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(54) Title: SILICONE PRESSURE SENSITIVE ADHESIVE COMPOSITION

(57) Abstract: A silicone pressure sensitive adhesive composition containing the condensation product of silanol-functional silicone resin, wherein the resin contains M structural units according to the formula $R_3SiO_{1/2}$, wherein R is a monovalent hydrocarbon radical, and Q structural units according to the formula $SiO_{4/2}$ in a ratio of M units to Q units of less than 1.1:1, a silanol-functional polydiorganosiloxane gum, and a crosslinker exhibits high tack and high lap shear strength.



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SILICONE PRESSURE SENSITIVE ADHESIVE COMPOSITION

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims rights of priority from U.S. Provisional Patent Application Serial No. 60/213,700, filed June 23, 2000.

TECHNICAL FIELD

The present invention is directed to a silicone composition, more specifically, to a silicone pressure sensitive adhesive composition that provides high tack and high lap shear strength as well as enabling a broad range of peel adhesion strengths.

BACKGROUND

Commercially available silicone pressure sensitive adhesives ("PSAs") are known for their superior stability characteristics at temperatures above 350°F, compared to organic polymer-based PSA. However, the silicone PSA's improved stability at elevated temperatures, for example, up to temperatures in the range of 500 to 550°F, is typically achieved only at the expense of reduced tack performance, particularly under low contact pressure and at short contact times, see, for example, the silicone PSAs described in U.S. Patent Nos. 5,441,811 and 5,506,288.

What is needed in the art is a PSA that exhibits high tack and high lap shear strength at high temperatures while retaining a broad range of peel adhesion strength.

SUMMARY OF THE INVENTION

In a first aspect, the present invention is directed to a silicone composition comprising the condensation product of:

- 5 (a) a silanol-functional silicone resin, said resin comprising M structural units according to the formula $R^1_3SiO_{1/2}$, wherein each R^1 is independently hydroxy or a monovalent hydrocarbon radical, and Q structural units according to the formula $SiO_{4/2}$ in a ratio of M units to Q units of less than 1.1:1,
- (b) a silanol-functional polydiorganosiloxane gum, and
- (c) a crosslinker.

10 In a second aspect, the present invention is directed to a method for providing a pressure sensitive adhesive composition, comprising condensing, at an elevated temperature in the presence of a base catalyst, a silanol-functional silicone resin, a silanol-functional polydiorganosiloxane gum and a crosslinker.

15 In a third aspect, the present invention is directed to an article, comprising a substrate and a layer of a silicone composition disposed on at least a portion of at least one surface of the substrate, said silicone composition comprising the condensation product of a silanol-functional silicone resin, said resin comprising M structural units according to the formula $R^1_3SiO_{1/2}$, wherein each R^1 is independently hydroxy or a monovalent hydrocarbon radical, and Q structural units according to the formula $SiO_{4/2}$ in a ratio of M units to Q units of less than 1.1:1, a silanol-functional polydiorganosiloxane gum and a crosslinker.

20

25 In a fourth aspect, the present invention is directed to method for making an article, comprising applying a layer of a silicone composition on at least a portion of at least one surface of a substrate, said silicone composition comprising the condensation reaction product of a silanol-functional silicone resin, said resin comprising M structural units according to the formula

$R^1_3SiO_{1/2}$, wherein each R^1 is independently hydroxy or a monovalent hydrocarbon radical, and Q structural units according to the formula $SiO_{4/2}$ in a ratio of M units to Q units of less than 1.1:1, a silanol-functional polydiorganosiloxane gum and a crosslinker.

5 The composition of the present invention provides a silicone PSA that exhibits high probe tack and high lap shear strength at high temperatures while retaining a broad range of peel adhesion strength.

DETAILED DESCRIPTION OF THE INVENTION

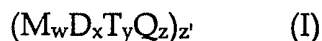
10 In a preferred embodiment, the composition comprises, based on 100 parts by weight ("pbw") of the composition, from 30 pbw to 80 pbw, more preferably from 35 pbw to 75 pbw and even more preferably from 65 pbw to 75 pbw of the silicone resin, from 20 pbw to 70 pbw, more preferably from 25 pbw to 65 pbw and even more preferably from 25 pbw to 35 pbw of the polydiorganosiloxane gum, and from 0.1 pbw to 5.0 pbw, more preferably from 0.5 pbw to 5.0 pbw and even more preferably from 0.5 pbw to 4.0 pbw of the crosslinker. In a preferred embodiment, the relative amount of resin and gum is from about 1.2 to 2.0, more preferably 1.2 to 1.8, pbw resin per pbw gum. The PSA composition may optionally comprise a volatile organic solvent in an amount of from 10 to 70 pbw, more preferably from 20 to 60 pbw of the total of the resin and gum composition.

20 Silicone resins suitable as the silanol-functional silicone resin of the present invention are those silicone resins containing a non-zero amount of silicon bonded hydroxy or "silanol" groups, preferably having silanol content of from about 0.2% to about 5%, more preferably from about 1% to about 3%, and even more preferably from about 1.5% to about 2.5% by weight, based on
25 the weight of such hydroxyl substituents and the total weight of the resin.

In a preferred embodiment, the silanol-functional silicone resin is a MQ resin. MQ resins are generically known in the art and contain M units, represented by the formula $R^1_3SiO_{1/2}$ and Q units, represented by the formula $SiO_{4/2}$. It is recognized that while the MQ resins are primarily made from M and Q units, there can be up to 5 mole percent of D units represented by the formula $R^2_2SiO_{2/2}$ and T units, represent by the formula $R^3SiO_{3/2}$, wherein each R^1 , R^2 and R^3 is independently hydroxyl or a monovalent hydrocarbon radical. Examples of preferred monovalent hydrocarbon radical include those monovalent hydrocarbon radicals having from about 1 to about 6 carbon atoms, such as alkyl radicals including methyl, ethyl, and isopropyl; alkenyl radicals including ethylene, propenyl, and hexenyl; cycloaliphatic radicals such as cyclopentyl cyclohexenyl; olefinic-containing radicals such as vinyl and allyl; and olefinic-containing radicals. Preferably, the monovalent hydrocarbon radical is methyl.

In a preferred embodiment, the silanol-functional silicone resin has a ratio of M units to Q units (an "M/Q ratio") of less than 1.1:1, more preferably from about 0.8:1 to less than 1.1:1, still more preferably from about 0.8:1 to about 1.0:1. Silanol-functional silicone resin blends having an M:Q ratio within a preferred range may be prepared by blending silicone MQ resins, one or more of which may individually have an M/Q ratio outside the preferred range.

In a preferred embodiment, the silanol-functional silicone resin comprises one or more compounds of the structural formula (I):



wherein:

M is $R^1_3SiO_{1/2}$;

D is $R^2SiO_{2/2}$;

T is $R^3SiO_{3/2}$;

and Q is $SiO_{4/2}$

each R^1 , R^2 and R^3 is independently hydroxy or a monovalent hydrocarbon radical, provided that the resin has a silanol content of 0.2% to about 5% by weight, and

w, x, y, z and z' are each numbers wherein w and z are each greater than 0 are chosen to provide an M/Q ratio from about 0.8:1.0 to less than 1.1:1.0, z' is such that a solution of about 60 percent by weight ("wt%") resin solids in toluene exhibits a viscosity of from 2 to 20 centiStokes ("cSt"), more preferably from 4 to 15 cSt, even more preferably from 5 to 12 cSt, wherein the quantity $((x + y)/(w + x + y + z))$ is less than 0.3.

Suitable hydrocarbon groups include acyclic hydrocarbon radicals, alicyclic hydrocarbon radicals and aromatic hydrocarbon radicals. Preferred hydrocarbon radicals are alkyl radicals, aryl radicals and aralkyl radicals.

As used herein, the terminology "acyclic hydrocarbon radical" means a straight chain or branched hydrocarbon radical, preferably containing from 1 to 60 carbon atoms per radical, which may be saturated or unsaturated and which may be optionally substituted or interrupted with one or more atoms or functional groups, such as, for example, carboxyl, cyano, hydroxy, halo and oxy. Suitable monovalent acyclic hydrocarbon radicals include, for example, alkyl, alkenyl, alkynyl, hydroxyalkyl, cyanoalkyl, carboxyalkyl, alkyloxy, oxaalkyl, alkylcarbonyloxaalkylene, carboxamide and haloalkyl, such as, for example, methyl, ethyl, sec-butyl, tert-butyl, octyl, decyl, dodecyl, cetyl, stearyl, ethenyl, propenyl, butynyl, hydroxypropyl, cyanoethyl, butoxy, 2,5,8-trioxadecanyl, carboxymethyl, chloromethyl and 3,3,3-fluoropropyl.

As used herein, the term "(C₁-C₆)alkyl" means a linear or branched alkyl group or fluoro-containing alkyl group from 1 to 6 carbons per group, such as, for example, methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, sec-butyl, tert-butyl, pentyl, hexyl, preferably methyl.

5 As used herein, the terminology "alicyclic hydrocarbon radical" means a radical containing one or more saturated hydrocarbon rings, preferably containing from 4 to 12 carbon atoms per ring, per radical which may optionally be substituted on one or more of the rings with one or more alkyl radicals, each preferably containing from 2 to 6 carbon atoms per alkyl
10 radical, halo radicals or other functional groups and which, in the case of a monovalent alicyclic hydrocarbon radical containing two or more rings, may be fused rings. Suitable monovalent alicyclic hydrocarbon radicals include, for example, cyclohexyl and cyclooctyl.

As used herein, the terminology "aromatic hydrocarbon radical"
15 means a hydrocarbon radical containing one or more aromatic rings per radical, which may, optionally, be substituted on the aromatic rings with one or more alkyl radicals, each preferably containing from 2 to 6 carbon atoms per alkyl radical, halo radicals or other functional groups and which, in the case of a monovalent aromatic hydrocarbon radical containing two or more
20 rings, may be fused rings. Suitable monovalent aromatic hydrocarbon radicals include, for example, phenyl, tolyl, 2,4,6-trimethylphenyl, 1,2-isopropylmethylphenyl, 1-pentalenyl, naphthyl, anthryl. As used herein, the term "aralkyl" means an aromatic derivative of an alkyl group, preferably a (C₂-C₆)alkyl group, wherein the alkyl portion of the aromatic derivative may,
25 optionally, be interrupted by an oxygen atom, such as, for example, phenylethyl, phenylpropyl, 2-(1-naphthyl)ethyl, preferably phenylpropyl, phenoxypropyl, biphenyloxypropyl.

In a preferred embodiment, the monovalent hydrocarbon radical is a monovalent (C₁-C₆)alkyl radical, most preferably, methyl.

Suitable silicone resins are made by methods known in the art, such as, for example, the method disclosed in U.S. Patent number 2,676,182 to Daudt et al. discloses a method in which a silica hydrosol is reacted under acidic conditions with a source of triorganosiloxy units such as hexaorganodisiloxane, e.g., hexamethyldisiloxane, or hydrolyzable triorganosiloxane, e.g. trimethylchlorosiloxane or mixtures thereof, and recovering a benzene soluble resin copolymer having M and Q units, and are commercially available, for example, the MQ resin is commercially available in solution form in a solvent such as xylene or toluene, generally at a 40% to 60% by weight solution.

Silicone gums suitable as the silanol-functional silicone gum component of the present invention are those silanol-functional polyorganosiloxanes having a viscosity from about 350,000 centiPoise (cps) to about 200,000,000 centipoise at 25°C. Gum viscosity may be characterized using, e.g., using a viscosity meter such as a Rheometrics rheometer.

In a preferred embodiment, the silanol-functional silicone gum comprises one or more silanol-terminated silicone compounds of the structural formula (II):



wherein:

M' is R⁴₃SiO_{1/2};

D' is R⁵₂SiO_{2/2};

25 T' is R⁶SiO_{3/2};

and Q' is $\text{SiO}_{4/2}$

each R^4 , R^5 and R^6 is independently hydroxy or a monovalent hydrocarbon radical, provided that at least one R^4 substituent per M' unit is hydroxy, and

a, b, c and d are integers effective to provide a gum which exhibits a viscosity
5 from about 350,000 to about 200,000,000 centipoise ("cps") at 25°C, more preferably, a viscosity from about 750,000 cps to about 2,000,000 cps.

Suitable monovalent hydrocarbon groups include monovalent acyclic hydrocarbon radicals, alicyclic hydrocarbon radicals and aromatic hydrocarbon radicals. Preferred hydrocarbon radicals are alkyl radicals,
10 monovalent aryl radicals and aralkyl radicals.

In a preferred embodiment, one R^4 substituent per M' group is hydroxyl and each of the remaining R^4 substituents and each R^5 and R^6 is independently alkyl, aryl or aralkyl. In a more highly preferred embodiment, one R^4 substituent per M' group is hydroxyl and each of the remaining R^4
15 substituents and each R^5 and R^6 is independently methyl, phenyl or phenylpropyl.

Suitable polydiorganosiloxane gums are known and are commercially available. For example, the polydiorganosiloxanes can be prepared according to the method disclosed in U.S. Patent No. 2,814,601, herein incorporated by
20 reference, wherein an appropriate siloxane is reacted with an aqueous acid in a closed system until the viscosity of the siloxane has become essentially constant. The product is then washed free of acid.

Compounds suitable for use as the polyalkoxysilane crosslinker of the present invention are those silane compounds with an alkoxy group on the
25 silicon atom.

In a preferred embodiment, the crosslinker of the present invention comprises one or more of:

silanes according to structural formula III:



5 wherein each R⁷ is independently hydroxy, alkoxy, preferably (C₁-C₆)alkoxy, or a monovalent (C₁-C₁₅)hydrocarbon radical, provided that at least two R⁷ substituents per molecule of the silane compound are each hydroxy or alkoxy,

poly(siloxanes) having structural units according to formula (IV):



wherein each R⁸ is independently hydroxy, alkoxy, preferably (C₁-C₆)alkoxy, and

poly(alkoxysiloxane-alkoxytitanate) copolymers containing first structural units according to formula (IV) and second structural units according to formula (V):



wherein each R⁹ is independently hydroxy or alkoxy, preferably (C₁-C₆)alkoxy and e is an integer from 0 to 2.

In a preferred embodiment, the crosslinker is dimethyldiethoxysilane, methyltriethoxysilane, a poly(diethoxysiloxane) or a poly(diethoxysiloxane-diethoxytitanoate) copolymer.

In a preferred embodiment, the composition of the present invention further comprises a volatile organic solvent or a mixture of solvents. As used herein, "volatile organic solvent" means any non-aqueous solvent or carrier

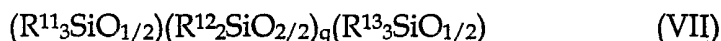
having a boiling point above 30°C. Examples of volatile organic solvents include volatile liquid hydrocarbon solvents such as volatile paraffinic hydrocarbons, e.g. pentane, the iso-pentanes, cyclopentane, hexane, the iso-hexanes, cyclohexane, heptane, the iso-heptanes, cycloheptane, octane, the
 5 iso-octanes, cyclo-octane and the like; volatile aromatic solvents such as benzene, toluene, the various xylenes, mesitylene and the like are examples of suitable hydrocarbon solvents that may be used. It is also possible to utilize low molecular weight oxygen containing solvents such as alcohols, ketones, aldehydes and the like. Additional non-reactive volatile solvents that may be
 10 employed may be selected from the group consisting of:

(1) cyclic diorganosiloxanes having the formula (VI):



wherein R^{10} is a monovalent hydrocarbon radical having from one to ten carbon atoms, preferably one to eight, more preferably one to six, and most
 15 preferably one to four carbon atoms; and p is an integer having values ranging from three to eight and

(2) linear volatile silicones having the formula (VII):



wherein each R^{11} , R^{12} and R^{13} is independently a monovalent hydrocarbon
 20 radical having from one to ten carbon atoms, preferably one to eight, more preferably one to six, and most preferably one to four carbon atoms and q is an integer of from 0 to 8.

Additional ingredients known in the art, such as, for example, antioxidants, pigments, stabilizers, fillers, may be added to the composition of
 25 this invention if desired. In one embodiment, the silicone composition of the present invention further comprises one or more of other silicone polymers in

addition to the above described condensation product and organic polymers, such as, for example, conventional silicone PSA polymers or organic PSA polymers.

5 The components of the compositions of this invention can be mixed in any manner such as in bulk or in organic solvent. Since the MQ resin is a solid and is conveniently prepared and handled in an organic solvent, the preparation of the composition of this invention preferably uses a volatile organic solvent for the mixing of the MQ resin and silicone gum. The mixing of the components can be accomplished by any of the techniques known in
10 the art, such as milling, blending, stirring, and the like, either in batch or in continuous process.

In a preferred embodiment, the silicone composition of the present invention is prepared by subjecting a mixture of the silicone resin, silicone gum, crosslinker to condensation conditions in the presence of a base catalyst.
15 Preferably, the mixture is heated to a temperature of from about 110 to 130°C, for example, by refluxing a mixture of the silicone resin, silicone gum, crosslinker, base catalyst and an organic solvent, such as, for example, toluene, for about one to three hours to condense the resin, gum and crosslinker

20 In an even more highly preferred embodiment, a mixture of the silicone resin, silicone gum, crosslinker, base catalyst and an organic solvent is heated to a temperature of from about 60 to 80°C for 2 to 4 hours. Water is added to the mixture, in molar excess based on moles of alkoxy groups of the reactants, and the resulting mixture is heated and mixed, in a preferred
25 example, for about 1 hour, to allow hydrolysis of any remaining alkoxy groups. The reaction mixture is then heated to a temperature of from about 110 to 130°C for about 1 to 3 hours to complete the condensation reaction.

The water formed during the condensation reaction is removed and the resulting condensation product is cooled, its solids content is adjusted, and the mixture is neutralized with acid.

Suitable base catalysts for silanol/alkoxysilane condensation reactions are known and include, for example, alkali metal hydroxides, e.g., sodium hydroxide, potassium hydroxide and the like; an aminofunctional silanes such as those disclosed in U.S. Patent No. 4,906,695 to Blizzard et al., which is hereby incorporated by reference. Suitable aminofunctional silanes include, for example, N-gamma-aminopropyltriethoxysilane, N-beta-aminoethyl-gamma-amino-isobutyltrimethoxysilane, and N-beta-aminoethyl-gamma-aminopropyltrimethoxysilane.

In a preferred embodiment, the base catalyst is sodium hydroxide, preferably in the form of an aqueous solution. The amount of base catalyst should be in the range of about 3 ppm to about 30 ppm, preferably about 8 ppm to about 20 ppm, based on the combined weight of the resin and gum.

In a preferred embodiment, the base catalyzed condensation reaction product mixture is neutralized by addition of an acid. Suitable acids for neutralizing the condensed mixture include mineral acids, such as hydrochloric acid, phosphoric acid, and the like and organic acids such as acetic acid, acetyl chloride, and the like, preferably phosphoric acid.

In a preferred embodiment, the silicone composition of the present invention further comprises free radical curing agent. Suitable free radical curing agents are those compounds that, upon thermal or radiation exposure, generate radicals which cause cure or crosslinking reactions within the silicone composition. Suitable free radical curing agents include, for example, peroxides and azo compounds. Specific peroxides include, for example, acetyl and benzoyl peroxide, cumyl peroxide, 2,4-dichlorobenzoyl peroxide.

The amount of cure catalyst is generally an amount effective to cause the cure or crosslinking of silicone adhesive and is typically about 0.5 to about 3.0% by weight of silicone composition solids.

5 The silicone composition of this invention is useful as a pressure sensitive adhesive for adhering a first substrate to a second substrate.

The silicone composition is applied to at least a portion of a surface of a first substrate in any convenient manner such as by roll coating, by knife-over-roll coating and the like, by dipping the base member in solution, or by brushing or spraying solution on the surface. In a preferred embodiment,
10 wherein the silicone composition comprises a free radical cure agent, the layer of silicone composition is then cured, for example, by heating to stabilize the layer on the substrate and prevent movement, for example, "creep" of the layer under applied pressure.

The first substrate and second a substrate are subsequently brought
15 together, so that the layer of silicone composition is in between the substrates and in contact with each of the substrates, to bond the substrates together.

The first and second substrates may be any known solid material such as metals, such as, for example, aluminum, silver, copper, iron and their alloys; porous materials such as, for example, paper, wood, leather, and
20 fabrics; polymeric materials such as, for example, polyolefins, such as polyethylene and polypropylene, fluorocarbon polymers such as polytetrafluoroethylene and polyvinylfluoride, polyimide, silicone elastomers, silicone resins, polystyrene, polyamides such as nylon, polyesters and acrylic polymers; painted surfaces; siliceous material such as concrete,
25 bricks, cinderblocks, and glass such as glass cloth. Porous materials such as glass cloth are often impregnated with a substance that will prevent the migration of the PSA from one surface to another surface of the support. It is

also well known to chemically treat the surface of fluorocarbon polymer support to enhance the adhesion of a PSA to said surface.

In a preferred embodiment, the first substrate comprises a flat substrate such as, for example, a sheet of paper, a woven or non-woven
5 textile, a polymer film or a metal foil.

Examples of articles made with the silicone composition of the present invention include pressure-sensitive adhesive tapes, labels, emblems and other decorative materials. The composition of the present invention is particularly useful as the adhesive layer of tapes for high temperature, high
10 stress applications, such as for example, slicing tapes for use in splicing rolls of paper in continuous printing processes.

The present invention is further directed to pressure sensitive adhesive formed from the cure of the composition of this invention. In addition, the present invention is directed to articles of manufacture containing a solid
15 support having deposited on at least one surface thereof the pressure sensitive adhesive of this invention. The preferred article of manufacture within the scope of this invention is a pressure sensitive tape containing a flexible material having deposited on at least one surface thereof the pressure sensitive adhesive of this invention.

20 The following examples are to illustrate the invention and are not to be construed as limiting the claims.

EXAMPLES

Components used in Examples 1 to 19

A	MQ resin solution (60% resin solids in toluene) having a viscosity of about 6.4 cSt, a M/Q ratio of 1.0:1 and a silanol content of about 2.8 wt%.
B	MQ resin solution (60% resin solids in toluene) having a viscosity in the range of from 9.5 to 10.5 centistokes and an M/Q ratio of 0.8:1.
C	MQ resin solution (60% resin solids in toluene) having a viscosity of about 6.1 cSt and a M/Q ratio of 1:1.
D	MQ resin solution (60% resin solids in toluene) having a viscosity of about 6.2 cSt and a M/Q ratio of 1.0:1.
E	Poly(dimethyl-co-diphenyl)siloxane gum having a diphenylsiloxy unit content of about 8 mole percent).
F	Polydimethylsiloxane gum blend (blend of a first gum having a viscosity in the range of from 150,000 to 350,000 cp, and a second gum having a viscosity in the range of from 65,000 to 175,000 cp).
G	Polydiethoxysiloxane crosslinker, 40-42% SiO ₂ content (Ethylsilicate 40).
H	Poly(diethoxysiloxane-diethoxytitanate) copolymer crosslinker, 92% SiO ₂ , 8% TiO ₂ content (Gelest).
I	Toluene.
J	10% NaOH solution.
K	1 % NaOH solution.
L	Methyltrimethoxysilane crosslinker.
M	MQ resin solution (60% resin solids in toluene) having a viscosity of about 6.5 cSt viscosity and an M/Q ratio of 1.0:1.
N	Poly(diethoxysilane) crosslinker, (Gelest, Inc. PSI-023).
O	MQ resin solution (60% resin solids in toluene) having a viscosity of about 6.0 cSt and an M/Q ratio of 1.0:1.
P	MQ resin solution (60% resin solids in toluene) having a viscosity of about 6.0 cSt and M/Q ratio of 1.0:1.
Q	MQ resin solution (60% resin solids in toluene) having a viscosity of about 9.6 centistokes and an M/Q ratio of 0.8:1.
R	MQ resin solution (60% resin solids in toluene) having a viscosity of 5.8 cSt and a M/Q ratio of 1.0:1.

Examples 1 to 4

To a 1 liter reactor, the MQ resin, polydiorganosiloxane gum and polyalkoxysilane crosslinker were charged in the amounts listed in Table 1. For comparative examples 1 and 2, no crosslinker was used. Solvent was added, and the contents were mixed until a homogeneous solution was formed. A solution catalyst and a trace amount of water were charged, and the mixture was heated to a reflux temperature of about 110°C and held for approximately two hours. The mixture was cooled and then neutralized to slightly acidic with phosphoric acid. Probe Tack, Peel Adhesion and Lap Shear results are shown in Table 2.

TABLE 1

	Ex. 1 (Comp.) Type	Amt. (Grams)	Ex. 2 (Comp.) Type	Amt. (Grams)	Ex. 3 Type	Amt. (Grams)	Ex. 4 Type	Amt. (Grams)
MQ resin	A	310	A B	155 155	A	310	A B	155 155
Gum	E	128.3	E	128.3	E	128.3	E	128.3
Crosslinker	None	0	None	0	G	5.7	G	5.7
Solvent	I	132	I	132	I	132	I	132
Catalyst	J	0.075	J	0.075	J	0.075	J	0.075
Mixture % Solids		56.1		55.6		56.6		55.6
Mixture Visc. (centipoise)		9920		13,100		13,800		12,000

Table 2 - Performance Properties

	Example 1 (Comp.)	Example 2 (Comp.)	Example 3	Example 4
Crosslinker	No	No	Yes	Yes
Probe Tack (g/cm ²)				
A weight	960	602	878	614
F weight	1056	755	922	745
Peel Adhesion (oz./in.)	31	37	35	35
500°F Lap Shear Holding Test (1"x1", 500 gram wt)	0.5 hr.	1.0 hr.	24 hrs.	24 hrs.

Performance Testing: To test the adhesion properties (Probe Tack, Peel Adhesion and Lap Shear Strength), the coating formulations were catalyzed with 2% of benzyl peroxide per solids (of total resin and gum) and diluted with toluene to a percent solids of 45%. The catalyzed mixture was coated onto 1 mil polyimide film in an amount equal to approximately 1.5 mil dry adhesive thickness. The probe tack adhesion was measured on a Polyken® Probe Tack instrument at 1.0 cm/sec pull speed with a 1.0 second dwell time. Two different contact pressures were applied - F weight (1000 g/cm²) and A weight (100 g/cm²). The high temperature lap shear strength was tested by preparing a 1 inch x 1 inch area of adhesive tape using 1 mil Kapton® polyimide, 1.4-1.7 mils dry adhesive build to steel to form a laminate, applying a 500 gram weight to the adhesive strip, then placing the laminate into a forced air oven (at 500°F or 550°F as required) until the either the adhesive slipped off of the steel plate, or 24 hours, whichever occurred first. The time in the oven before the adhesive slipped off, or 24 hours, is the lap shear strength. The peel adhesion was measured by performing a 180° peel test of the adhesive against a clean steel plate at a rate of 12 inches per minute.

Examples 5 to 8

To a 1 liter reactor, the MQ resin, polydiorganosiloxane gum and polyalkoxysilane crosslinker were charged in the amounts listed in Table 3. Solvent was added, and the contents were mixed until a homogeneous solution was formed. A solution catalyst and water were charged, and the mixture was heated to a reflux temperature of about 110°C and held for approximately two hours. The mixture was cooled, isopropanol was added, and then it was neutralized to slightly acidic with phosphoric acid. Probe Tack, Peel Adhesion and Lap Shear results are shown in Table 4.

Table 3

	Ex. 5	Amt.	Ex. 6	Amt.	Ex. 7	Amt.	Ex. 8	Amt.
	Type	(Grams)	Type	(Grams)	Type	(Grams)	Type	(Grams)
MQ resin (75/25 or 80/20 mixture)	C B	225.2 75.1	C B	225.2 75.1	D B	216.8 54.2	D B	155 155
Gum	E	138.6	E	138.6	F	101.7	F	101.7
Crosslinker	G	5.8	G	5.8	H	6.5	H	6.5
Solvent	I	95	I	95	I	90	I	90
Catalyst	K	0.81	K	0.81	J	0.07	J	0.07
Water		0.40		0.80		3.0		3.0
Isopropanol		1.10		1.10		0.80		0.80
Mixture % Solids		60.2		59.2		60.0		60.0

Table 4 - Performance Properties

	Example 5	Example 6	Example 7	Example 8
Resin/Gum ratio	1.30	1.30	1.60	1.50
Crosslinker	G	G	H	H
Probe Tack (g/cm ²)				
A weight	767	749	519	413
F weight	867	799	731	683
Peel Adhesion (oz./in.)	27	30	33	29
500°F	24 hrs.	24 hrs.	24 hrs.	24 hrs.
550°F	24 hrs.	24 hrs.	24 hrs.	<0.5 hr.
Lap Shear Holding Test (1"x1", 500 gram wt)				

Examples 9 to 15

Examples 9 to 12 were prepared in the same manner as Examples 5 to 8 discussed previously. Examples 13, 14 and 15 were prepared by repeating the composition of Example 4, except that the crosslinker level was varied, and in
5 Examples 14 and 15, the crosslinker was added after the PSA was made, instead of initially with the resin, gum and solvent. The crosslinker and the PSA were blended at room temperature and tested as described above. Amounts of the components used and performance results of the product are
10 shown in Tables 5 to 7 below.

Table 5

	Ex. 9 Type	Amt. (Grams)	Ex. 10 Type	Amt. (Grams)	Ex. 11 Type	Amt. (Grams)	Ex. 12 Type	Amt. (Grams)
MQ resin (mixture)	D	173.4	M	229.3	O	232.5	C	163.0
	B	43.3	B	25.0	B	77.5	B	69.3
Gum	F	81.4	F	101.7	E	128.3	E	106.6
Crosslinker	L	4.5	N	6.5	G	11.4	G	12.3
Solvent	I	90	I	90	I	132	I	118
Catalyst	J	0.06	J	0.07	K	0.75	K	0.70
Water		3.0		3.0		2.3		0
Isopropanol		0.7		0.8		0		0
Mixture % Solids		60.0		60.0		58.3		55.6

Table 6 - Performance Properties

	Example 9	Example 10	Example 11	Example 12
Resin/Gum ratio	1.60	1.50	1.45	1.30
Crosslinker*	L (2.1 wt%)	M (2.6 wt%)	G (3.6 wt%)	G (5.0 wt%)
Probe Tack (g/cm ²)				
A weight	456	300	811	796
F weight	672	553	903	861
Peel Adhesion (oz./in.)	35.5	30	29	27
Lap Shear Holding Test (1"x1", 500 gram wt)				
500°F	6 hrs.	5 hrs.	--	24 hrs.
550°F	<0.5 hrs.	<0.5 hrs.	24 hrs.	24 hrs.

*per silicone solids

Table 7 - Performance Properties

	Example 13	Example 14**	Example 15**
Resin/Gum ratio	1.50	1.30	1.28
Crosslinker*	G (7.5 wt%)	G (3.6 wt%)	G (4.5 wt%)
Probe Tack (g/cm ²)			
A weight	610	687	764
F weight	736	720	815
Peel Adhesion (oz./in.)	39	38	28
500°F	24 hrs.	24 hrs.	24 hrs.
550°F	24 hrs.	--	--
Lap Shear Holding Test (1"x1", 500 gram wt)			

* per silicone solids

**For Example 14, 1.0 g of crosslinker G was added to 50.0 g of the adhesive of Example 4, and blended at room temperature. For Example 15, 1.0 g of crosslinker G was added to 40.0 g of the adhesive of Example 4 (with the resin/gum ratio adjusted to 1.28), and blended at room temperature.

Example 16

This example illustrates that an adhesive prepared according to the invention can be blended with a commercial adhesive to impart improved lap shear properties.

A composition similar to that of Example 4 was made as follows. To a 1 liter reactor, the following ingredients were charged: 212.4 grams of resin solution P; 70.8 grams of resin Q; 126.8 grams of gum F; 6.9 grams of

crosslinker G; 93.9 grams of solvent I; and 0.08 grams of catalyst J. The components were mixed and the mixture was heated to approximately 70°C for four hours, 3.0 g water were then added, mixing was continued for 1 hr and the mixture was then refluxed at about 110°C for 2 hours. The mixture
5 was then cooled and 0.1 g of a 10% solution of phosphoric acid was added, yielding an adhesive with a viscosity of 24,800 centipoise at 59.8 wt% solids.

A commercially available PSA (56.0 wt% solids) was blended in varying amounts with the above adhesive and tested in the same manner as the previous examples. Results are shown in Table 8.

Table 8 - Performance Properties of PSA Blend

	16A	16B	16C	16D	Comparative Example
PSA of 50.0 grams	37.5 grams	25.0 grams	12.5 grams	--	
Example 16					
Commercial PSA	--	13.6 grams	27.3 grams	40.9 grams	50 grams
Probe Tack (g/cm ²)	756	617	599	568	512
A weight	848	925	805	745	658
F weight					
Peel Adhesion (oz./in.)	27	20	24	26	27
Lap Shear Holding Test					1.5
(1"x1", 500 gram wt)	> 24 hours	> 24 hours	> 24 hours	6 hours	hours
550°F					
Examples 17 to 19					

Examples 17 to 19 compare methyl PSAs made by the conventional process (no crosslinker) with methyl PSAs of the invention at different crosslinker levels. Examples 17 to 192 were prepared in the same manner as Examples 5 to 8 discussed previously. Amounts of the components used and performance results of the product are shown in Tables 9 and 10 below.

Table 9 - Amounts of Components

	Ex. 17 Type	Amt. (Grams)	Ex. 18 Type	Amt. (Grams)	Ex. 19 Type	Amt. (Grams)
MQ resin	R	1197.8	C	237.3	C	237.3
Gum	F	410.6	F	86.3	E	86.3
Crosslinker		0	G	10.2	G	3.3
Solvent	I	389.9	I	98.8	I	98.8
Catalyst	J	0.36	J	0.06	K	0.06
Isopropanol		0		0.70		0.70
Mixture % Solids		55.0		57.5		57.1

Table 10 - Performance Properties

	Example 17	Example 18	Example 19
Resin/Gum ratio	1.70	1.65	1.65
Crosslinker*	None	G (4.5 wt%)	G (1.4 wt%)
Probe Tack (g/cm ²)			
A weight	839	630	784
F weight	934	862	874
Peel Adhesion (oz./in.)	37.5	34.5	34.5
500°F 550°F Lap Shear Holding Test (1"x1", 500 gram wt)	1 hr. (at 450°F)	24 hrs. 24 hrs.	< 0.5 hrs. ≤ 0.25 hrs. (24 hrs. at 450°F)

* per silicone solids

The composition of the present invention provides a silicone PSA that exhibits high probe tack and high lap shear strength at high temperatures while retaining a broad range of peel adhesion strength.

CLAIMS:

1. A silicone composition comprising the condensation product of:

(a) a silanol-functional silicone resin, said resin comprising M structural units according to the formula $R^1_3SiO_{1/2}$, wherein each R^1 is independently hydroxy or a monovalent hydrocarbon radical, and Q structural units according to the formula $SiO_{4/2}$ in a ratio of M units to Q units of less than 1.1:1,

(b) a silanol-functional polydiorganosiloxane gum, and

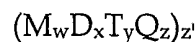
(c) a crosslinker.

2. The composition of claim 1, wherein the composition comprises, based on 100 parts by weight of the composition, from 30 to 80 parts by weight of the silicone resin, from 20 to 70 parts by weight of the polydiorganosiloxane gum, and from 0.1 to 5.0 parts by weight of the crosslinker.

3. The composition of claim 1, wherein the resin and gum are present in a relative amount of from about 1.2 to 2.0 parts by weight resin per parts by weight gum.

4. The composition of claim 1, wherein the ratio of M units to Q units is from 0.8:1 to less than 1.1:1.

5. The composition of claim 1, wherein the silanol-functional silicone resin comprises one or more compounds of the structural formula:



wherein:

5 M is $R^1_3SiO_{1/2}$;

D is $R^2_2SiO_{2/2}$;

T is $R^3SiO_{3/2}$;

and Q is $SiO_{4/2}$

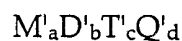
each R^1 , R^2 and R^3 is independently hydroxy or a monovalent hydrocarbon
10 radical, provided that the resin has a silanol content of 0.2% to about 5% by weight, and

w , x , y , z and z' are each numbers wherein w and z are each greater than 0 are chosen to provide an M/Q ratio from about 0.8:1.0 to less than 1.1:1.0, z' is such that a solution of about 60 percent by weight resin solids in toluene
15 exhibits a viscosity of from 2 to 20 centiStokes, more preferably from 4 to 15 cSt, even more preferably from 5 to 12 cSt, wherein the quantity $((x + y)/(w + x + y + z))$ is less than 0.3.

6. The composition of claim 5, wherein each R^1 , R^2 and R^3 is independently hydroxy or a monovalent (C_1 - C_6)alkyl radical.

20 7. The composition of claim 1, wherein the silanol-functional polydiorganosiloxane gum comprises a silanol-functional polyorganosiloxane polymer having a viscosity from about 350,000 to about 200,000,000 centipoise at 25°C.

8. The composition of claim 1, wherein the silanol-functional silicone gum comprises one or more silanol-terminated silicone compounds of the structural formula:



5 wherein:

M' is $R^4_3SiO_{1/2}$;

D' is $R^5_2SiO_{2/2}$;

T' is $R^6SiO_{3/2}$;

and Q' is $SiO_{4/2}$

10 each R^4 , R^5 and R^6 is independently hydroxy or a monovalent hydrocarbon radical, provided that at least one R^4 substituent per M' unit is hydroxy, and a , b , c and d are integers effective to provide a gum which exhibits a viscosity from about 350,000 to about 200,000,000 centipoise at 25°C.

9. The composition of claim 8, wherein one R^4 substituent per M' group is
15 hydroxyl and each of the remaining R^4 substituents and each R^5 and R^6 is independently methyl, phenyl or phenylpropyl.

10. The composition of claim 1, wherein the crosslinker comprises one or more compounds selected from:

(a) silanes according to structural formula:



5 wherein each R^7 is independently hydroxy, alkoxy, preferably (C₁-C₆)alkoxy, or a monovalent (C₁-C₁₅)hydrocarbon radical, provided that at least two R^7 substituents per molecule of the silane compound are each hydroxy or alkoxy,

(b) poly(siloxane)s having structural units according to formula:



wherein each R^8 is independently hydroxy, alkoxy, preferably (C₁-C₆)alkoxy, and

(c) poly(alkoxysiloxane-alkoxytitanate) copolymers containing first structural units according to formula (IV) and second structural units
15 according to formula:



wherein each R^9 is independently hydroxy or alkoxy, preferably (C₁-C₆)alkoxy and e is an integer from 0 to 2.

11. The composition of claim 1, wherein the condensation product is made
20 by contacting the silanol-functional silicone resin, silanol-functional polydiorganosiloxane gum and crosslinker at an elevated temperature in the presence of a base catalyst.

12. The composition of claim 1, further comprising a free radical curing agent..

13. A method for providing a pressure sensitive adhesive composition, comprising condensing, at an elevated temperature in the presence of a base catalyst, a silanol-functional silicone resin, said resin comprising M structural units according to the formula $R^1_3SiO_{1/2}$, wherein each R^1 is independently
5 hydroxy or a monovalent hydrocarbon radical, and Q structural units according to the formula $SiO_{4/2}$ in a ratio of M units to Q units of less than 1.1:1, a silanol-functional polydiorganosiloxane gum and a crosslinker.
14. The method of claim 13, wherein the elevated temperature is from about 110 to 130°C.
- 10 15. The method of claim 13, comprising:
- (a) heating a mixture of the resin, gum, crosslinker, base catalyst and an organic solvent to a first elevated temperature to begin condensation of the resin, gum and crosslinker,
 - (b) adding a molar excess, based on moles of alkoxy groups of the
15 resin, gum and crosslinker of the mixture of step (a), of water to the mixture of step (a),
 - (c) heating the mixture of step (c) to allow hydrolysis of any remaining alkoxy groups, and
 - (d) heating the mixture of step (c) to a second elevated temperature
20 to drive condensation of the resin, gum and crosslinker toward completion.
16. The method of claim 15, wherein the mixture of step (a) is heated to a first elevated temperature of from 60 to 80°C for a time period of from 2 to 4 hours prior to step (b).

17. The method of claim 15, wherein the mixture of step (d) is heated to a second elevated temperature of from about 110 to 130°C for a time period of from about 1 to 3 hours.

18. An article, comprising a substrate and a layer of a silicone composition disposed on at least a portion of at least one surface of the substrate, said silicone composition comprising the condensation product of a silanol-functional silicone resin, said resin comprising M structural units according to the formula $R^1_3SiO_{1/2}$, wherein each R^1 is independently hydroxy or a monovalent hydrocarbon radical, and Q structural units according to the formula $SiO_{4/2}$ in a ratio of M units to Q units of less than 1.1:1, a silanol-functional polydiorganosiloxane gum and a crosslinker.

19. The article of claim 18, wherein the substrate comprises paper, a woven textile, a non-woven textile, a polymer film or a metal foil.

20. The article of claim 18, wherein the silicone composition further comprises a free radical curing agent.

21. A method for making an article, comprising applying a layer of a silicone composition on at least a portion of at least one surface of a substrate, said silicone composition comprising the condensation reaction product of a silanol-functional silicone resin, said resin comprising M structural units according to the formula $R^1_3SiO_{1/2}$, wherein each R^1 is independently hydroxy or a monovalent hydrocarbon radical, and Q structural units according to the formula $SiO_{4/2}$ in a ratio of M units to Q units of less than 1.1:1, a silanol-functional polydiorganosiloxane gum and a crosslinker.

INTERNATIONAL SEARCH REPORT

tional Application No

PCT/US 01/15014

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09J183/04

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 C09J C08L

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)

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	DE 44 14 653 A (GENERAL ELECTRIC) 17 November 1994 (1994-11-17) page 3, line 29; example 3 page 4, line 14 - line 38 page 5, line 62 page 6, line 29	1-14, 18-21
X	EP 0 628 617 A (DOW CORNING) 14 December 1994 (1994-12-14) claim 1; example 3	1-3,5,6, 9-11,13, 14,18-21
X	EP 0 787 774 A (DOW CORNING TORAY) 6 August 1997 (1997-08-06) claim 1	1-10,18, 19



Further documents are listed in the continuation of box C.



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INTERNATIONAL SEARCH REPORT

In ional Application No
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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 4414653	A	17-11-1994	DE 4414653 A1	17-11-1994
			FR 2705355 A1	25-11-1994
			GB 2277933 A ,B	16-11-1994
			JP 7053941 A	28-02-1995
			US 5580915 A	03-12-1996
EP 628617	A	14-12-1994	US 5905123 A	18-05-1999
			CA 2125365 A1	12-12-1994
			DE 69410347 D1	25-06-1998
			DE 69410347 T2	07-01-1999
			EP 0628617 A2	14-12-1994
			JP 7053942 A	28-02-1995
EP 787774	A	06-08-1997	JP 9268256 A	14-10-1997
			EP 0787774 A2	06-08-1997
			US 5705587 A	06-01-1998