extended periods of time.

25. The method of Claim 24, wherein said precipitated calcium carbonate is used in an amount from about 1% to about 60% by weight.

26. The method of Claim 24, wherein said forming step further includes forming a seal about a surface in a two cycle engine that is exposed to fuel.

27. A method of using a fuel resistant sealing composition to form a seal between two or more surfaces, the steps of which comprise:

a. applying therebetween said composition comprising a room temperature condensation curing silanol terminated silicone polymer, a plasticizer, a crosslinker and an effective amount of precipitated calcium carbonate to impart fuel resistance to said composition; and

b. allowing said composition to cure to form a fuel resistant elastomer.

28. The method of Claim 27, wherein said fuel resistant elastomer is formed between carburetor flanges and/or intake manifold flanges.

29. A silicone composition comprising:

- a. a silanol terminated silicone fluid;
- b. an effective amount of an organic plasticizer to maintain adhesion of said composition after immersion in oil;
- c. a crosslinker; and
- d. an effective amount of precipitated calcium carbonate to impart fuel resistance to said composition.

30. The silicone composition of Claim 29, further comprising a catalyst.

31. A cured fuel and oil resistant elastomer formed the composition of Claim 29.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/11889

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08K 3/14; C08J 5/00
US CL : 264/331.11; 524/788

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)

U.S. : C08K 3/14; C08J 5/00

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,641,832 A (NAGAOKA et al.) 24 June 1997.	1-31
X	US 4,514,529 A (BEERS et al.) 30 April 1985, see entire document.	1-31

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	*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
A document defining the general state of the art which is not considered to be of particular relevance	*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
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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)	*&* document member of the same patent family
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	

Date of the actual completion of the international search 30 JUNE 1999	Date of mailing of the international search report 27 JUL 1999
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