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(54) Title: RESIN MODIFIED SILICONE ELASTOMERS

(57) Abstract: Resin modified elastomers, methods of making them and their uses are disclosed. The method for making the elastomers comprises reacting in a diluent an  $\equiv\text{SiH}$  functional siloxane; a diene, diyne or ene-yne compound, a resin having the formula  $(\text{R}^1_3\text{SiO}_{1/2})_x(\text{SiO}_{4/2})_y(\text{R}^1\text{SiO}_{3/2})_z$  where  $\text{R}^1$  is independently a monovalent hydrocarbon group having 1 to 30 carbon atoms or an unsaturated hydrocarbon group having 2 to 30 carbon atoms  $x \geq 1$ ,  $y \geq 0$ ,  $z \geq 0$  and  $y+z \geq 1$ .

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## RESIN MODIFIED SILICONE ELASTOMERS

[0001] This invention relates to resin modified elastomers, methods of making them and their uses. The method for making the elastomers comprises reacting in a diluent an  $\equiv\text{SiH}$  functional siloxane; a diene, diyne or ene-yne compound, a resin having the formula  $(\text{R}^1_3\text{SiO}_{1/2})_x(\text{SiO}_{4/2})_y(\text{R}^1\text{SiO}_{3/2})_z$  where each  $\text{R}^1$  is independently a monovalent hydrocarbon group having 1 to 30 carbon atoms or an unsaturated hydrocarbon group having 2 to 30 carbon atoms  $x \geq 1$ ,  $y \geq 0$ ,  $z \geq 0$  and  $y + z \geq 1$ .

[0002] Silicone based materials comprising cross-linked siloxanes dispersed in a diluent are known in the art. One such material, made by polymerization of certain organohydrogenpolysiloxanes along with organopolysiloxanes having aliphatic unsaturated groups while in the presence of certain low viscosity silicones, is disclosed in U.S. Patent No. 4,987,169 to Kuwata et al. Another such material is disclosed in U.S. Patent No. 5,760,116 to Kilgour et al. In this last instance, certain alkenyl stopped polyorganosiloxanes are hydrosilylated with  $\equiv\text{SiH}$  containing "MQ" silicone resins in the presence of certain other silicones.

[0003] There are of course many variations possible in these materials and the synthesis of such materials. For example, the  $\equiv\text{SiH}$  groups and the aliphatic unsaturation may be on either or even both hydrosilylation reactants, as may other functionality. Sometimes, this allows for the synthesis of the same or a very similar type material using very different reactants in the same type of reaction. For example, what could be called a variant of Kilgour is seen in EP 1 057 476 by Fry, wherein the unsaturation appears in the resin and the  $\equiv\text{SiH}$  functionality appears in the other hydrosilylation reactant.

[0004] As with many other silicone based materials, it has been found that inclusion of certain functional groups in the silicone material can impart or enhance desirable properties. One example, where the polyether functionality is used, can be seen in U.S. Patent No. 5,811,487 to Schulz et al. Here, the polyether functionality was introduced by hydrosilylation prior to cross-linking. It may also be of note that the cross-linker may be purely hydrocarbon as was the case in this last mentioned material.

[0005] The present invention provides resin modified silicone based elastomers capable of suitably enhancing durability of personal care products while providing desirable aesthetics. Because the nature in which the resin functionality is introduced into the elastomer it is

possible by the instant invention to produce materials having a variety of aesthetic properties for use in the personal care formulations.

[0006] This invention pertains to resin modified silicone elastomers. The resin modified elastomers comprise:

(A) a cross-linked siloxane comprising:

- (i) a siloxane polymer,
- (ii) resin functionality having the formula  $(R_3SiO_{1/2})_x(SiO_{4/2})_y(RSiO_{3/2})_z$  and
- (iii) cross-links, -E-Y-E-, with each end of the cross-link is bonded to a silicon atom, wherein, each R is independently a divalent hydrocarbon group having 2 to 30 carbon atoms or a monovalent hydrocarbon group having 1 to 30 carbon atoms; wherein when R is a divalent hydrocarbon group it is bonded to the resin and to the siloxane polymer or a cross-link; each E is a divalent group independently selected from -CH<sub>2</sub>CH<sub>2</sub>- or -CH=CH-; Y is a divalent group that is a hydrocarbon, a siloxane or some combination of these; and  $x \geq 1$ ,  $y \geq 0$ ,  $z \geq 0$  and  $y + z \geq 1$ ; and

(B) a diluent.

[0007] This invention further pertains to methods of making the resin modified elastomers. One method comprises cross-linking, in the presence of a hydrosilylation catalyst,

- (1) an  $\equiv SiH$  functional siloxane,
- (2) a diene, diyne or ene-yne compound,
- (3) a resin having the formula  $(R^1_3SiO_{1/2})_x(SiO_{4/2})_y(R^1SiO_{3/2})_z$  where each R<sup>1</sup> is independently a monovalent hydrocarbon group having 1 to 30 carbon atoms or a unsaturated hydrocarbon group having 2 to 30 carbon atoms, x, y, and z are as defined above; wherein (1), (2) and (3) are dispersed in a diluent, and there is 0.1 to 100 weight parts of diluent per weight part of (1), (2) and (3).

[0008] In addition, the invention relates to personal care products containing the compositions of the present invention.

[0009] Component (A) of the resin modified elastomer of present invention is a cross-linked siloxane comprising:

- (i) a siloxane polymer,
- (ii) resin functionality having the formula  $(R_3SiO_{1/2})_x(SiO_{4/2})_y(RSiO_{3/2})_z$  and
- (iii) cross-links, -E-Y-E-, with each end of the cross-link is bonded to a silicon atom,

wherein, each R is independently a divalent hydrocarbon group having 2 to 30 carbon atoms or a monovalent hydrocarbon group having 1 to 30 carbon atoms; wherein when R is a divalent hydrocarbon group it is bonded to the resin and to the siloxane polymer or a cross-link; each E is a divalent group independently selected from  $-\text{CH}_2\text{CH}_2-$  or  $-\text{CH}=\text{CH}-$ ; Y is a divalent group that is a hydrocarbon, a siloxane or some combination of these; and  $x \geq 1$ ,  $y \geq 0$ ,  $z \geq 0$  and  $y + z \geq 1$ .

[0010] The siloxane polymer (i) is typically comprised of  $\text{R}^3_2\text{SiO}$  units but may also contain units of the formula  $\text{R}^3_3\text{SiO}_{1/2}$ ,  $\text{R}^3\text{SiO}_{3/2}$  and  $\text{SiO}_{4/2}$  where  $\text{R}^3$  is a monovalent hydrocarbon group, alternatively a monovalent hydrocarbon group having 1 to 30 carbon atoms.

[0011] The resin functionality (ii) in the cross-linked siloxane may be chemically bonded or blended into the cross-linked siloxane. When the resin functionality is chemically bonded into the cross-linked siloxane at least one R in the resin is a divalent hydrocarbon group having 2 to 30 carbon atoms. R as a divalent hydrocarbon group ( $\text{R}'$ ) may be exemplified by, but not limited to, alkylene groups such as ethylene, hexenylene, propylene, and mixtures thereof, preferably ethylene ( $-\text{CH}_2\text{CH}_2-$ ). The remaining R groups are independently monovalent hydrocarbons groups having 1 to 30 carbon atoms, preferably methyl, alternatively phenyl, or alternatively combinations thereof. Typically one of the R groups is ethylene and two are methyl, alternatively one of the R groups is ethylene, one is methyl and one is phenyl.

[0012] When the resin functionality is chemically bonded into the cross-linked siloxane it is typically bonded into the backbone of the siloxane polymer but it may be bonded in the cross-links or both the backbone of the siloxane polymer and cross-links. It is possible a particular siloxane molecule may have several different types of backbone elements as well as several different cross-linker elements. The resin functionality can be distributed among these in any fashion as long as present somewhere in the cross-linked siloxane molecule.

[0013] When the resin functionality is blended into the cross-linked siloxane all of the R groups are monovalent hydrocarbon groups having 1 to 30 carbon atoms. R as a monovalent hydrocarbon group ( $\text{R}''$ ) may be exemplified by, but not limited to, alkyl groups such as methyl, ethyl, isopropyl; phenyl and mixtures thereof, preferably methyl ( $\text{CH}_3-$ ).

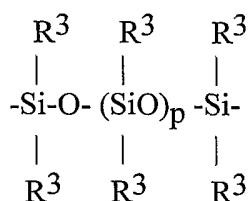
[0014] It is also possible to have the resin functionality both chemically and covalently bonded into the cross-linked siloxane by using a mixture of resins.

[0015] The resin functionality is comprised of at least one  $R_3SiO_{1/2}$  unit and at least one unit selected from  $SiO_{4/2}$  and  $RSiO_{3/2}$ . The resin functionality may be exemplified by, but not limited to, resins of the formula  $(R_3SiO_{1/2})_x(SiO_{4/2})_y$  where x and y have a ratio of from 0.5:1 to 1.5:1 and by resins of the formula  $(R_3SiO_{1/2})_x(RSiO_{3/2})_z$ .

[0016] The amount of resin functionality in the siloxane is from 1 to 30 mole%, alternatively 5 to 20 mole% based on the moles of siloxane units in the siloxane polymer.

[0017] The cross-linked siloxane also contain crosslinks of the formula -E-Y-E- where each E is a divalent hydrocarbon group independently selected from -CH<sub>2</sub>CH<sub>2</sub>- or -CH=CH- and Y is a divalent group that is a hydrocarbon, a siloxane or some combination of these. Typically each E is -CH<sub>2</sub>CH<sub>2</sub>- and Y is a hydrocarbon group having 1 to 30 carbon atoms alternatively 1 to 10 carbon atoms. The cross-links may be exemplified by, but not limited to pentylene, hexylene, heptylene, octylene, decylene, dodecylene, tetradecylene and others.

When Y is a siloxane it typically has the formula

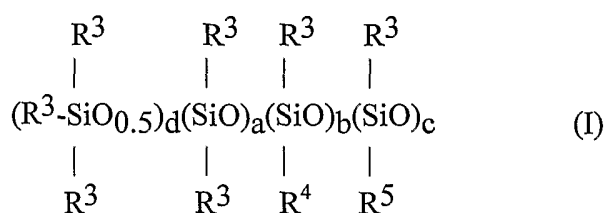


where  $R^3$  is a monovalent hydrocarbon group and p is 0 to 20,000, alternatively 0 to 500.

[0018] The amount of cross-link functionality in the siloxane is from 1 to 20 mole%, alternatively 3 to 10 mole% based on the moles of siloxane units in the siloxane polymer.

[0019] The resin modified elastomers also comprise a diluent (B). Suitable examples include silicones, both linear and cyclic (other than the corresponding cross-linked siloxane (A)), organic oils, organic solvents and mixtures of these. Specific examples of diluents may be found in U.S. Patent No. 6,200,581. Non-reactive or relatively non-reactive diluents are preferred. For purposes here, non-reactive is used in reference to the associated cross-linking reaction and used relative to the (other) reactants therein. A relatively non-reactive diluent would be less than one tenth as reactive with the other reactants as the others are with each other in the associated cross-linking reaction. The weight ratio range for (A):(B) is typically 1:100 to 10:1, alternatively 1:50 to 2:1, alternatively 1:20 to 1:1.

[0020] One embodiment of the resin modified elastomer is where the cross-linked siloxane (A) has the average formula:



where,

$\text{R}^3$  is a monovalent hydrocarbon group having 1 to 30 carbon atoms;

$\text{R}^4$  is resin functional group having the formula  $(\text{R}'\text{R}''_2\text{SiO}_{1/2})_x(\text{SiO}_{4/2})_y$  where  $\text{R}'$ ,  $\text{R}''$ ,  $x$  and  $y$  are as defined above and where  $x$  and  $y$  have a ratio of from 0.5:1 to 1.5:1.

$\text{R}^5$  is a cross-link -E-Y-E- or a siloxane containing (somewhere in its structure as pendant, internal, terminal or otherwise) -E-Y-E-; where E and Y are as defined above where one end of the cross-link is bonded into the siloxane (I) and the other end of the cross-link is bonded into a unit having the formula  $(\equiv\text{SiO}_{1/2})$  wherein the remaining two bond sites on the Si in this unit are selected from oxygen,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^5$  or any combination thereof; and

$a$  is 0 to 100,000,000 (alternatively 100 to 10,000,000);

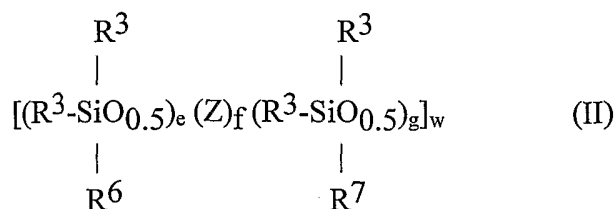
$b$  is 1 to 50,000,000 (alternatively 1 to 5,000,000);

$c$  is 1 to 10,000,000 (alternatively 1,000,000); and

$4 \leq d \leq 2c+2$ .

[0021] In the above formula (I)  $\text{R}^3$  is preferably a monovalent hydrocarbon group having 1 to 30 carbons, alternatively 1 to 18 carbons and in particular alkyl, aryl, alkaryl, aralkyl, or combinations thereof. Alternatively  $\text{R}^3$  is methyl. Y is preferably a divalent hydrocarbon group having 1 to 30 carbon atoms.

[0022] Another embodiment of the resin modified elastomer is where the cross-linked siloxane (A) has the average formula:



where,  $\text{R}^3$  is a monovalent hydrocarbon group having 1 to 30 carbon atoms;

each  $\text{R}^6$  is independently a monovalent hydrocarbon group or  $\text{R}^4$  wherein  $\text{R}^4$  is as defined above with the proviso that at least one  $\text{R}^6$  group is  $\text{R}^4$ ;

$R^7$  is a cross-link having the formula  $-E-R^8-Y-R^9-E-$ , or a siloxane containing a cross-link having the formula  $-E-R^8-Y-R^9-E-$ ; where E and Y are as defined above and one end of the cross-link is bonded into the siloxane (II) and the other end of the cross-link is bonded to a unit having the formula  $(\equiv SiO_{1/2})$  wherein the remaining two bond sites on the Si in this unit are selected from oxygen,  $R^3$ ,  $R^4$ ,  $R^7$  or any combination thereof;

Z is on average at least 80 mole percent ( $SiO_2$ ) with the balance made up of one or more other types of siloxane units;

$R^8$  and  $R^9$  are independently divalent hydrocarbon groups or nullities;

w is 1 to 100 (alternatively 1 to 70);

e is 1 to 500 (alternatively 2 to 300);

f is 1 to 1,000 (alternatively 1 to 500); and

g is 1 to 100 (alternatively 1 to 50);

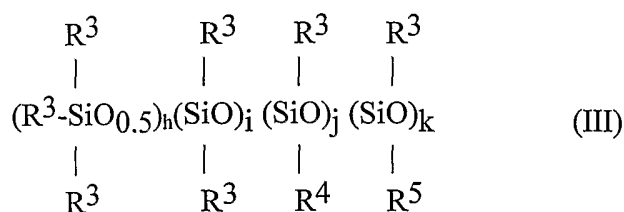
with the proviso that the ratio of  $e+f : g$  is 0.5 to 4.0 (alternatively 0.6 to 3.5).

[0023] In the above siloxane (II),  $R^3$  and  $R^6$  are typically monovalent hydrocarbon groups having 1 to 30, alternatively 1 to 20 carbons.  $R^8$  and  $R^9$  are typically divalent hydrocarbon groups having 1 to 8 carbons. Y is preferably a divalent hydrocarbon group having 1 to 30 carbon atoms.

[0024] It should be understood that in this disclosure and the claims that follow that "siloxane units" refers to one of the silicon based building blocks found in siloxanes and polysiloxanes. These are commonly referred to in the art as "M" ( $\equiv SiO_{1/2}$ ), "D" ( $=SiO$ ), "T" ( $-SiO_{3/2}$ ) and "Q" ( $SiO_2$ ) units, as well as functionalized and/or substituted versions of these. One particular "T" type siloxane unit of interest in siloxane (II) is "T-OH" ( $HO-SiO_{3/2}$ ).

[0025] In the context of a divalent R or similarly designated divalent group, it should be understood that "nullity" means "nothing there". For example, in  $-E-R^8-Y-R^9-E-$ , if  $-R^8-$  is a nullity, then  $-E-R^8-Y-R^9-E-$  is the same as  $-E-Y-R^9-E-$ .

[0026] Another embodiment of the resin modified elastomer is where the cross-linked siloxane (A) has subunits of the formula:



where,  $R^3$ ,  $R^4$ , and  $R^5$  are as described above;

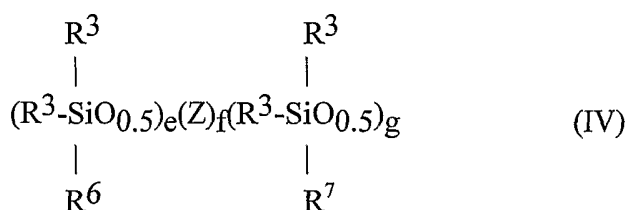
$i$  is 0 to 1,000;

$j$  is 1 to 500;

$k$  is 1 to 100; and

$4 \leq h \leq 2k+2$ .

[0027] Another embodiment of the resin modified elastomer is where the cross-linked siloxane (A) has subunits of the formula



where  $R^3$ ,  $R^6$ ,  $R^7$ ,  $Z$ , and  $e$ ,  $f$ , and  $g$  are as described above.

[0028] The present invention also relates to methods of making the resin modified elastomers. One method comprises reacting, in the presence of a hydrosilylation catalyst,

(1) an  $\equiv SiH$  functional siloxane and,

(2) a diene, diyne or ene-yne compound

(3) a resin having the formula  $(R^1_3SiO_{1/2})_x(SiO_{4/2})_y(R^1SiO_{3/2})_z$  where  $R^1$  is

independently a monovalent hydrocarbon group having 1 to 30 carbon atoms or an unsaturated hydrocarbon group having 2 to 30 carbon atoms, and  $x \geq 1$ ,  $y \geq 0$ ,  $z \geq 0$  and  $y + z \geq 1$ ;

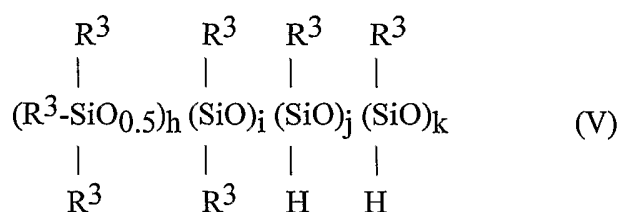
wherein (1), (2) and (3) are dispersed in a diluent, and there is 0.1 to 100 weight parts of diluent per weight part of (1), (2) and (3).

[0029] Any hydrosilylation catalyst, of which many are well known in the art, may be utilized, such as those based on noble metals like platinum, notably Karstedt's catalyst. Karstedt's catalyst, a platinum divinyl tetramethyl disiloxane based composition, is described extensively in the art such as in U.S. Patent No. 5,654,362. Homogeneous, heterogeneous or mixtures of homogeneous and heterogeneous form catalysts may be employed. The hydrosilylation catalysts are used in amounts from 0.00001 to 0.5 parts per 100 weight parts of the  $\equiv SiH$  functional siloxane, alternatively 0.00001 to 0.02 parts, alternatively 0.00001 to 0.002 parts.

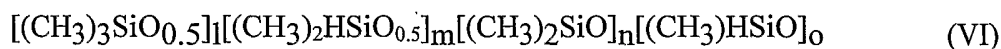
[0030] It may be advantageous in some instances to control reaction using a catalyst quencher. Quenching of this type is presented in U.S. Patent No. 5,929,164. It is not essential that a quencher be used in the methods of the present invention, but one may be employed if desired.

[0031] In component (1), the  $\equiv\text{SiH}$  functionality may be pendant, internal, terminal or otherwise or some combination of these. The  $\equiv\text{SiH}$  functional siloxane includes those comprising at least one unit selected from  $\text{R}^3\text{HSiO}_{2/2}$ ,  $\text{HSiO}_{3/2}$  and  $\text{R}^3_2\text{HSiO}_{1/2}$  where  $\text{R}^3$  is as previously described. Typically the  $\equiv\text{SiH}$  functional siloxane contains  $\geq 2$  of these units, alternatively 2 to 600 of these units.

[0032] The  $\equiv\text{SiH}$  functional siloxane may be exemplified by, but not limited to



where  $\text{R}^3$ ,  $h$ ,  $i$ ,  $j$ , and  $k$  are as described previously;  
and more specifically by



where

$l$  is 0 to 2;

$m$  is 0 to 2;

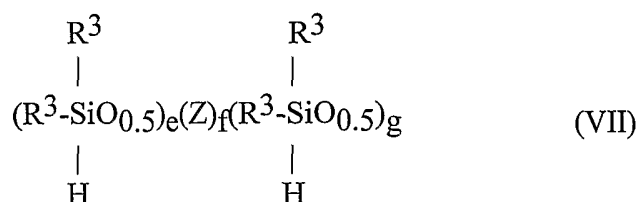
$l+m = 2$ ;

$n$  is 0 to 20,000 (alternatively 100 to 5000 or 500 to 5000);

$o$  is 0 to 2000 (alternatively 0 to 200); and

$m+o \geq 2$ ;

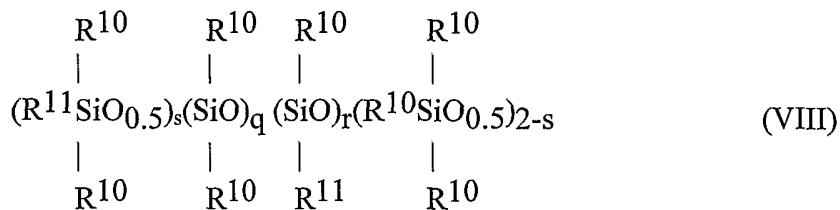
and by



where  $\text{R}^3$ ,  $Z$ ,  $e$ ,  $f$  and  $g$  are as described above.

[0033] Component (2) is a diene, diyne or ene-yne compound. Diene, diyne or ene-yne compounds are those compounds wherein there is at least two aliphatic unsaturated groups

with some separation between the groups. Structurally, component (2) can be, in the "alpha, omega diene" case, HC=C-Y-C=CH, where Y is a divalent group that is a hydrocarbon, siloxane or some combination of these. The unsaturation could be at an end or pendant if part of a polymer molecule. Component (2) may be exemplified by, but not limited to, E<sup>1</sup>-Y-E<sup>1</sup> where each E<sup>1</sup> is independently CH<sub>2</sub>=CH- or CH≡C- and Y is as defined above; a siloxane containing two E<sup>1</sup>-Y-E- groups; a siloxane having the formula



where q is 0 to 20,000 (alternatively 100 to 20,000 or 100 to 5000);

r is 0 to 2000,

s is 0 to 2,

2 ≤ s+r ≤ 2000,

R<sup>10</sup> is a monovalent hydrocarbon having 1 to 30 carbons and

R<sup>11</sup> is a monovalent, terminally aliphatic unsaturated hydrocarbon having from two to twelve carbons;

and a siloxane having the formula



where l, m and n are as previously defined and t is 0 to 1000 (alternatively 0 to 50) and l+t ≥ 2. In formula (IX) n is preferably 0 to 500.

[0034] Component (2) may be further exemplified by, but not limited to 1,4-pentadiene, 1,5-hexadiene; 1,6-heptadiene; 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,11-dodecadiene, 1,13-tetradecadiene, and 1,19-eicosadiene, 1,3-butadiyne, 1,5-hexadiyne (dipropargyl), and 1-hexene-5-yne.

[0035] Component (3) is a resin having the formula (R<sup>1</sup><sub>3</sub>SiO<sub>1/2</sub>)<sub>x</sub>(SiO<sub>4/2</sub>)<sub>y</sub>(R<sup>1</sup>SiO<sub>3/2</sub>)<sub>z</sub> where R<sup>1</sup>, x, y, and z are as defined above. In addition to the R<sup>1</sup><sub>3</sub>SiO<sub>1/2</sub>, SiO<sub>4/2</sub> and R<sup>1</sup>SiO<sub>3/2</sub> units, the resins may contain hydroxyl or alkoxy functional units and even some divalent siloxane units (R<sup>1</sup><sub>2</sub>SiO), provided however, that these units are present only in small amounts.

[0036] R<sup>1</sup> may be exemplified by alkyl radicals such as methyl or ethyl; the phenyl radical and alkenyl radicals such as vinyl, allyl and hexenyl. Typically R<sup>1</sup> is selected from the group consisting of methyl and vinyl. When it is desirable to chemically bond the resin into the

elastomer at least one  $R^1$  is an alkenyl group, typically a vinyl group. These resins will contain 0.01 to 22 wt% alkenyl functionality, alternatively 0.6 to 20 wt% alkenyl functionality or 0.6 to 8 wt% alkenyl functionality. When it is desirable to have the resin blended into the elastomer  $R^1$  is typically methyl, phenyl or any combination thereof.

[0037] One example of resins useful herein have the formula  $(R^1_3SiO_{1/2})_x(SiO_{4/2})_y$ . The mole ratio of  $(R^1_3SiO_{1/2})$  units to  $(SiO_{4/2})$  units in this resin has a value of from 0.5:1 to 1.5:1, alternatively 0.6:1 to 1.1:1. These mole ratios are easily measured by  $^{29}Si$  NMR spectroscopy. Typically the presence of silicon-bonded hydroxyl groups (i.e.  $HOR^{10}_2SiO_{1/2}$  or  $HOSiO_{3/2}$ ) is kept below 0.7 wt% based on the total weight of the resin, alternatively below 0.3 wt%.

[0038] The reaction to produce the resin modified elastomer is carried out in a diluent (B). Suitable diluents include silicones, both linear and cyclic, organic oils, organic solvents and mixtures of these. Specific examples of diluents may be found in U.S. Patent No. 6,200,581, which is hereby incorporated by reference for this purpose. Non-reactive or relatively non-reactive diluents are preferred.

[0039] Specifically, the diluent may be a low viscosity silicone typically having a viscosity in the range of 100 to 1,000  $mm^2/sec$  such as hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane, tetradecamethylhexasiloxane, hexadecamethylheptasiloxane, heptamethyl-3- $\{(trimethylsilyl)oxy\}$ trisiloxane, hexamethyl-3,3,bis $\{(trimethylsilyl)oxy\}$ trisiloxane pentamethyl $\{(trimethylsilyl)oxy\}$ cyclotrisiloxane as well as polydimethylsiloxanes, polyethylsiloxanes, polymethylethylsiloxanes, polymethylphenylsiloxanes, polydiphenylsiloxanes.

[0040] Typically the diluent is a volatile silicone. By volatile it is meant having a boiling point less than about  $250^\circ C$  and a viscosity of about 0.65 to 5.0  $mm^2/s$ .

[0041] Organic diluents may be exemplified by, but not limited to, aromatic hydrocarbons, aliphatic hydrocarbons, alcohols, aldehydes, ketones, amines, esters, ethers, glycols, glycol ethers, alkyl halides and aromatic halides.

[0042] The amount of diluent is such that there is 0.1 to 100 weight parts of diluent per weight part of (1), (2) and (3), alternatively 0.5 to 50 parts of diluent, alternatively 1 to 20 parts.

[0043] The method for producing the resins is not critical. Typically the  $\equiv\text{SiH}$  functional siloxane, resin and diluent and hydrosilylation catalyst are combined and the reaction is carried out to produce a resin-modified  $\equiv\text{SiH}$  functional siloxane. The amount of resin used is typically from 0.1 to 50 mole% resin based on the total moles of SiH in component (1), alternatively 5 to 20 mole%.

[0044] Thereafter the diene, diyne or ene-yne compound (2) is added to cross-link the resin modified  $\equiv\text{SiH}$  functional siloxane to produce the resin modified elastomer. Component (2) is used in an amount to provide 0.7 to 1.3 part of unsaturation in (2) per part  $\equiv\text{SiH}$  functionality. Typically (2) is used in an amount to provide 0.8 to 1.1 part of unsaturation in (2) per part  $\equiv\text{SiH}$ . Typically the reaction is carried out with an excess of unsaturation per part  $\equiv\text{SiH}$ .

[0045] Alternatively the  $\equiv\text{SiH}$  functional siloxane, resin, diene, diyne or ene-yne compound, diluent and hydrosilylation catalyst are combined and the reaction is carried out to produce the resin modified elastomer.

[0046] In any case it is necessary to add the resin to the reaction mixture prior to or during the cross-linking reaction.

[0047] Typically the reaction is carried out at a temperature of 40°C to 100°C, alternatively 65°C to 95°C.

[0048] Another method for producing the resin modified elastomers comprises cross-linking, in the presence of a hydrosilylation catalyst,

(1) a  $\equiv\text{SiH}$  functional siloxane containing  $\text{R}^4$  groups where  $\text{R}^4$  is as defined previously, and

(2) a diene, diyne or ene-yne compound,

wherein (1) and (2) are dispersed in a diluent, and there is 0.1 to 100 weight parts of diluent per weight part of (1) and (2). The resin modified elastomers may be prepared by first reacting the  $\equiv\text{SiH}$  functional siloxane with the resin described as component (3) above. Component (2) is used in an amount to provide 0.7 to 1.3 parts unsaturation in (2) per part  $\equiv\text{SiH}$  functionality. Typically (2) is used in an amount to provide 0.8 to 1.1 parts unsaturation in (2) per part  $\equiv\text{SiH}$  functionality.

[0049] It is sometimes convenient to express a composition (implicitly) in terms of a method to make it. This invention includes compositions that are the product of (made by, prepared by, etc.) any of the methods of the present invention.

[0050] The resin modified elastomers of the present invention are often clear and nearly solid materials. These may be diluted with a suitable diluent ("second diluent") to form pastes, gels or fluids as required. The second diluent may be selected from the diluents described above that are used in the preparation of the resin modified elastomer. Typically the second diluent is added in an amount of 1% to 50% based on weight solids in the resin modified elastomer.

[0051] The resin modified elastomers may be thermodynamically stable. By thermodynamically stable it is meant a material comprising a cross-linked polymer and a diluent that is homogeneous immediately after shearing and remains as such for at least 72 hours after being sheared, where homogeneous refers to something with a constant bulk viscosity (the type measured in units of cP, mPa s or equivalent units such as in a Brookfield device and sometimes referred to as absolute viscosity as opposed to kinematic viscosity) throughout a given sample within +/- 10 percent at any given point in time.

[0052] One method for determining such thermodynamic stability is wherein a sample of material is first sheared then visually inspected for homogeneity. If the sheared material is found to be visually homogeneous, then viscosity is measured using a statistically significant number of random samples of the sheared material taken immediately after the visual inspection and again 72 hours later. The material is considered thermodynamically stable if all viscosity measurements (for accuracy's sake, these are taken as, respectively, the mean of several measurements at the same point) from the initial sampling and the sampling 72 hours later are within +/- 10 percent of their respective means.

[0053] The invention also includes compositions, such as personal care products, made from any of the compositions of the present invention previously described herein. This would include hair, skin and underarm care products, more specifically conditioners, moisturizers, body washes, cosmetic foundations, blushes, lipsticks, eye liners, mascaras, eye shadows, antiperspirants and deodorants. Other examples of products that can be made using the compositions of the present invention are the same as can be made from the materials disclosed in U.S. Patent No. 6,200,581.

[0054] The personal care products contain the resin modified elastomer of the instant invention and at least one personal care product ingredient. Examples of personal care product ingredients include, but are not limited to, ester waxes, oils and fats of animal or vegetable origin, fatty alcohols, fatty acids, alkyl esters of fatty acids; hydrocarbon oils and

waxes; water, organic solvents, perfumes, surfactants, oil-soluble vitamins, water-soluble vitamins, oil-soluble drugs, water-soluble drugs, actives, pharmaceutical compounds and others.

[0055] It should be understood that in the context of a chemical formula that Me stands for methyl. Further, compositions expressed in percent should be taken as being in weight percent, unless otherwise indicated.

[0056] In reference to polymer formulae "average" should be understood to be a number or molar average, unless otherwise indicated. Also, it should be understood that formulae given for polymers (such as the one for the cross linked siloxane given just above) should be regarded as only semi-structural such that the subscripts for various subunits indicate merely the number present in the molecule as opposed to the particular position shown. Further, no stereospecificity is intended by what is shown in such formulae.

[0057] The following non-limiting examples are provided so that one skilled in the art may more readily understand the invention.

#### EXAMPLES

[0058] In the following examples, MQ means a resin having the general formula  $(\text{Me}_2\text{ViSiO}_{1/2})_x(\text{SiO}_{4/2})_y$ .

[0059] Into a vessel was added 36.2 g of a MQ resin ( $M_n = 2,700$ , 2.16 weight percent vinyl) and 400 g of decamethylcyclopentasiloxane. The mixture was heated to 70°C and upon complete dissolution of the resin, 57.8 g of the dimethyl methylhydrogen siloxane copolymer (DP = 93, 6.6 mole percent methyl hydrogen groups) was added followed by 10 ppm of platinum catalyst. The mixture was held at 70 °C with mixing for 1 hour. Next, 1.2 g of 1,5-hexadiene was added and the mixture was stirred for an additional 3 hours. Next, additional decamethylcyclopentasiloxane is added to achieve the desired level of solid. The resulting product is a clear thick paste.

[0060] Into a vessel was added 18.8 g of a MQ resin ( $M_n = 2,690$ , 0.88 weight percent vinyl) and 26.8 g of a second MQ resin ( $M_n = 4,320$ , 0.96 weight percent vinyl) and 415 g of decamethylcyclopentasiloxane. The mixture was heated to 70°C and upon complete dissolution of the resin, 38.4 g of a dimethyl methylhydrogen siloxane copolymer (DP = 188, 6.5 mole percent methyl hydrogen groups) was added followed by 10 ppm of platinum catalyst. The mixture was held at 70 °C with mixing for 1 hour. Next, 0.9 g of 1,5-hexadiene

was added and the mixture was stirred for an additional 3 hours. Next, additional decamethylcyclopentasiloxane is added to achieve the desired level of solids. The resulting product is a thick paste.

[0061] Into a vessel was added 26.5 g of a MQ resin ( $M_n = 4,200$ , 0.0 weight percent vinyl) and 430 g of decamethylcyclopentasiloxane. The mixture was heated to 70°C and upon complete dissolution of the resin, 42.0 g of the dimethyl methylhydrogen siloxane copolymer (DP = 93, 6.6 mole percent methyl hydrogen groups) was added followed by 10 ppm of platinum catalyst. The mixture was held at 70°C with mixing for 1 hour. Next, 1.5 g of 1,5-hexadiene was added and the mixture was stirred for an additional 3 hours. Next, additional decamethylcyclopentasiloxane is added to achieve the desired level of solids.

[0062] Into a vessel was added 33.2 g of a MQ resin ( $M_n = 4,180$ , 2.09 weight percent vinyl) and 430 g of decamethylcyclopentasiloxane. The mixture was heated to 70°C and upon complete dissolution of the resin, 36.5 g of the dimethyl methylhydrogen siloxane copolymer (DP = 93, 6.6 mole percent methyl hydrogen groups) was added followed by 10 ppm of platinum catalyst. The mixture was held at 70°C with mixing for 1 hour. Next, 0.65 g of 1,5-hexadiene was added and the mixture was stirred for an additional 3 hours. Next, additional decamethylcyclopentasiloxane is added to achieve the desired level of solids.

[0063] Into a vessel was added 45.4 g of a MQ resin ( $M_n = 4,180$ , 2.09 weight percent vinyl) and 400 g of decamethylcyclopentasiloxane. The mixture was heated to 70°C and upon complete dissolution of the resin, 53.7 g of a dimethyl methylhydrogen siloxane copolymer (DP = 265, 6.0 mole percent methyl hydrogen groups) was added followed by 10 ppm of platinum catalyst. The mixture was held at 70 °C with mixing for 1 hour. Next, 0.9 g of 1,5-hexadiene was added and the mixture was stirred for an additional 3 hours. Next, additional decamethylcyclopentasiloxane is added to achieve the desired level of solids.

[0064] Into a vessel was added 52.4 g of a MQ resin ( $M_n = 2,650$ , 0.0 weight percent vinyl) and 400 g of decamethylcyclopentasiloxane. The mixture was heated to 70°C and upon complete dissolution of the resin, 46.1 g of the dimethyl methylhydrogen siloxane copolymer (DP = 93, 6.6 mole percent methyl hydrogen groups) was added followed by 10 ppm of platinum catalyst. The mixture was held at 70 °C with mixing for 1 hour. Next, 1.5 g of 1,5-hexadiene was added and the mixture was stirred for an additional 3 hours. Next, additional decamethylcyclopentasiloxane is added to achieve the desired level of solids.

[0065] Into a vessel was added 96.6 g of the dimethyl methylhydrogen siloxane copolymer (DP = 99, 6.0 mole percent methyl hydrogen groups) and 400 g of decamethylcyclopentasiloxane. The mixture was heated to 70 °C with mixing. To this mixture was added 10 ppm of platinum catalyst. Next, 3.40 g of 1,5-hexadiene was added and the mixture was stirred for an 3 hours. Next, additional decamethylcyclopentasiloxane is added to achieve the desired level of solids.

## CLAIMS:

## 1. A resin modified elastomer comprising:

## (A) a cross-linked siloxane comprising:

- (i) a siloxane polymer,
  - (ii) resin functionality having the formula  $(R_3SiO_{1/2})_x(SiO_{4/2})_y(RSiO_{3/2})_z$  and
  - (iii) cross-links, -E-Y-E-, with each end of the cross-link is bonded to a silicon atom,
- wherein,

each R is independently a divalent hydrocarbon group having 2 to 30 carbon atoms or a monovalent hydrocarbon group having 1 to 30 carbon atoms; wherein when R is a divalent hydrocarbon group it is bonded to the resin and to the siloxane polymer or a cross-link;

each E is a divalent group independently selected from -CH<sub>2</sub>CH<sub>2</sub>- or -CH=CH-;

Y is a divalent group that is a hydrocarbon, a siloxane or some combination of these;

and

x is  $\geq 1$ , y  $\geq 0$ , z  $\geq 0$  and y + z  $\geq 1$ ;

and

## (B) a diluent.

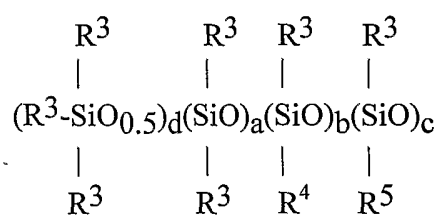
2. The resin modified elastomer of claim 1 wherein the resin functionality has the formula  $(R_3SiO_{1/2})_x(SiO_{4/2})_y$  where x and y have a ratio of from 0.5:1 to 1.5:1.

3. The resin modified elastomer of claim 1 wherein the cross-linked siloxane contains 1 to 30 mole % of resin functionality based on the moles of siloxane units in the siloxane polymer.

4. The resin modified elastomer of claim 1 wherein the cross-link is selected from pentylene, hexylene, heptylene, octylene, decylene, dodecylene and tetradecylene.

5. The resin modified elastomer of claim 1 wherein the cross-linked siloxane contains 1 to 20 mole % cross-link based on the moles of siloxane units in the siloxane polymer.

6. The resin modified elastomer of claim 1 wherein the diluent is selected from silicones, organic solvents or mixtures thereof.
7. The resin modified elastomer of claim 1 wherein the cross-linked siloxane and diluent are present in a weight ratio of 1:100 to 10:1.
8. The resin modified elastomer of claim 1 wherein (A) has the average formula



where,

$R^3$  is a monovalent hydrocarbon group;

$R^4$  is resin functional group having the formula  $(R'R''_2SiO_{1/2})_x(SiO_{4/2})_y$  where  $R'$  is a divalent hydrocarbon group having 2 to 30 carbon atoms, each  $R''$  is independently a monovalent hydrocarbon group having 1 to 30 carbon atoms and  $x$  and  $y$  have a ratio of from 0.5:1 to 1.5:1;

$R^5$  is a cross-link -E-Y-E- or a siloxane containing -E-Y-E-; where one end of the cross link is bonded into the siloxane and the other end of the cross-link is bonded into a unit having the formula  $(\equiv SiO_{1/2})$  wherein the remaining two bond sites on the Si in this unit may be oxygen,  $R^3$ ,  $R^4$ ,  $R^5$  or any combination thereof; and

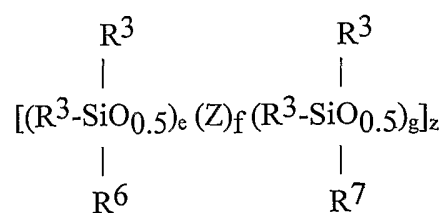
$a$  is 0 to 100,000,000;

$b$  is 1 to 50,000,000;

$c$  is 1 to 10,000,000; and

$4 \leq d \leq 2c+2$ .

9. The resin modified elastomer of claim 1 wherein (A) is a cross-linked siloxane of average formula:



where,

$R^3$  is a monovalent hydrocarbon group;

$R^6$  is a monovalent hydrocarbon group or  $R^4$  wherein  $R^4$  is resin functional group having the formula  $(R'R''_2SiO_{1/2})_x(SiO_{4/2})_y$  where  $R'$  is a divalent hydrocarbon group having 2 to 30 carbon atoms and  $R''$  is a monovalent hydrocarbon group having from 1 to 30 carbon atoms, and x and y have a ratio of from 0.5:1 to 1.5:1; with the proviso that at least one  $R^6$  group is  $R^4$ .

$R^7$  is a cross-link having the formula  $-E-R^8-Y-R^9-E-$ , or a siloxane containing a cross-link having the formula  $-E-R^8-Y-R^9-E-$ ; wherein each E is a divalent group independently selected from  $-CH_2CH_2-$  or  $-CH=CH-$ ; Y is a divalent group that is a hydrocarbon, a siloxane or some combination of these;  $R^8$  and  $R^9$  are independently divalent hydrocarbon groups or nullities and where one end of the cross-link is bonded into the siloxane (A) and the other end of the cross-link is bonded to a unit having the formula  $(\equiv SiO_{1/2})$  wherein the remaining two bond sites on the Si in this unit may be oxygen,  $R^3$ ,  $R^4$ ,  $R^7$  or any combination thereof; Z is on average at least 80 mole percent  $(SiO_2)$  with the balance made up of one or more other types of siloxane units;

w is 1 to 100;

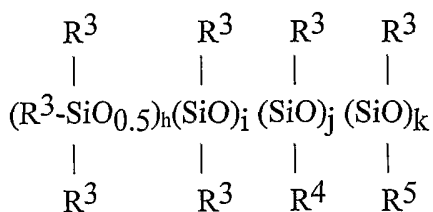
e is 1 to 500;

f is 1 to 1,000; and

g is 1 to 100; with the proviso that  $e+f : g$  is 0.5 to 4.0.

10. The resin modified elastomer of claim 1 wherein:

(A) is a cross-linked siloxane comprising subunits of formula:



where,

$R^3$  is a monovalent hydrocarbon group;

$R^4$  is resin functional group having the formula  $(R'R''_2SiO_{1/2})_x(SiO_{4/2})_y$  where  $R'$  is a divalent hydrocarbon group having 2 to 30 carbon atoms, each  $R''$  is a monovalent hydrocarbon group having 1 to 30 carbon atoms and  $x$  and  $y$  have a ratio of from 0.5:1 to 1.5:1;

$R^5$  is a cross-link -E-Y-E- or a siloxane containing -E-Y-E-; where one end of the cross link is bonded into the siloxane and the other end of the cross-link is bonded into a unit having the formula  $(=SiO_{1/2})$  wherein the remaining two bond sites on the Si in this unit may be oxygen,  $R^3$ ,  $R^4$ ,  $R^5$  or any combination thereof;

$i$  is 0 to 1,000;

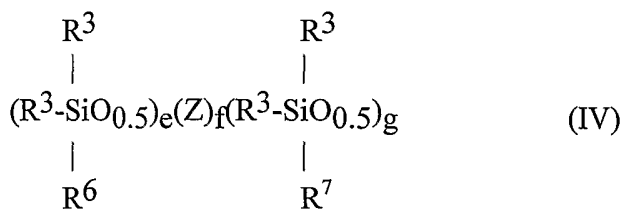
$j$  is 1 to 500;

$k$  is 1 to 100; and

$4 \leq h \leq 2k+2$ .

11. The resin modified elastomer of claim 1 wherein

(A) is a cross-linked siloxane comprising subunits of formula:



$R^3$  is a monovalent hydrocarbon group;

$R^6$  is a monovalent hydrocarbon group or  $R^4$  wherein  $R^4$  is resin functional group having the formula  $(R'R''_2SiO_{1/2})_x(SiO_{4/2})_y$  where  $R'$  is a divalent hydrocarbon group having 2 to 30 carbons, each  $R''$  is a monovalent hydrocarbon group having 1 to 30 carbons, and  $x$  and  $y$  have a ratio of from 0.5:1 to 1.5:1;

$R^7$  is a cross-link having the formula -E- $R^8$ -Y- $R^9$ -E-, or a siloxane containing a cross-link having the formula -E- $R^8$ -Y- $R^9$ -E-; wherein each E is a divalent group independently selected from -CH<sub>2</sub>CH<sub>2</sub>- or -CH=CH-; Y is a divalent group that is a hydrocarbon, a siloxane or some combination of these;  $R^8$  and  $R^9$  are independently divalent hydrocarbon groups or nullities and where one end of the cross-link is bonded into the siloxane (A) and the other end of the cross-link is

bonded to a unit having the formula ( $\equiv\text{SiO}_{1/2}$ ) wherein the remaining two bond sites on the Si in this unit may be oxygen,  $\text{R}^3$ ,  $\text{R}^4$ ,  $\text{R}^7$  or any combination thereof; Z is on average at least 80 mole percent ( $\text{SiO}_2$ ) with the balance made up of one or more other types of siloxane units;

e is 1 to 500;

f is 1 to 1,000; and

g is 1 to 100; with the proviso that  $e+f : g$  is 0.5 to 4.0.

12. A method of making a resin modified elastomer, the method comprising reacting, in the presence of a hydrosilylation catalyst;

- (1) an  $\equiv\text{SiH}$  functional siloxane,
- (2) a diene, diyne or ene-yne compound,
- (3) a resin having the formula  $(\text{R}^1_3\text{SiO}_{1/2})_x(\text{SiO}_{4/2})_y(\text{R}^1\text{SiO}_{3/2})_z$  where  $\text{R}^1$  is independently a monovalent hydrocarbon group having 1 to 30 carbon atoms or an unsaturated hydrocarbon group having 2 to 30 carbon atoms, and  $x \geq 1$ ,  $y \geq 0$ ,  $z \geq 0$  and  $y + z \geq 1$ ;

wherein (1), (2) and (3) are dispersed in a diluent, and there is 0.1 to 100 weight parts of diluent per weight part of (1), (2) and (3).

13. The method as claimed in claim 12 wherein component (2) is  $\text{E}^1\text{-Y-E}^1$  or a siloxane containing aliphatic unsaturated groups with some separation between the groups, where

$\text{E}^1$  are independently  $\text{CH}_2=\text{CH-}$  or  $\text{CH}\equiv\text{C-}$ ; and

Y is a multivalent group that is a hydrocarbon, a siloxane or some combination of these.

14. A method of making a resin modified elastomer, the method comprising reacting in the presence of a hydrosilylation catalyst

- (1) a  $\equiv\text{SiH}$  functional siloxane containing  $\text{R}^4$  groups where  $\text{R}^4$  is resin functional group having the formula  $(\text{R}_3\text{SiO}_{1/2})_x(\text{SiO}_{4/2})_y(\text{RSiO}_{3/2})$  where, each R is independently a divalent hydrocarbon group having 2 to 30 carbon atoms or a

monovalent hydrocarbon group having 1 to 30 carbon atoms; with the proviso that at least one R is a divalent hydrocarbon group;

and

(2) a diene, diyne or ene-yne compound,

wherein (1) and (2) are dispersed in a diluent, and there is 0.1 to 100 weight parts of diluent per weight part of (1) and (2).

15. A composition comprising

(1) the resin modified elastomer as claimed in claim 1;

(2) a second diluent selected from the group consisting of silicones, organic oils, organic solvents or mixtures thereof.

16. A personal care product comprising (1) the resin modified elastomer as claimed in claim 1 and (2) at least one personal care product ingredient.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 03/25949

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08L83/14 C08G77/50 C08K3/34

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08L C08G C08K

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

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

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 057 476 A (WACKER CHEMIE GMBH) 6 December 2000 (2000-12-06) cited in the application paragraphs '0001!, '0014!, '0015!, '0020!-'0022!; claims; examples ---	1-3, 5-16
X	US 4 987 169 A (SAKUTA KOJI ET AL) 22 January 1991 (1991-01-22) cited in the application examples 5,6 ---	1-3, 5-7, 12, 13, 15, 16
X	EP 0 827 983 A (GEN ELECTRIC) 11 March 1998 (1998-03-11) cited in the application claims; examples; tables 1-4 -----	1-3, 5-16

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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- \*P\* document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

20 January 2004

Date of mailing of the international search report

27/01/2004

Name and mailing address of the ISA

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Authorized officer

Kolitz, R

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/25949

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1057476	A	06-12-2000	US 6423322 B1	23-07-2002
			AT 235221 T	15-04-2003
			BR 0002442 A	02-01-2001
			CA 2307996 A1	22-11-2000
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