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(57) Claim

1. A curable sealant composition comprising a mixture of an allyl ester, at least one methylhydrosiloxane, a Group VIII metal catalyst and a filler.

3. A method of preparing a curable sealant composition which comprises mixing an allyl ester, at least one methylhydrosiloxane, a Group VIII metal catalyst and a filler and heating at a temperature in excess of 125°C.

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Complete Specification for the invention entitled:

SILICONE SEALANTS

The following statement is a full description of this invention, including the best method of performing it known to :- us

SILICONE SEALANTS

This invention relates to silicone sealants and, more particularly, to sealants which include certain cross-linked methylhydrosiloxanes.

The cross-linking of silicones to form higher molecular weight polymers has been used to prepare many useful silicone products. One example is the hydrolysis of reactive chloro, alkoxy and amino, silanes to form various fluids, resins and elastomers through silanol condensation. Low molecular weight resinous silicones have been formulated with high viscosity silanol fluids to prepare pressure sensitive adhesives. These pressure sensitive adhesives have medical utility such as surgical dressings as well as various non-medical applications. The cross-linking reaction of vinyl endblocked silicone fluids of about one thousand centistoke viscosity with methyl/hydrogen silicones in the presence of a platinum catalyst provides "psuedo" interpenetrating network gels. These gels are used in applications ranging from breast implants to paper coatings. Condensation curing has been employed to prepare room temperature vulcanizing sealants and adhesives. The room temperature vulcanizing and curable silicones have been composed of cross-linkers with moisture sensitive groups on silicon and are typically catalyzed by tin, zinc, titanium, iron or carboxylate salt catalysts. High temperature vulcanizing cures involves a method in which a peroxide initiates cure of a silcon hydride and an olefin substituted silicone at elevated temperature. Such technology has found application in penile prosthesis, for example.

Since one of the major cure reactions used in sealants is acetoxy hydrolysis known as moisture curing, it

has been unexpectedly discovered that the foregoing technology for converting a silicon hydride to a silicon ester could be applied in a new and novel manner for creating an "in situ" acetoxy cure. Thus, and in accordance with the concept of the present invention, the silicon hydrogens on a silicone are converted to acetoxy groups and exposed to air and the material cures and cross-links through silanols to form new siloxane bonds.

Silicone sealants are old in the art and such sealants generally include a mixture of a silicone polymer, one or more fillers, a crosslinking component such as a reactive silane and a catalyst. The silicone polymer has a siloxane backbone and includes pendant alkyl, alkoxy or acetoxy groups. Such groups are hydrolyzed to silanol groups which form larger chains by condensation. The sealants may be applied by means of a caulking gun and are cured by exposure in moist air. The cured products are employed as flexible space fillers. The silicone sealants have low shrinkage characteristics and may be applied and used over a wide temperature range. Representative formulations of such silicone sealants are set forth in more detail and may be found may be found by reference to U.S. Patent No. 3,642,692, issued February 15, 1972; U.S. Patent No. 3,697,473, issued October 10, 1972; U.S. Patent No. 3,734,881, issued May 22, 1973; and U.S. Patent No. 4,711,928, issued December 8, 1987. While the present invention relates to a silicone sealant, the sealant of this invention differs from prior art sealants in that a new mechanism is provided, as noted previously in detail, for achieving a cure. Thus, in accordance with the present invention, a separate crosslinking component is not required as the combination of the methylhydrosiloxane and the allyl acetate provides the acetoxy group which cross-links the siloxane to higher molecular weight polymers.

composition

This invention relates to a silicone sealant, and to a process of curing and cross-linking methylhydrosiloxanes by contacting and forming a mixture of an allyl ester with at least one methylhydrosiloxane in the presence of a Group VIII metal catalyst and heating the mixture of the allyl ester, the methylhydrosiloxane and the Group VIII metal catalyst, in the presence of ambient moisture until the methylhydrosiloxane becomes cured and cross-linked. In the process, the mixture of the allyl ester, the methylhydrosiloxane and the Group VIII metal catalyst, is heated at a temperature in excess of about 125°C. There is also included in the mixture at least one filler.

For purposes of the present invention, "bulk" is defined as curing in a container to a depth in excess of about one-eighth of an inch.

These and other features, objects and advantages, of the herein described invention will become more apparent when considered in light of the accompanying detailed description thereof.

As noted hereinabove, a mixture is prepared including certain silicones that is employed as a sealant. The sealant is prepared in accordance with a process of curing and cross-linking methylhydrosiloxanes by contacting and forming a mixture of either an allyl amide or an allyl ester with at least one methylhydrosiloxane in the presence of a Group VIII metal catalyst and heating the mixture of the allyl amide or the allyl ester, the methylhydrosiloxane, a filler and the Group VIII metal catalyst, in the presence of ambient moisture until the methylhydrosiloxane becomes cured and cross-linked.

The allyl ester employed in the process can be allyl butyrate, allyl acetate, allyl methacrylate, vinyl

acetate, allyl acrylate, vinyl butyrate and other known allyl esters.

For purposes of the present invention, the siloxanes which may be used are methylhydrosiloxanes among which are bis(trimethylsiloxy)dimethyldisiloxane, bis(trimethylsiloxy)methylsilane, diphenyldimethyldisiloxane, diphenyltetrakis(dimethylsiloxy)disiloxane, heptamethyltrisiloxane, hexamethyltrisiloxane, methylhydrocyclosiloxanes, methyltris(dimethylsiloxy)silane, octamethyltetrasiloxane, pentamethylcyclopentasiloxane, pentamethyldisiloxane, phenyltris(dimethylsiloxy)silane, polymethylhydrosiloxane, tetrakis(dimethylsiloxy)silane, tetramethylcyclotetrasiloxane, tetramethyldisiloxane and methylhydrodimethylsiloxane copolymers.

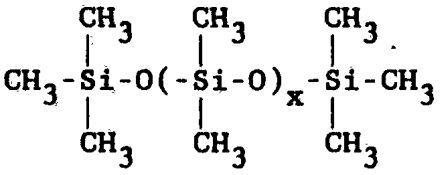
The preferred Group VIII metal catalyst is $RhCl_3$, although other appropriate catalyst systems may be employed such as $ClRh(PPh_3)_3$; H_2PtCl_6; a complex of 1,3-divinyl tetramethyl disiloxane and H_2PtCl_6; and alkyne complexes of H_2PtCl_6. A more exhaustive list of appropriate catalyst systems is set forth in the '750 patent. The most effective concentration of the Group VIII metal catalyst has been found to be from about ten parts per million to about two thousand parts per million on a molar basis relative to the allyl ester.

As used herein, the term chemically inert polyorganosiloxane is intended to denote a polymer of the formula

$$(R_nSiO_{\frac{4-n}{2}})_m$$

wherein n is an integer between zero and three and m is two or more. The simplest silicone materials are the

polydimethylsiloxanes. Polydimethylsiloxanes have the structure



where x is an integer of from one to about one hundred thousand. The repeating unit of the polymer is the dimethylsiloxane unit. The terminal unit is the trimethylsiloxy group. At low molecular weights, silicones are fluids and at high molecular weights, they are gums which may be cross-linked to form elastomeric products. The methyl group in a silicone may be substituted by a variety of other substituents including for example, phenyl or ethyl. Conventional silicones are the trimethylsiloxy terminated polydimethylsiloxanes. Such materials are available in viscosities ranging from 0.65 to 2,500,000 centistokes. Substituents on the silicon consist of methyl groups. Termination of the polymer chain prevents viscosity change and other alterations of the physical properties of the silicone polymeric materials. The polydimethylsiloxanes exhibit characteristic properties of low viscosity change with temperature; thermal stability; oxidative stability; chemical inertness; non-flammability; low surface tension; high compressibility; shear stability; and dielectric stability.

The polydimethylsiloxane fluid used herein as the chemically inert polyorganosiloxane is a high molecular weight polymer having a viscosity in the range from about 20 to 2,000,000 centistokes, preferably from about 500 to 50,000 centistokes, more preferably about 50 centistokes at 25°C. The siloxane polymer is generally end-blocked with

trimethylsilyl groups but other end-blocking groups are also suitable. The polymer can be prepared by various techniques such as the hydrolysis and subsequent condensation of dimethyldihalosilanes or by the cracking and subsequent condensation of dimethylcyclosiloxanes.

For purposes of the present invention, the term "skinned over" is defined as curing to a solid film on top of a fluid that can be touched and which does not leave a visibly wet residue, which is not tacky, but which is not fully cured. "Cured" is defined as the formation of a solid film that does not leave a visibly wet residue when touched. "Cheesy" is defined as a cured solid that when rubbed has the texture of cheese. "Tacky" is defined as cured to a gelatinous texture that adheres to the fingers when touched. "Orange peel" is defined as cured to a clear undulant appearance. "Spongy" is defined as cured to a porous solid.

Following are examples illustrating the process of the present invention as well as the products produced in accordance with the present invention. For the sake of simplicity, tetrahydrofuran has been referred to as THF.

Example 1

A catalyst was prepared by stirring 10 grams of $RhCl_3$ $3H_2O$ in 1200 grams of THF at room temperature for 12 hours. This catalyst was employed in the examples unless otherwise specified. A solution of 20 grams of polymethylhydrosiloxane having a viscosity of about thirty centistokes, hereinafter referred to as PMHS, 2 grams of allyl acetate and 0.2 gram catalyst was prepared and about 30 drops of this cloudy, yellow fluid was used to coat the bottom of a 2 inch aluminum weighing pan. The pan was immediately placed in a 125°C. oven for 5 minutes. Upon removal, the material had cured to a smooth, clear and colorless film.

Example 2

A mixture of 2.0 grams of PMHS, 3.5 g of allyl acetate and 0.02 gram of catalyst were combined. The material was coated in a 2 inch aluminum weighing pan and placed in a 125°C. oven for 5 minutes. The material cured and was very brittle.

Example 3

A mixture of 2.0 grams $Me_3SiO(SiMe_2O)_{54}(SiMeHO)_6SiMe_3$, 0.3 gram allyl acetate and 0.02 gram catalyst were combined. The mixture was used to coat the bottom of a 2 inch aluminum weighing pan. The pan was placed in an oven at 175°C. oven and provided a cured coating after 5 minutes which had a cheesy texture and an orange peel appearance. A 12 minute cure at this temperature yielded the same results.

Example 4

A mixture of 2.0 grams of $Me_3SiO(SiMe_2O)_{27}(SiMeHO)_3SiMe_3$, 0.3 gram of allyl acetate and 0.02 gram of catalyst were combined and used to coat a 2 inch aluminum weighing pan. The pan was placed in a 175°C. oven for 10 minutes after which time the material had cured to a cheesy coating with an orange peel appearance.

Example 5

A mixture of 2 grams of $Me_3SiO(SiMe_2O)_{97}(SiMeHO)_{22}SiMe_3$, 0.39 gram of allyl acetate, and 2 drops catalyst were combined. The formulation was coated in a 2 inch aluminum weighing pan and cured to a smooth appearance which had a cheesy texture at 125°C. for 10 minutes.

Example 6

A mixture of 2 grams of $Me_3SiO(SiMe_2O)_{86}(SiMeHO)_{22}SiMe_3$, 0.62 gram of allyl acetate and 3 drops of catalyst were combined. A portion of the formulation was coated on a 2 inch aluminum weighing pan and

heated at 125°C. for 10 minutes. This cured to a smooth appearance resulting in a cheesy textured coating.

Example 7

A solution of 3.0 grams of $Si(OSiMe_2H)_4$, 0.6 gram of allyl acetate and 0.3 gram of catalyst was prepared in a glass vial. This solution is hereinafter referred to as "Stock A". To 0.15 gram of Stock A was added 0.75 gram of $HSiMe_2O(SiMe_2O)_{13}SiMe_2H$. The resulting formulation was poured into a 2 inch aluminum weighing pan and placed in an over at 126°C. The material skinned over in 10 minutes and was fully cured in 60 minutes providing an undulant film.

Example 8

To 0.15 gram of the Stock A was added 0.75 gram of $Me_3SiO(SiMe_2O)_{70}(SiMeHO)_3SiMe_3$. The resulting formulation was poured into a 2 inch aluminum weighing pan and placed in an over at 126°C. The material was tacky after 60 minutes.

Example 9

To 0.15 gram of Stock A was added 0.75 gram of $Me_3SiO(SiMe_2O)_{100}(SiMeHO)_9SiMe_3$. The resulting formulation was poured into a 2 inch aluminum weighing pan and placed in an over at 126°C. The material skinned over in 10 minutes and was fully cured in 60 minutes providing a smooth film.

Example 10

A portion of the solution from Example 1 was applied to super calendared Kraft paper with a number 8 wire wound rod and cured in an oven at 125°C. for 5 minutes. This provided a cured coating of a thickness of about 0.6 lbs/ream which showed good adhesive release.

Example 11

A portion of the solution from Example 6 was applied to super calendared Kraft paper with a number 8 wire wound rod and provided a smooth cured coating when cured for 10 minutes at 175°C.

Example 12

A portion of the solution from Example 1 was applied to MYLAR polyethylene terephthalate with a number 8 wire wound rod and cured in an oven at 125°C. for 5 minutes. This provided a cured coating which showed good adhesive release. This procedure was followed with the coatings from Examples VI and VII. Both provided smooth films on MYLAR when cured for ten minutes but the coating from Example 6 was heated in the oven to 175°C. instead of 125°C.

Example 13

A portion the solution from Example 1 was applied to an isopropanol cleaned Lexan polycarbonate plate which was placed in a 125°C. oven for 10 minutes. Upon removal, the solution cured to a smooth film.

Example 14

A portion of the solution from Example 1 was applied to an isopropanol cleaned Plexiglass G acrylic plate and allowed to remain in a 125°C. oven for 10 minutes at which time curing occurred, although a slight warping of the acrylic plate was apparent.

Example 15

In this example and Examples 16 and 17, a full medicine dropper containing about 0.65 gram is used as the unit of measurement. The medicine dropper employed was a 2 ml three inch Fisher brand eyedropper with a tapered black rubber bulb. The procedure used was to prepare the formulation and to transfer the formulation with the eyedropper to either a 5 dram or 2 dram vial which was heated in an oven. Thus, a mixture of 20 grams PMHS, 2 grams allyl acetate and 0.2 gram catalyst were combined. A total of 2 eyedroppers full cured at 125°C. for 60 minutes to form a spongy clear material having a little residual liquid. This same amount cured at 175°C. without residual liquid. A half

full 5 dram vial at 175°C. cured clear and spongy and was gelatinous on the bottom of the vial. A full 2 dram vial also cured and was spongy, slightly tacky and somewhat gelatinous. All times unless otherwise specified were 60 minutes.

Example 16

A mixture of 10 grams of PMHS, 17.5 grams allyl acetate and 0.1 gram of catalyst were combined. A total of 2 eyedroppers resulted in a spongy brittle cavitated foam upon curing at 175°C. for 60 minutes. A total of 3 eyedroppers resulted in a spongy brittle and cavitated foam at 175°C. A half full 5 dram vial foamed out of the vial and cured at 175°C. A half full 5 dram vial at 125°C. provided the same results. All times were 60 minutes unless otherwise specified.

Example 17

A total of 2 medicine droppers full of the mixture from Example 5 was transferred to a 5 dram vial. When heated at 175°C. for 60 minutes the material cross-linked to a tacky fluid. A mixture of 2 medicine droppers full of the mixture from Example 6 was transferred to a 2 dram vial. Heating at 175°C. for 60 minutes resulted in the material cross-linking to form a non-tacky gel.

Example 18

A mixture of 19.6 grams of PMHS, 0.4 gram of polydimethylsiloxane having a viscosity of about fifty centistokes at 25°C., 2.0 grams of allyl acetate and 0.2 gram of catalyst was prepared and thermally cured in an aluminum weighing pan at 175°C. for 10 minutes. The cured coating contained cracks and was flexible.

Example 19

A mixture of 1 gram of $Me_3SiO(Me_2SiO)_{97}(MeSiHO)_{11}SiMe_3$, 1 gram of

polydimethylsiloxane having a viscosity of about fifty centistokes, 0.39 gram of allyl acetate and 2 drops of catalyst was prepared. Curing in a 2 inch aluminum weighing pan resulted in a cheesy non-tacky coating at 175°C. for 15 minutes.

Example 20

A mixture of 1 gram of $Me_3SiO(Me_2SiO)_{97}(MeSiHO)_{11}SiMe_3$, 0.5 gram of fifty centistoke polydimethylsiloxane, 0.195 grams allyl acetate and 2 drops catalyst was prepared. Curing in an aluminum weighing pan at 175°C. for 15 minutes resulted in a slightly tacky material which contained a liquid residue.

Example 21

A mixture of 1 gram of $Me_3SiO(Me_2SiO)_{97}(MeSiHO)_{11}SiMe_3$, 0.3 gram of polydimethylsiloxane of fifty centistoke viscosity, 0.195 grams of allyl acetate and 2 drops catalyst was prepared and cured in a 2 inch aluminum weighing pan resulting in a slightly tacky material.

Example 22

In the following examples, the catalyst employed was a 0.1 N solution of H_2PtCl_6 in isopropanol. Accordingly, a mixture of 1.0 gram of PMHS, 0.10 gram of allyl acetate and 0.01 gram of catalyst was prepared. A total of 10 drops of each the formulation was coated in an aluminum weighing pan. The formulation cured at 5 minutes at 125°C. and in repetitive examples with 30 drops of the platinum formulation, curing occurred between 5 seconds and 10 seconds at 125°C. The films formed with platinum were hard, very brittle and contained cavities.

Example 23

A mixture of 10 grams of PMHS, 1.0 gram of allyl acetate and 0.1 gram of the platinum catalyst was prepared in

a 5 dram vial and placed in an oven at 125°C. At the end of one hour the material cured. The cured formulation bubbled out of the vial, was hard, contained cavities and was very brittle.

The following additional examples and the table set forth hereinbelow, relate to the preparation and testing of particular paper coating films in accordance with the present invention.

The catalyst was prepared by dissolving 1 gram of rhodium chloride crystals in 120 grams of THF. This was stirred for 24 hours and filtered. A solution, Stock C, was prepared by mixing 20 grams of allyl acetate with 2 grams of catalyst in a 10 dram vial and shaking vigorously. A solution, Stock D, of 20 grams of allyl acetate and 4 grams of rhodium catalyst was prepared by mixing the two reagents in a vial.

Example 24

A mixture of 2 grams of $Me_3SiO(SiMe_2O)_{97}(SiMeHO)_{11}SiMe_3$, 2 grams of $HMe_2SiO(SiMe_2O)_{15}SiMe_2H$ and 0.22 grams of the Stock C was placed in a 5 dram vial and shaken vigorously. A portion of the mixture was coated on a sheet of 54.5 pound Nicolet paper using a number 8 wire wound rod. This was placed in an oven at 135°C. for 6 minutes. The sheets felt waxy. The release force data and coating thickness is shown in Table I.

Example 25

A mixture of 2 grams $Me_3SiO(SiMe_2O)_{97}(SiMeHO)_{11}SiMe_3$, 2 grams pentamethylcyclosiloxane and 0.22 gram of the Stock C was placed in a 5 dram vial and shaken vigorously. A portion of the mixture was coated on a sheet of 54.5 pound Nicolet paper using a number 8 wire wound rod. This was placed in the oven at 138°C. for

6 minutes. The sheet was smooth and felt waxy. The release force data and coating thickness is shown in Table I.

Example 26

A mixture of 2 grams of $Me_3SiO(SiMe_2O)_{97}(SiMeHO)_{11}SiMe_3$, 2 grams of $Si(OSiMe_2H)_4$ tetrakis(dimethylsiloxy)silane and 0.22 gram of the Stock C was placed in a 5 dram vial and shaken vigorously. A portion of the mixture was coated on a sheet of 54.5 pound Nicolet paper using a number 8 wire wound rod. This was placed in the oven at 138°C. for 5 minutes. The sheet felt waxy. The release force data is shown in Table I.

Example 27

A mixture of 0.2 gram of Stock D, 1 gram of $Me_3SiO(SiMe_2O)_{86}(SiMeHO)_{22}SiMe_3$ and 1 gram of $(MeHSiO)_5$ pentamethylcyclosiloxane was mixed in a 5 dram vial and shaken vigorously. A portion of the mixture was coated on a sheet of 54.5 pound Nicolet paper using a number 8 wire wound rod. This was placed in the oven at 135°C. for 6 minutes. The sheets were smooth and felt waxy. The release force data is shown in Table I.

Example 28

A mixture of 0.2 gram of Stock D, 1 gram of $Me_3SiO(SiMe_2O)_{86}(SiMeHO)_{22}SiMe_3$ and 2 grams of $HMe_2SiO(SiMe_2O)_{15}SiMe_2H$ was mixed in a 5 dram vial and shaken vigorously. A portion of the mixture was coated on a sheet of 54.5 pound Nicolet paper using a number 8 wire wound rod. This was placed in the oven at 135°C. for 6 minutes. The sheets were smooth and felt rubbery. The release force data is shown in Table I.

Example 29

A mixture of 0.2 gram of Stock D, 1 gram of $Me_3SiO(SiMe_2O)_{86}(SiMeHO)_{22}SiMe_3$ and 2 grams of tetrakis(dimethylsiloxy)silane was mixed in a 5 dram vial and

shaken vigorously. A portion of the mixture was coated on a sheet of 54.5 pound Nicolet paper using a number 8 wire wound rod. This was placed in the oven at 137°C. for 6 minutes. The sheets were smooth and felt waxy. The release force data is shown in Table I.

An acrylate adhesive and a styrene-butadiene adhesive, were used to prepare laminates of the sheets in Examples 28-33. The adhesives were applied in 3 mil wet thicknesses with a Bird Bar and cured at 70°C. in a forced air oven after standing 1 minute at room temperature. This resulted in a 1 mil dry thickness for the adhesive. Sixty pound matte-litho stock was applied to the adhesive coated paper using a 4.5 pound rubber roller. This final laminate was allowed to stand 24 hours at room temperature before testing for release. After 24 hours at room temperature, each laminate was cut into one-inch wide strips. The release force, measured in gram/inch, was determined by pulling the silicone coated sheet at an angle of 180°C. from the matte-litho stock at a a speed of 400 inches per minute on a Scott Tester.

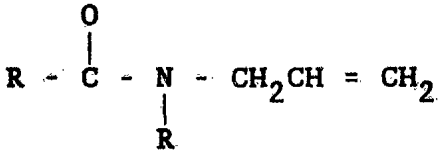
TABLE I

Example	Adhesive	Coating Thickness (pounds/3000ft^2)	Release Force (grams/inch)
28	SB*	6.53	10
29	AC**	6.53	15
	SB	3.03	5
	AC	3.03	10
30	SB	----	10
	AC	----	10
31	SB	----	11
	AC	----	15
32	SB	----	5
	AC	----	15
33	SB	----	10
	AC	----	17

* = styrene-butadiene adhesive SBR 36-6045, manufactured by Monsanto Co., St. Louis, MO.

** = acrylate adhesive GMS-263, manufactured by National Starch & Chemical Corp., Bridgewater, NJ.

As noted hereinabove, allyl amides may be employed in the method of the present invention for curing and crosslinking methylhydrosiloxanes. The most preferred allyl amide is of the type illustrated by the following generic formula:



wherein R is selected from the group consisting of hydrogen, alkyl radicals having one to eight carbon atoms and aryl radicals. A preferred allyl amide species of this type is, for example, N-allyl-N-methylacetamide of the above formula in which R is methyl.

There is also included in the mixture a filler in order to strengthen, toughen or otherwise reinforce the endproduct. Typical of the fillers which may be employed in the compositions of the present invention are, for example, carbon black, silica aerogels, silica soots, treated silicas, alumina, clays, metal oxides, metal carbonates and metal silicas. Specific filler materials may be ground quartz, reinforcing silicas, titanium dioxide, diatomaceous earth, iron oxide, fume silica, precipitated silica and silica xerogel.

The mixture can further include other materials which have been found to be useful in order to strengthen, toughen or otherwise reinforce the endproduct. Such materials which have been found useful are various silicone gums, silanol functional silicones, silane treated silicates and curable silicone resin compositions. Exemplary of a silane treated silicate is trimethylchlorosilane treated sodium silicate referred to hereinafter and in the examples as TMC treated silicate. A preferred silanol functional silicone is a silanol functional polydimethylsiloxane having a viscosity of about 90 centistokes measured at 25°C. and having the formula $HOSiMe_2(OSiMe_2)_xSiMe_2OH$ in which Me is methyl and x is an integer having a value of about thirty to forty. This silanol functional silicone is referred to in the examples as SFS fluid. The particular details of the silicone gums and the curable silicone resin compositions which may be employed in accordance with the present invention are set forth below.

The polydiorganosiloxane gum most suitable for use in the present invention is a polydimethylsiloxane gum. The polydiorganosiloxane gum can be represented by an average unit formula

$$R_a^3SiO_{\frac{4-a}{2}}$$

where each R^3 is a methyl radical, a vinyl radical, a phenyl radical, an ethyl radical or a 3,3,3-trifluoropropyl radical and a has an average value of 1.95 to 2.005 inclusive. Since the polydiorganosiloxane gums are essentially polydimethylsiloxane gums, at least 90 percent of the total R^3 groups are methyl radicals and the remaining R_3 groups are vinyl, phenyl, ethyl or 3,3,3-trifluoropropyl. Small amounts of other groups can be present such as 1 or 2 percent of the total R_3, where such groups are other monovalent hydrocarbon groups, such as propyl, butyl, hexyl cyclohexyl, beta-phenylethyl, octadecyl and the like; other halogenated monovalent hydrocarbon radicals, such as chloromethyl, bromophenyl, α,α,α-trifluorotolyl, perfluoroheptylethyl, dichlorophenyl and the like; cyanoalkyl; alkoxyl, such as, methoxy, propoxy, ethoxy, hexoxy and the like; ketoxime; halogen; hydroxyl; and acyloxy. The groups which are present in small amounts are considered as incidental and not producing any significant characteristic changes of the polydimethylsiloxane gum.

The polydiorganosiloxane gums suitable for the present invention are essentially composed of dimethylsiloxane units with the other units being represented by monomethylsiloxane, trimethylsiloxane, methylvinylsiloxane, methylethylsiloxane, diethylsiloxane, methylphenylsiloxane, diphenylsiloxane, ethylphenylsiloxane, vinylethylsiloxane, phenylvinylsiloxane, 3,3,3-trifluoropropylmethylsiloxane, dimethylphenylsiloxane, methylphenylvinylsiloxane, dimethylethylsiloxane, 3,3,3-trifluoropropyldimethylsiloxane, mono-3,3,3-trifluoropropylsiloxane, monophenylsiloxane, monovinylsiloxane and the like.

The polydiorganosiloxane gums are well known in the art and can be obtained commercially and have viscosities greater than 1,000,000 cs. at 25°C., preferably greater than 5,000,000 cs. at 25°C.

The resinous composition of the present invention is disclosed in U.S. Patent No. 4,322,518, issued March 30, 1982. This curable silicone resin composition can be best described as a mixture of (i) a resinous polymeric siloxane containing silicon-bonded hydroxyl radicals and consisting essentially of $R_3SiO_{1/2}$ siloxane units and $SiO_{4/2}$ siloxane units wherein the ratio of the number of said $R_3SiO_{1/2}$ siloxane units to the number of said $SiO_{4/2}$ siloxane units has a value of from 0.6/1 to 0.9/1 and each R denotes, independently, a monovalent hydrocarbon radical and (ii) an organohydrogenpolysiloxane wherein each organic radical is, independently, a monovalent hydrocarbon radical, there being an average of at least one silicon-bonded hydrogen radical per molecule of said organohydrogenpolysiloxane.

Following are additional examples illustrating the concept of the present invention in which an allyl amide is included in the mixture for curing and crosslinking methylhydrosiloxanes.

Example 30

A mixture was prepared including $HSiMe_2O(SiMe_2O)_{13}SiMe_2H$, the catalyst of Example 1 and N-allyl-N-methylacetamide solution and a curable silicone resin composition as defined above. The catalyst was prepared in accordance with the procedure of Example 1. A solution of N-allyl-N-methylacetamide and the $RhCl_3$/THF catalyst was prepared in a five dram vial by combining the allyl amide and the catalyst in a weight ratio of 1:0.2. This solution is referred to in the examples as the catalyst of Example 1 and N-allyl-N-methylacetamide solution. The ingredients of the mixture including the siloxane, the catalyst-allyl amide solution and the curable silicone resin were combined in the weight ratio of 1:0.2:1. Thirty drops of the combined mixture was coated in an aluminum weighing

pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full, soft and flexible cure had been obtained.

Example 31

A mixture was prepared including $HSiMe_2O(SiMe_2O)_{13}SiMe_2H$, the catalyst of Example 1 and N-allyl-N-methylacetamide solution and TMC treated silicate as defined above. The ingredients of the mixture were combined in the weight ratio of 1:0.2:1. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a smooth and tacky cure had been obtained.

Example 32

A mixture was prepared including $HSiMe_2O(SiMe_2O)_{13}SiMe_2H$ and the catalyst of Example 1 and N-allyl-N-methylacetamide solution. The ingredients of the mixture were combined in the weight ratio of 1:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full, soft and flexible cure had been obtained.

Example 33

A mixture was prepared including polymethylhydrosiloxane having a viscosity of about thirty centistokes measured at 25°C. hereinafter referred to as PMHS, the catalyst of Example 1 and N-allyl-N-methylacetamide solution and a curable silicone resin composition as defined above. The ingredients of the mixture were combined in the weight ratio of 1:0.2:1. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in

a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full, soft and flexible cure had been obtained.

Example 34

A mixture was prepared including PMHS, the catalyst of Example 1 and N-allyl-N-methylacetamide solution and TMC treated silicate as defined above. The ingredients of the mixture were combined in the weight ratio of 1:0.2:1. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a hard and brittle cure had been obtained.

Example 35

A mixture was prepared including PMHS, the catalyst of Example 1 and N-allyl-N-methylacetamide solution and SFS fluid as defined above. The ingredients of the mixture were combined in the weight ratio of 1:0.2:1. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a soft and flexible cure had been obtained.

Example 36

A mixture was prepared including PMHS, the catalyst of Example 1 and N-allyl-N-methylacetamide solution and fumed silica. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full soft and grainy cure had been obtained.

Example 37

A mixture was prepared including PMHS, the catalyst of Example 1 and N-allyl-N-methylacetamide solution and porous precipitated silica. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full soft and flexible cure had been obtained.

Example 38

A mixture was prepared including $HSiMe_2O(SiMe_2O)_{13}SiMe_2H$, the catalyst of Example 1 and N-allyl-N-methylacetamide solution and fumed silica. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full soft cure had been obtained.

Example 39

A mixture was prepared including $HSiMe_2O(SiMe_2O)_{13}SiMe_2H$, the catalyst of Example 1 and N-allyl-N-methylacetamide solution and porous precipitated silica. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full soft cure had been obtained.

Example 40

A mixture was prepared including PMHS, the catalyst of Example 1 and N-allyl-N-methylacetamide solution and a silicone gum as defined above. The ingredients of the

mixture were combined in the weight ratio of 1:0.2:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full cure had been obtained.

Example 41

A mixture was prepared including PMHS, a polydimethylsiloxane fluid having a viscosity of fifty centistokes and the catalyst of Example 1 and N-allyl-N-methylacetamide solution. The ingredients of the mixture were combined in the weight ratio of 1:0.25:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full soft, cheesy, nontacky and flexible cure had been obtained. The same mixture was also placed into a four ounce vial and after thirty minutes in the oven, a solid brittle cure was obtained.

Example 42

A mixture was prepared including $HSiMe_2O(SiMe_2O)_{13}SiMe_2H$, a polydimethylsiloxane fluid having a viscosity of fifty centistokes and the catalyst of Example 1 and N-allyl-N-methylacetamide solution. The ingredients of the mixture were combined in the weight ratio of 1:0.25:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a soft cure had been obtained.

Example 43

A mixture was prepared including $Me_3SiO(SiMe_2O)_{27}(SiMeHO)_3SiMe_3$ and the catalyst of Example 1

and N-allyl-N-methylacetamide solution. The ingredients of the mixture were combined in the weight ratio of 1:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for ten minutes. At the end of this time, the pan was removed from the oven evidencing that a soft, cheesy and flexible cure had been obtained.

Example 44

A mixture was prepared including $Me_3SiO(SiMe_2O)_{27}(SiMeHO)_3SiMe_3$ and the catalyst of Example 1 and N-allyl-N-methylacetamide solution. The ingredients of the mixture were combined in the weight ratio of 1:0.2. Ten drops of the combined mixture was coated on various substrates including paper, glass and MYLAR. Each of the substrates including the mixture was placed in a 135°C. oven for ten minutes. At the end of this time, the substrates were removed from the oven evidencing that a cure had been obtained in each instance. The coating on all of the substrates was soft. The paper and glass substrate coatings were both smooth and shiny and showed good adhesion. The MYLAR coating was cheesy and flexible and showed good adhesion.

Example 45

A mixture was prepared including PMHS and the catalyst of Example 1 and N-allyl-N-methylacetamide solution. The ingredients of the mixture were combined in the weight ratio of 1:0.2. Thirty drops of the combined mixture was coated on various substrates including polycarbonate, acrylic and paper. A thin coating was applied to each substrate with a number eight wire wound rod. Each coated substrate was placed in a 135°C. oven for five minutes. At the end of this time, the substrates were removed from the oven evidencing that a cure had been obtained in each instance. The coating

on all of the substrates was smooth and shiny and showed good adhesion.

Example 46

A mixture was prepared including PMHS, $Me_3SiO(SiMe_2O)_{27}(SiMeHO)_3SiMe_3$ and the catalyst of Example 1 and N-allyl-N-methylacetamide solution. The ingredients of the mixture were combined in the weight ratio of 1:0.5:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for ten minutes. At the end of this time, the pan was removed from the oven evidencing that a soft cure had been obtained. The same mixture was also placed into a four ounce vial and after thirty minutes in the oven, a solid brittle cure was obtained.

Example 47

A mixture was prepared including PMHS, $Me_3SiO(SiMe_2O)_{27}(SiMeHO)_3SiMe_3$ and the catalyst of Example 1 and N-allyl-N-methylacetamide solution. The ingredients of the mixture were combined in the weight ratio of 1:0.5:0.2. Ten drops of the combined mixture was coated on various substrates including polycarbonate, poly(ethylene terephthalate), paper and glass. A thin coating was applied to each substrate with a number eight wire wound rod. Each coated substrate was placed in a 135°C. oven for five minutes. At the end of this time, the substrates were removed from the oven evidencing that a cure had been obtained in each instance. The coating on all of the substrates except glass was soft, shiny and showed good adhesion.

The following example illustrates a procedure for preparing the allyl amide N-allyl-N-methylacetamide employed in the foregoing procedures.

Example 48

Four hundred-fifty milliliters of toluene was placed in a one liter three neck round bottom flask equipped with a stirring bar, condenser and addition funnel. The flask was heated and 14.7 grams of sodium was added to the flask and allowed to melt. A mixture including 47.2 grams of N-methylacetamide and twenty milliliters of toluene was added. Heat to the flask was discontinued and the contents were allowed to cool to room temperature. Seventy grams of allyl bromide mixed with 75 milliliters of toluene was added to the flask and stirred overnight. The flask contents was placed in a medium frit funnel containing filter aid and the filtrate was distilled in a one liter three neck round bottom flask equipped with a stirring bar, J-head distillation apparatus, thermometer and stopper. Forty-one grams of product was isolated and the product was identified as N-allyl-N-methylacetamide by gas chromatographic mass spectroscopy, nuclear magnetic resonance and infrared analysis.

The following examples illustrate the preparation of some additional compositions in accordance with the present invention.

Example 49

A mixture was prepared of $HSiMe_2O(SiMe_2O)_{13}SiMe_2H$, the catalyst of Example 1 and allyl acetate solution and a curable silicone resin composition as defined above. The catalyst was prepared in accordance with the procedure of Example 1. A solution of allyl acetate and the $RhCl_3$/THF catalyst of Example 1 and was prepared in a five dram vial by combining allyl acetate and the catalyst in a weight ratio of 1:0.2. This solution is referred to in the examples as the catalyst of Example 1 and acetate solution. The ingredients of the mixture including the siloxane, the catalyst-allyl acetate solution and the curable silicone resin were combined

in the weight ratio of 1:0.2:1. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for seven minutes. At the end of this time, the pan was removed from the oven evidencing that a full, soft and flexible cure had been obtained. Seven grams of the mixture was placed in a five dram vial. After ninety minutes in the oven, one-eighth inch of foam had cured.

Example 50

A mixture was prepared including PMHS, the catalyst of Example 1 and allyl acetate solution and fumed silica. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full and flaky cure had been obtained.

Example 51

A mixture was prepared including PMHS, the catalyst of Example 1 and allyl acetate solution and porous precipitated silica. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full soft and flaky cure had been obtained.

Example 52

A mixture was prepared including $HSiMe_2O(SiMe_2O)_{13}SiMe_2H$, the catalyst of Example 1 and allyl acetate solution and fumed silica. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven

for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full soft and flexible cure had been obtained.

Example 53

A mixture was prepared including $HSiMe_2O(SiMe_2O)_{17}SiMe_2H$, the catalyst of Example 1 and allyl acetate solution and porous precipitated silica. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full soft and flexible cure had been obtained.

Example 54

A mixture was prepared including PMHS, the catalyst of Example 1 and allyl acetate solution and SFS fluid as defined above. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.5. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a soft and flexible cure had been obtained. The mixture was coated on paper and cured to a smooth uniform coating. The mixture was placed in a five dram vial and cured in sixty minutes.

Example 55

A mixture was prepared including PMHS, the catalyst of Example 1 and allyl acetate solution and TMC treated silicate as defined above. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.5. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven

evidencing that a soft cure had been obtained. Cures were also obtained when the mixture was coated on paper and placed in a vial as in Example 54.

Example 56

A mixture was prepared including polymethylhydrosiloxane having a viscosity of about thirty centistokes measured at 25°C. referred to as PMHS, the catalyst of Example 1 and allyl acetate solution and a curable silicone resin composition as defined above. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.5. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full cure had been obtained. As in the previous example, coated papers and vials of the mixture cured.

Example 57

A mixture was prepared including PMHS, the catalyst of Example 1 and allyl acetate solution and a silicone gum as defined above. The ingredients of the mixture were combined in the weight ratio of 1:0.2:0.2. Thirty drops of the combined mixture was coated in an aluminum weighing pan and the pan was placed in a 135°C. oven for five minutes. At the end of this time, the pan was removed from the oven evidencing that a full cure had been obtained.

Example 58

A mixture was prepared including a higher molecular weight methylhydrodimethylsiloxane copolymer of the formula $Me_3SiO(SiMe_2O)_{301}(SiMeHO)_{34}SiMe_3$ and the catalyst of Example 1 and allyl acetate solution. The copolymer had a viscosity of about 792 centistokes measured at 25°C. The ingredients were combined in the weight ratio of 1:0.2. Thirty drops of the combined mixture was placed between two bricks and the

bricks were placed in a 135°C. oven for ten minutes. At the end of this time, the bricks were removed from the oven and were found to be sealed one to the other. The bricks were placed in an INSTRON tensile strength testing apparatus and could be separated one from the other upon slight tightening of the apparatus grips on the bricks.

Example 59

A mixture was prepared including a higher molecular weight methylhydrodimethylsiloxane copolymer of the formula $Me_3SiO(SiMe_2O)_{301}(SiMeHO)_{34}SiMe_3$, the catalyst of Example 1 and allyl acetate solution and silica. The ingredients were combined in the weight ratio of 1:0.2:0.015. Thirty drops of the combined mixture was placed between two bricks and the bricks were placed in a 135°C. oven for ten minutes. At the end of this time, the bricks were removed from the oven and were found to be sealed one to the other. The bricks were placed in an INSTRON tensile strength testing apparatus and were separated one from the other upon application of about thirty-one pounds of force to the bricks.

Example 60

A mixture was prepared including a higher molecular weight methylhydrodimethylsiloxane copolymer of the formula $Me_3SiO(SiMe_2O)_{301}(SiMeHO)_{34}SiMe_3$, the catalyst of Example 1 and allyl acetate solution and silica. The ingredients were combined in the weight ratio of 1:0.2:0.05. Thirty drops of the combined mixture was placed between two bricks and the bricks were placed in a 135°C. oven for ten minutes. At the end of this time, the bricks were removed from the oven and were found to be sealed one to the other. The bricks were placed in an INSTRON tensile strength testing apparatus and were separated one from the other upon application of forty-four pounds of force to the bricks.

It will be apparent from the foregoing that many other variations and modifications may be made in the compounds, compositions and methods described herein without departing substantially from the essential feature and concepts of the present invention. Accordingly, it should be clearly understood that the forms of the invention described herein are exemplary only and are not intended as limitations on the scope of the present invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A curable sealant composition comprising a mixture of an allyl ester, at least one methylhydrosiloxane, a Group VIII metal catalyst and a filler.

2. The composition according to Claim 1 in which the mixture includes a material to strengthen, toughen or reinforce the cured and crosslinked methylhydrosiloxane, the material being selected from the group consisting of silicone gums, silanol functional silicones, silane treated silicates and curable silicone resin compositions.

3. A method of preparing a curable sealant composition which comprises mixing an allyl ester, at least one methylhydrosiloxane, a Group VIII metal catalyst and a filler and heating at a temperature in excess of 125°C.

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