

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
31 December 2003 (31.12.2003)

PCT

(10) International Publication Number  
**WO 2004/000959 A1**

(51) International Patent Classification<sup>7</sup>: **C09D 183/04**,  
C08L 83/04, D06M 15/643

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,  
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE,  
SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,  
VC, VN, YU, ZA, ZM, ZW.

(21) International Application Number:  
PCT/US2003/019372

(22) International Filing Date: 19 June 2003 (19.06.2003)

(25) Filing Language: English

(26) Publication Language: English

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,  
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(30) Priority Data:  
60/390,073 19 June 2002 (19.06.2002) US

**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations*
- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*
- *of inventorship (Rule 4.17(iv)) for US only*

(71) Applicant (*for all designated States except US*): **DOW CORNING CORPORATION** [US/US]; 2200 West Salzburg Road, Midland, MI 48686-0994 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **BLACKWOOD, William** [US/US]; 2403 Plymouth, Midland, MI 48642 (US). **FEY, Kenneth** [US/US]; 2605 Dilloway Drive, Midland, MI 48640 (US). **SCHMIDT, Randall** [US/US]; 813 Honeysuckle Circle, Midland, MI 48642 (US). **STARK-KASLEY, Lori** [US/US]; 2683 East Mier Road, Midland, MI 48642 (US).

(74) Common Representative: **SCADUTO, Patricia, M.**; Patent Department - Mail CO 1232, Dow Corning Corporation, 2200 West Salzburg Road, Midland, MI 48686-0994 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,

**Published:**

- *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: FIRE AND STAIN RESISTANT COMPOSITIONS

(57) Abstract: A composition comprising (A) 100 parts by weight of at least one organosiloxane copolymer; (B) 10 to 120 parts by weight of at least one polyorganosiloxane; and (C) 10 to 150 parts by weight of at least one metal alkoxide. Methods for preparing the abovedescribed composition and for treating substrates are also disclosed.



WO 2004/000959 A1

## FIRE AND STAIN RESISTANT COMPOSITIONS

### DESCRIPTION

**[0001]** The present invention relates to a composition comprising (A) 100 parts by weight of at least one organosiloxane copolymer; (B) 10 to 120 parts by weight of at least one polyorganosiloxane; and (C) 10 to 150 parts by weight of at least one metal alkoxide. Methods for preparing the above-described composition and for treating substrates are also disclosed.

**[0002]** Compositions for making textiles water repellent have been prepared from many types of organic and silicone components. Compositions using silicone resins containing significant amounts of Q units and various combinations of M, D, and T units have been utilized, however, these types of silicone resins do not provide water repellent compositions having optimum properties, particularly flame retardancy. In addition these Q-containing silicone resins were found to impart stiffness to treated fabric. It has now been found that water repellent compositions comprising silicone resins containing little or no Q units have improved properties including providing flame retardancy and less stiffness to treated fabrics. Another object of the invention is to provide a water repellent composition having improved shelf life.

**[0003]** The present invention relates to a composition comprising (A) 100 parts by weight of at least one organosiloxane copolymer; (B) 10 to 120 parts by weight of at least one polyorganosiloxane; and (C) 10 to 150 parts by weight of at least one metal alkoxide. Methods for preparing the above-described composition and for treating substrates are also disclosed.

**[0004]** One embodiment of the present invention is a composition comprising (A) 100 parts by weight of at least one organosiloxane copolymer having a general formula (I)  $R^1_nSiO_{(4-n)/2}$ , where each  $R^1$  is independently chosen from a hydrogen atom or a monovalent hydrocarbon group comprising 1 to 10 carbon atoms, provided greater than 80 mole percent of  $R^1$  are methyl groups, n is a value from 0.8 to 1.5, greater than 50 mole percent of the copolymer comprises  $R^1SiO_{3/2}$  units, and having a hydroxyl content from 0.2 to 5 weight percent; (B) 10 to 120 parts by weight of at least one polyorganosiloxane having a general formula (II)  $R^2R^3_2SiO(R^3_2SiO_{2/2})_a(R^3SiO_{3/2})_bSiR^3_2R^2$  where each  $R^2$  is an

independently chosen hydrogen atom, monovalent hydrocarbon group comprising 1 to 10 carbon atoms, hydroxy group, or alkoxy group, each  $R^3$  is independently chosen from a hydrogen atom or a monovalent hydrocarbon group comprising 1 to 10 carbon atoms, a is an integer from 2 to 2000, and b is chosen such that  $b/(a+b)$  is from 0 to 0.05; and (C) 10 to 150 parts by weight of at least one metal alkoxide.

[0005] Component (A) comprises 100 parts by weight of at least one organosiloxane copolymer having a general formula (I)  $R^1_nSiO_{(4-n)/2}$ , where each  $R^1$  is independently chosen from a hydrogen atom or a monovalent hydrocarbon group comprising 1 to 10 carbon atoms, provided greater than 80 mole percent of  $R^1$  are methyl groups, n is a value from 0.8 to 1.5 (see comments on n above), provided greater than 50 mole percent of the copolymer comprises  $R^1SiO_{3/2}$  units, and having a hydroxyl content from 0.2 to 5 weight percent.

[0006] Component (A) comprises at least one organosiloxane copolymer having a general formula (I)  $R^1_nSiO_{(4-n)/2}$ . As used herein, the term "copolymer" means a polymer comprising at least two different organosiloxane units described by  $R^1_3SiO_{1/2}$  (M units),  $R^1_2SiO_{2/2}$  (D units),  $R^1SiO_{3/2}$  (T units), and  $SiO_{4/2}$  (Q units). Component (A) may be a single organosiloxane copolymer species or a mixture of different organosiloxane copolymers.

[0007] Each  $R^1$  of general formula (I) is independently chosen from a hydrogen atom or a monovalent hydrocarbon group comprising 1 to 10 carbon atoms, provided greater than 80 mole percent of  $R^1$  are methyl groups. The monovalent hydrocarbon group represented by  $R^1$  may be substituted with halogen atoms or unsubstituted. Examples of monovalent hydrocarbon group represented by  $R^1$  include alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, hexyl, 3,3,3-trifluoropropyl, chloromethyl, and octyl; alkenyl groups such as vinyl, allyl, and butadienyl; cycloalkyl groups such as cyclobutyl, cyclopentyl, and cyclohexyl; cycloalkenyl groups such as cyclopentenyl and cyclohexenyl; aryl groups such as phenyl and xylyl; aralkyl groups such as benzyl; and alkaryl groups such as tolyl and styryl. Alternatively, each  $R^1$  is independently chosen from alkyl groups comprising 1 to about 8 carbon atoms. Alternatively, each  $R^1$  is a methyl group.

[0008] Subscript n of the organosiloxane copolymer of component (A) allows for various mixtures of the M, D, T, and Q units provided the overall mixture of units would fall in the specified range. Generally, n is a value from 0.8 to 1.5, provided greater than 50 mole percent of the organosiloxane copolymer comprises  $R^1SiO_{3/2}$  units. Alternatively, n is a value from 1 to 1.5. Alternatively, n is a value from 1 to 1.3 and greater than 70 mole percent of the organosiloxane copolymer comprises  $R^1SiO_{3/2}$  units. Alternatively, n is a value from 1 to 1.3, greater than 70 mole percent of the organosiloxane copolymer comprises  $R^1SiO_{3/2}$  units, and the organosiloxane copolymer comprises essentially no  $SiO_{4/2}$  units.

[0009] The organosiloxane copolymer of component (A) can have a hydroxyl content from 0.2 to 5 weight percent. Alternatively, the hydroxyl content of the organosiloxane copolymer is from 0.3 to 3 weight percent. In addition to hydroxyl groups, the organosiloxane copolymer may contain up to 5 weight percent of alkoxy groups.

[0010] The organosiloxane copolymers useful in this invention may be prepared by methods well known in the art. The copolymerization of these units is generally accomplished by hydrolysis and subsequently the condensation of either chlorosilanes or alkoxy silanes. For example, organosiloxane copolymers may be prepared by the hydrolysis and condensation of appropriate amounts of  $R^1SiCl_3$ ,  $R^1_2SiCl_2$ ,  $R^1_3SiCl$ , and  $SiCl_4$  where  $R^1$  is as described above. A review of this process can be found in "The Chemistry and Technology of Silicones," pp. 192-198, by W. Noll (1968). When using chlorosilanes as a starting material HCl is generated as a by-product and must be neutralized or otherwise removed. One can neutralize HCl using an aqueous solution of base, such as a bicarbonate or carbonate salt of a metal such as sodium or potassium or calcium, or by repeated washing with water. Both methods may also be employed together. When made from alkoxy silanes, residual alcohol can be distilled overhead. Those skilled in the art will recognize that catalysts such as minerals, acids, and bases can be used to facilitate the hydrolysis/condensation process. A neutral solvent such as toluene may also be used to facilitate the reaction. A solvent may also be used when various reactive capping agents are used to reduce residual silanols in the organosiloxane copolymer. The solvent may then be removed by known methods such as distillation after the organosiloxane copolymer's manufacture is complete.

[0011] Component (B) comprises at least one polyorganosiloxane having a general formula (II)  $R^2R^3_2SiO(R^3_2SiO_{2/2})_a(R^3SiO_{3/2})_bSiR^3_2R^2$  where each  $R^2$  is an independently chosen hydrogen atom, monovalent hydrocarbon group comprising 1 to 10 carbon atoms, hydroxy group, or alkoxy group, each  $R^3$  is independently chosen from a hydrogen atom and a monovalent hydrocarbon group comprising 1 to 10 carbon atoms, a is an integer from 2 to 2000, and b is chosen such that  $b/(a+b)$  is from 0 to 0.05.

[0012] Component (B) comprises at least one polyorganosiloxane having a general formula (II)  $R^2R^3_2SiO(R^3_2SiO_{2/2})_a(R^3SiO_{3/2})_bSiR^3_2R^2$ . The polyorganosiloxanes may be homopolymers or copolymers (as defined above). The polyorganosiloxanes may be a single species or a mixture of different polymers.

[0013] Each  $R^2$  group of component (B) is an independently chosen hydrogen atom, monovalent hydrocarbon group comprising 1 to 10 carbon atoms, hydroxy group, or alkoxy group. The monovalent hydrocarbon group represented by  $R^2$  may be substituted with halogen atoms or unsubstituted. Examples of monovalent hydrocarbon groups represented by  $R^2$  are as described above for the monovalent hydrocarbon groups of  $R^1$ .

[0014] The alkoxy group represented by  $R^2$  may be described by  $-OR^5$  where  $R^5$  is an alkyl group comprising 1 to 5 carbon atoms. The alkyl group represented by  $R^5$  may be substituted with halogen atoms or unsubstituted. Examples of alkyl groups include methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, and chloropropyl. Examples of useful alkoxy groups include methoxy, ethoxy, propoxy, iso-propoxy, n-butoxy, and iso-butoxy.

Alternatively, each  $R^2$  of component (B) is an independently chosen alkyl group comprising 1 to 8 carbon atoms. Alternatively, each  $R^2$  is methyl.

[0015] Each  $R^3$  group of component (B) is independently chosen from a hydrogen atom or a monovalent hydrocarbon group comprising 1 to 10 carbon atoms. The monovalent hydrocarbon group represented by  $R^3$  may be substituted with halogen atoms or unsubstituted. Examples of monovalent hydrocarbon groups represented by  $R^3$  are as described above for the monovalent hydrocarbon groups of  $R^1$ . Alternatively, each  $R^3$  is an independently selected alkyl group comprising 1 to 8 carbon atoms. Alternatively, each  $R^3$  is methyl.

[0016] The polyorganosiloxanes of component (B) comprise repeating siloxy units described by  $(R^3_2SiO_{2/2})_a$  and  $(R^3SiO_{3/2})_b$ , where  $R^3$  is as described above, a is an integer from 2 to 2000, alternatively, from 3 to 300, and b is chosen such that  $b/(a+b)$  is from 0 to 0.05. Generally, the viscosity of the polyorganosiloxane of component (B) is from 1 to 250,000 mPa.s as measured at 25° C. Alternatively, the viscosity of the polyorganosiloxane of component (B) is from 10 to 1000 mPa.s as measured at 25° C.

[0017] Generally, the present composition comprises 10 to 120 parts by weight of component (B) per 100 parts by weight of component (A). Alternatively, the present composition comprises 50 to 110 parts of component (B) on the same basis. The polyorganosiloxanes of Component (B) are commercially available or may be made by methods known in the art.

[0018] Component (C) comprises at least one metal alkoxide. As used herein, the term "metal alkoxide" includes non-hydrolyzed metal alkoxides, partially hydrolyzed metal alkoxides and mixtures thereof. The metal alkoxide may be a single species or a mixture of different metal alkoxides. Particularly useful metal alkoxides are substantially soluble in aliphatic hydrocarbon solvents

[0019] Alternatively, metal alkoxides useful in the present composition have the formula  $M(OR^4)_4$ , where M is titanium or zirconium and each  $R^4$  is independently chosen from alkyl groups comprising 1 to 12 carbon atoms or hydroxylated alkyl groups comprising 1 to 12 carbon atoms and containing less than 4 hydroxyl groups.

[0020] Each  $R^4$  is independently chosen from alkyl groups comprising 1 to 12 carbon atoms or hydroxylated alkyl groups comprising 1 to 12 carbon atoms and containing less than 4 hydroxyl groups. The alkyl groups represented by  $R^4$  may be substituted with halogen atoms or unsubstituted. Examples of the alkyl groups comprising 1 to 12 carbon atoms of  $R^4$  include methyl, ethyl, propyl, iso-propyl, n-butyl, and iso-butyl, hexyl, 2-ethylhexyl, octyl, decyl, and dodecyl. Examples of useful titanium alkoxides include tetramethyl titanate, tetraethyl titanate, tetrapropyl titanate, tetraisopropyl titanate, tetrabutyl titanate, tetradecyl titanate, tetraoctyl titanate, tetra 2-ethylhexyl titanate, and tetradodecyl titanate. Examples of useful zirconium alkoxides include tetramethyl zirconate, tetraethyl zirconate, tetrapropyl zirconate, tetraisopropyl zirconate, tetrabutyl zirconate, tetradecyl zirconate, tetraoctyl zirconate, tetra 2-ethylhexyl zirconate, and tetradodecyl zirconate. Alternatively, component

(C) metal alkoxides useful in the present composition have the formula  $M(OR^4)_4$ , where M is titanium and each  $R^4$  is an alkyl group comprising 6 to 12 carbon atoms.

[0021] Generally, the present composition comprises 10 to 150 parts by weight of component (C) per 100 parts by weight of component (A). Alternatively, the present composition comprises 50 to 140 parts of component (C) on the same basis. It is also preferable that the amount of Component C in the composition be equal to or greater than the amount of Component B; that is, that the ratio of Component C to Component B is greater or equal to 1.0. Component (C) is commercially available or may be made by methods known in the art.

[0022] In an alternative embodiment the present composition may further comprise (D) at least one carrier chosen from water, organic solvents, and silicone compounds.

[0023] Suitable organic solvents include hydrocarbons such as aromatic hydrocarbons exemplified by toluene, benzene, and xylene; aliphatic hydrocarbons such as hexane, heptane, naphtha, and mineral spirits; ketones such as acetone, methyl ethyl ketone, and methylisobutyl ketone; and alcohols such as butanol, hexanaol, or octanol. Suitable silicone compounds include dimethylcyclsiloxanes having a DP of 3 to 8. Solvents that are preferred are ketones, aromatic hydrocarbons and aliphatic hydrocarbons. Most preferable are aliphatic hydrocarbons, which are odorless.

[0024] The present composition may contain up to 400 parts by weight of component (D) per 100 parts by weight of component (A). Alternatively, the present composition comprises 10 to 400 parts by weight of component (D) on the same basis. Alternatively, the present composition comprises 40 to 200 parts by weight of component (D) on the same basis.

[0025] Other additional ingredients may also be added to the present composition provided that the properties of the composition are not significantly reduced. Examples of such ingredients include fillers such as silica and titanium dioxide, silicone or organic-based waxes, fluorocarbons, and stainblockers.

[0026] One of the uses of the present composition is treating different substrates. The present composition can have any suitable form to enable treatment of various substrates. For example, the composition can be applied to the substrate neat. However, the composition can also be a solution, dispersion, or emulsion.

[0027] This invention further relates to a method for preparing a composition comprising mixing components (A), (B), (C) and any optional ingredients. Components (A), (B), (C) are as described above.

[0028] The order of addition of these ingredients is not critical. Alternatively, to facilitate ease of handling, Component (A) may be first mixed with an organic solvent (component (D)) and then mixed with component (B). Component (C) is then added to the mixture of components (A), (B), and optionally (D). The composition may be prepared as a one-part or have multiple parts if desired.

[0029] The mixing of ingredients can be done using any equipment known in the art. The temperature that the reaction is run is also not critical. Alternatively, to expedite mixing, one can perform the reaction at temperatures up to 60° C.

[0030] This invention further relates to a method for treating substrates and the treated substrates. The method comprises applying a composition comprising components (A), (B), (C) and any optional ingredients to a substrate. Alternatively, the method comprises applying a composition comprising components (A), (B), (C), and (D) to a substrate. Alternatively, the method comprises applying a composition comprising components (A), (B), (C), and (D) to a substrate and then removing component (D) after applying the composition to the substrate. Application of the composition to a substrate can be done in any known fashion, including spraying and dipping.

[0031] Many different kinds of substrates can be treated with the present composition. These treated substrates exhibit various improved properties including mildew resistance, stain repellency, water repellency and fire resistance. Examples of useful substrates include leather, wood, textile fabrics, fibers, and masonry. Alternatively, the useful substrates include textile fabrics and fibers.

[0032] The fibers that can be treated with the present composition are not specifically restricted. Suitable fibers include natural fibers such as cotton, silk, linen, and wool; regenerated fibers such as rayon and acetate; synthetic fibers such as polyesters, polyamides, polyacrylonitriles, polyethylenes, nylon, and polypropylenes; and combinations and blends thereof.

[0033] The form of the fibers is also not specifically restricted. The present treatment method is suitable for threads, filaments, tows, yarns, woven fabrics, knitted materials, nonwoven materials, and others.

[0034] Examples of applications include carpet protection, fabric protection in automotive and home furnishings, breathable water repellency for woven and nonwoven substrates and stain resistance in masonry. Benefits also include colorfastness on silk and durable stain and water repellency on silk substrates. Carpet protection requires that the carpet have mildew resistance, water repellency and stain resistance and can pass the flammability test.

[0035] The following examples are disclosed to further teach, but not limit, the invention, which is properly delineated by the appended claims.

[0036] NMR: The nuclear magnetic resonance (NMR) analysis was done using a Mercury 400 MHz super conducting spectrometer. The instrument uses a silicon-free probe.

Characterization of these materials was done using  $^{29}\text{Si}$  and  $^{13}\text{C}$  experiments. Samples were prepared using a 60/40 ratio of deuterated chloroform ( $\text{CDCl}_3$ ) to sample material. The NMR sample contained 0.02 molar chromium (III) acetylacetonate ( $\text{Cr}(\text{acac})_3$ ). This compound was used as a relaxation agent to increase the efficiency of the experiments. NMR samples were prepared in Teflon tubes to eliminate the silicon signal in the Q region that occurs with glass tubes. In most cases, the acquisition time was 1 to 2 hours. Similar procedures for sample preparation were also used for  $^{13}\text{C}$  NMR.

[0037] Percent (%) Solids: 2-3 grams of the sample resin solution was placed into a pre-weighted aluminum dish. The sample was then heated in an oven at atmospheric pressure for 4 hours at  $105^\circ\text{C}$ . At that time the amount of weight loss was measured. The percent solids is the weight of the remaining portion of the sample relative to the original sample weight.

Stability ratings: Excellent: Clear;

Very Good: Clear with slight solids

Poor: Phase separation

These ratings were done by eye.

[0038] Resin A: 28 grams of methyltrichlorosilane and 3.2 grams of dimethyldichlorosilane were hydrolyzed in the presence of 45.8 grams of toluene, 10.9 grams of water, and 11.5 grams of isopropanol. The reaction temperature was allowed to rise to  $80^\circ\text{C}$  and held there for three hours. The acid layer consisting of  $\text{HCl}$ , water and isopropanol was then removed and the product solution then azeotropically stripped to remove the remaining traces of water.

The resin solids is 50%, the level of silanol is about 2.6% wt as determined by  $\text{Si}^{29}$  NMR. The molar distribution of D and T units in Resin A are described in Table 1.

[0039] Resin B: 18.6 grams of methyltrichlorosilane and 2.8 grams of dimethyldichlorosilane were hydrolyzed in the presence of 31.0 grams of toluene, 4.2 grams of water, and 8.8 grams of isopropanol. Azeotropic distillation removes residual acid, water, isopropanol and toluene. The resin solids was adjusted to 50%, the level of silanol was about 4.6 % weight (wt) as determined by  $^{29}\text{Si}$  NMR. The molar distribution of D and T units in Resin B are described in Table 1.

[0040] Resin C: 29 grams of methyltrimethoxysilane and 3.0 grams of dimethylcyclsiloxane were equilibrated and then hydrolyzed in the presence of 31.0 grams of toluene, 36.9 grams of water, and 0.05 grams of trifluoromethanesulfonic acid. After the reaction was completed the trifluoromethanesulfonic acid was neutralized with calcium carbonate (0.1 grams). The resin was then bodied in the presence of toluene to remove traces of water and residual alkoxy and silanol groups. The molar distribution of D and T units in Resin C are described in Table 1.

[0041] Resin D (Comparison) Sodium silicate and hexamethyldisiloxane were hydrolyzed and bodied to form a resin consisting of  $\text{M}_x$  and Q siloxy units where  $x = 1.27$  to  $1.32$ . The resin was used as a 70% solids solution in toluene. The silanol content was 2.5 %.wt. The molar distribution of M and Q units in Resin D are described in Table 1.

[0042] Resin A was dissolved in odorless mineral spirits at a solids of 50%wt for Examples 1 to 11. Examples 12, 13, 14 were prepared at solids of 25, 23 and 38% respectively. To the resin solution was added polydimethylsiloxane fluid, 350cs, with simple mixing; and then to that mixture was added tetraisopropyltitanate. The parts of each component added are provided in Table 2. Adding too little titanate results in gels or hazy solutions which over time become two phases. Solutions containing more titanate than polydimethylsiloxane fluid are favored for their stability.

[0043] Resin A preparations were made using the same mix sequence as for Examples 1 to 14. In this dataset, Table 3, the resin was dissolved in odorless mineral spirits at a solids of 71.5%wt. The parts of 350 cs polydimethylsiloxane and tetraisopropyltitanate used in the examples are listed in Table 3. In all cases the resulting solutions were hazy and without continuous mixing phase separate. Addition of more Component D, odorless mineral spirits, by measured aliquots allowed one to demonstrate the point at which a clear solution was achieved. It was also at that point the maximum water repellent solids were achieved. This data shows that one can maximize the effective water repellent solids by adjusting the level

of titanate. This has the added benefit of introducing a more highly crosslinked resin matrix upon coating a substrate and curing the resin.

[0044] Table 4 lists the parts of the components used and results of Tests A and B (described below). Resin A was used at 50% solids in odorless mineral spirits. In this dataset, 5 tetra-2-ethylhexyl titanate was used to compatibilize the resin and fluid components. The data shows that an excess of titanate to polydimethylsiloxane fluid ratio is favored to achieve acceptable solution stability.

[0045] Test A: The static water drop test involves placing a predetermined amount of water on to a flat horizontal piece of fabric. The test may be performed on treated or untreated 10 fabric. A pipette is used to place a droplet of water on to the fabric. The water is placed on to the fabric from a close distance so that the droplet does not splatter on the surface. Sufficient water is dropped on to the fabric to create a droplet from 0.2 – 1.0 centimeter in diameter. Preferred is a droplet diameter of 0.5 centimeter. This amount could be reliably applied from a glass pipette, applying two drops of water from a height of 1 centimeter over the fabric.

15 Immediately an assessment is made of the shape of the droplet and an approximation of the droplet's contact angle with the fabric surface. For example, a droplet with a high contact angle will be rounded and have a minimum area of contact between the water and the fabric surface. This indicates a very water repellent surface on the fabric. As the contact angle and the water repellency decreases, the shape of the droplet becomes flatter and the area of 20 contact between the water and the fabric increases. A fabric surface with no water repellency will show the water soaking into the fabric, either partially or completely. It is also useful to reassess the character of the droplet after some period of time: from 5 minutes up to several hours. The data presented in Table 4 are readings of 5 minutes.

[0046] Test B: Approximately one gram of Heinz® Ketchup was placed on the fabric as a 25 droplet, ie., a mound. This was let set at 23C for 17 hours. After this exposure period, the residue was washed off with water and gentle agitation. It was determined at this time whether any stain remained. If so, the spot was washed with gentle agitation using a 5gm Joy® dishwashing liquid in 100 gm of distilled water solution. After drying the area was re-examined for staining. This test was used for samples summarized in Table 4.

30 [0047] Examples 24, 25, 26, 32, 33, 34, 38 and 39 were repeated except that Resin A was used at 71.5% solids in mineral spirits. The higher solids solutions upon mixing with 350 cs polydimethylsiloxane and tetra-2-ethylhexyl titanate resulted in hazy, unstable water repellent

solutions. Measured aliquots of additional odorless mineral spirits, Component D, were added back to these examples until solution clarity and stability were achieved. The parts for all components are in Table 5. One saw that as the titanate to polydimethylsiloxane fluid ratio increases, the effective water repellent solids level increases. This demonstrates that correct use of metal alkoxides to compatibilize the resin / fluid mixtures resulted in lower carrier solvent use.

[0048] 40 parts of Resin A solution, at a solids level of 70%wt in odorless mineral spirits, was mixed with 30 parts each of 350 cs polydimethylsiloxane and tetra-2-ethylhexyl titanate. The ratio of resin solids to polydimethylsiloxane fluid was 0.93; the ratio of titanate to polydimethylsiloxane fluid was 1.0. This solution was diluted in odorless mineral spirits to 5-7% wt.

[0049] Resin D (40 parts) was formulated as a 70% solids solution in xylene with 30 parts of 350 cs polydimethylsiloxane fluid and 30 parts of tetra-2-ethylhexyl titanate. The ratio of resin solids to polydimethylsiloxane fluid is 0.93; the ratio of titanate to polydimethylsiloxane fluid is 1.0. The solution, though initially clear, over time yielded crystals which precipitated from solution.

[0050] The following tests also demonstrate the utility of the invention. If one skilled in the art dilutes the composition of Example 49 to 5-10% wt solids with toluene, and then applies the resulting solution to a substrate with overlapping spray, allowing the substrate to dry for 15 minutes, then spraying the substrate again and finally allowing it to dry at room temperature (23°C) for 24 hours, one would expect the following test results to be obtained. Coating weight of the treatment on the substrate would be approximately 1% wt. The composition of Comparison Resin Water Repellent can be applied to the same substrate and cured in the same manner. Both treated substrates were then tested for comparison.

[0051] Test 1: A 4"x4" piece of 65/35 Polyester/Cotton Woven (7435) substrate was treated by the procedure noted above with Example 49, and another piece of the same fabric was treated with the Comparison Resin Water Repellent. Both were tested for Mildew Resistance by the AATCC Method 30. Results in Table 6 show that the Example 49 composition provides superior mildew resistance.

[0052] Test 2: The 12 Second Vertical Flammability Test in Compliance with FR 25.853 was used to evaluate 4" x 4" wool carpet samples, some which had been treated with Example 49 and some with the Comparison Resin Water Repellent. As shown in Table 6,

while the Comparison Resin Water Repellent burned, the carper treated with Example 49 did not.

**[0053]** Test 3: 100% Cotton Woven (429W) 65/35 Polyester/Cotton Woven (7435) treated with both Example 49 and the Comparison Resin Water Repellent were evaluated for water repellency using the Water Repellency Spray Test per AATCC Method 22-1996. As shown in Table 6, both samples gave ratings of 100 which are excellent.

**[0054]** Test 4: 4"x 4" sections of wool carpet, when treated per the described method with either Example 49 or the Comparison Resin Water Repellent, were evaluated for stain release as shown in Table 6 using a selection of different stain media and found to release the staining agents with only a mild detergent and water solution. The stain media consisted of French®'s mustard being applied to the carpet which immediately formed a 1/8" bead. The mustard was then wiped away with a towel dampened with detergent solution and no mark or trace of mustard was evident. This test was repeated using coffee and also Diet Coke® with the stain media beading up and wiped off with no trace of stain present.

**TABLE 1: Description of Component (A) Resin**

| <u>Resin</u> | <u>M</u> | <u>D</u> | <u>T*</u> | <u>Q</u> | $(R^{1n}SiO((4-n)/2))$<br><u>Average n</u> | <u>Wt%</u><br><u>OZ**</u> | <u>Weight Av</u><br><u>Mw</u> |
|--------------|----------|----------|-----------|----------|--------------------------------------------|---------------------------|-------------------------------|
| A            | 0        | 0.134    | 0.866     | 0        | 1.134                                      | 2.6 - 2.8                 | 15,000                        |
| B            | 0        | 0.147    | 0.853     | 0        | 1.147                                      | 4.4 - 4.8                 | 20,000                        |
| C            | 0        | 0.160    | 0.840     | 0        | 1.160                                      |                           |                               |
| D            | 0.43     | 0        | 0         | 0.570    | 1.29                                       | 2.5                       | 15,000                        |

\* includes D(OZ) which is a T unit with one uncondensed silanol group

\*\* includes both alkoxy and hydroxyl on silicon

**TABLE 2**

| Example | Component A<br>(parts) | Component B<br>(parts) | Component C<br>(parts) | Stability | % Component A in<br>Component D |
|---------|------------------------|------------------------|------------------------|-----------|---------------------------------|
| 1       | 100.0                  | 50.0                   | 83.3                   | Good      | 50.0                            |
| 2       | 100.0                  | 54.5                   | 109.0                  | Good      | 50.0                            |
| 3       | 100.0                  | 70.4                   | 103.7                  | Good      | 50.0                            |
| 4       | 100.0                  | 66.7                   | 84.3                   | Excellent | 50.0                            |
| 5       | 100.0                  | 80.0                   | 120.0                  | Good      | 50.0                            |
| 6       | 100.0                  | 66.7                   | 66.7                   | Excellent | 50.0                            |
| 7       | 100.0                  | 80.0                   | 120.0                  | Good      | 50.0                            |
| 8       | 100.0                  | 86.8                   | 94.3                   | Good      | 50.0                            |
| 9       | 100.0                  | 83.6                   | 83.6                   | Good      | 50.0                            |
| 10      | 100.0                  | 100.0                  | 100.0                  | Excellent | 50.0                            |
| 11      | 100.0                  | 120.0                  | 80.0                   | Excellent | 50.0                            |
| 12      | 100.0                  | 75.0                   | 25.0                   | Excellent | 25.0                            |
| 13      | 100.0                  | 200.7                  | 33.5                   | Poor      | 23.0                            |
| 14      | 100.0                  | 121.5                  | 20.3                   | Poor      | 38.0                            |

Notes: Comp. A: Resin A in a solution in mineral spirits (Component D).

Comp. B: polydimethyl siloxane fluid, 350 cs.

Comp. C: Tetraisopropyl Titanate

Comp. D: odorless mineral spirits from Exxon Mobil Chemicals

**TABLE 3**

| Example | Component A<br>(parts) | Component B<br>(parts) | Component C<br>(parts) | Stability<br>(initial) | Initial % Component<br>A in Component D | Post Added<br>Component D | Stability (final) | % Component<br>A in<br>Component D<br>(final) |
|---------|------------------------|------------------------|------------------------|------------------------|-----------------------------------------|---------------------------|-------------------|-----------------------------------------------|
| 15      | 100.0                  | 50.0                   | 66.5                   | Poor                   | 71.5                                    | 8.3                       | Good              | 67.5                                          |
| 16      | 100.0                  | 50.0                   | 50.0                   | Poor                   | 71.5                                    | 20.3                      | Good              | 62.4                                          |
| 17      | 100.0                  | 50.0                   | 33.5                   | Poor                   | 71.5                                    | 45.0                      | Good              | 54.1                                          |
| 18      | 100.0                  | 79.9                   | 99.9                   | Poor                   | 71.5                                    | 14.0                      | Good              | 65.0                                          |
| 19      | 100.0                  | 79.9                   | 79.9                   | Poor                   | 71.5                                    | 34.0                      | Good              | 57.5                                          |
| 20      | 100.0                  | 79.9                   | 59.9                   | Poor                   | 71.5                                    | 57.9                      | Good              | 50.6                                          |
| 21      | 100.0                  | 125.0                  | 145.8                  | Poor                   | 71.5                                    | 31.6                      | Good              | 58.3                                          |
| 22      | 100.0                  | 125.0                  | 125.0                  | Poor                   | 71.5                                    | 55.9                      | Good              | 51.1                                          |

Notes: Comp. A: Resin A in a solution in mineral spirits (Component D).

Comp. B: polydimethyl siloxane fluid, 350 cs.

Comp. C: Tetraisopropyl Titanate

Comp. D: is odorless mineral spirits from Exxon Mobil Chemicals

TABLE 4

| Example          | Component A | Component B | Component C | % Component A in Component D | Stability | Static Water Drop | 18 Hour, 25C Ketchup | Avg Treatment Weight |
|------------------|-------------|-------------|-------------|------------------------------|-----------|-------------------|----------------------|----------------------|
| 23               | 100         | 50.0        | 83.3        | 50                           | Excellent | B                 | VVS                  | 1.23                 |
| 24               | 100         | 50.0        | 66.7        | 50                           | Excellent | A                 | VVS                  | 1.35                 |
| 25               | 100         | 50.0        | 50.0        | 50                           | Excellent | B                 | VS                   | 2.97                 |
| 26               | 100         | 50.0        | 33.3        | 50                           | Poor      | B                 | VVS                  | 1.46                 |
| 27               | 100         | 54.5        | 109.0       | 50                           | Excellent | A                 | VVS                  | 1.54                 |
| 28               | 100         | 66.7        | 84.3        | 50                           | Excellent | A                 | VVS                  | 1.55                 |
| 29               | 100         | 70.4        | 103.7       | 50                           | Excellent | A                 | VVS                  | 1.57                 |
| 30               | 100         | 66.7        | 66.7        | 50                           | Excellent |                   |                      |                      |
| 31               | 100         | 80.0        | 120.0       | 50                           | Excellent |                   |                      |                      |
| 32               | 100         | 80.0        | 100.0       | 50                           | Excellent | B                 | VS                   | 0.64                 |
| 33               | 100         | 80.0        | 80.0        | 50                           | Fair      | C                 | S                    | 1.31                 |
| 34               | 100         | 80.0        | 60.0        | 50                           | Poor      | B                 | VS                   | 1.51                 |
| 35               | 100         | 83.6        | 83.6        | 50                           | Excellent | B                 | VS                   | 1.45                 |
| 36               | 100         | 86.8        | 94.3        | 50                           | Excellent |                   |                      |                      |
| 37               | 100         | 100.0       | 100.0       | 50                           | Fair      |                   |                      |                      |
| 38               | 100         | 120.0       | 140.0       | 50                           | Excellent | B                 | VS                   | 3.39                 |
| 39               | 100         | 120.0       | 120.0       | 50                           | Fair      | B                 | VS                   | 1.20                 |
| 40               | 100         | 120.0       | 80.0        | 50                           | Poor      | B                 | S                    | 1.35                 |
| Untreated Fabric |             |             |             |                              |           | D                 | M                    | --                   |

Notes: Comp. A: Resin A in a solution of mineral spirits A = Very high contact angle, water bead moves easily over surface

Comp. B: polydimethyl siloxane fluid, 350 cs. B = High contact angle, bead moves over the surface

Comp. C: tetra-2-ethylhexyl titanate C = Bead flattens out on the surface

Comp. D odorless mineral spirits from Exxon Mobil Chemicals D = Water soaks

VVS = Very, very slight stain, VS = Very slight stain, S = Stains, M = Stains heavily

| TABLE 5    |             |             |             |                        |                                         |                           |                      |                                            |
|------------|-------------|-------------|-------------|------------------------|-----------------------------------------|---------------------------|----------------------|--------------------------------------------|
| Examp<br>e | Component A | Component B | Component C | Stability<br>(initial) | Initial % Component<br>A in Component D | Post Added<br>Component D | Stability<br>(final) | % Component A<br>in Component D<br>(final) |
| 41         | 100         | 50.0        | 66.5        | Poor                   | 71.5                                    | 17.0                      | Good                 | 63.8                                       |
| 42         | 100         | 50.0        | 50.0        | Poor                   | 71.5                                    | 54.6                      | Good                 | 51.4                                       |
| 43         | 100         | 50.0        | 33.5        | Poor                   | 71.5                                    | 109.2                     | Good                 | 40.1                                       |
| 44         | 100         | 76.9        | 96.2        | Poor                   | 71.5                                    | 21.2                      | Good                 | 62.1                                       |
| 45         | 100         | 76.9        | 76.9        | Poor                   | 71.5                                    | 65.5                      | Good                 | 48.7                                       |
| 46         | 100         | 76.9        | 57.7        | Poor                   | 71.5                                    | 115.5                     | Good                 | 39.2                                       |
| 47         | 100         | 125.0       | 146.3       | Poor                   | 71.5                                    | 113.9                     | Good                 | 39.4                                       |
| 48         | 100         | 125.0       | 125.0       | Poor                   | 71.5                                    | 101.9                     | Good                 | 41.4                                       |

Notes: Comp. A: Resin A in a solution in mineral spirits (Component D).

Comp. B: polydimethyl siloxane fluid, 350 cs.

Comp. C: Tetraisopropyl Titanate

Comp. D: odorless mineral spirits from Exxon Mobil Chemicals

**Table 6**

|                                         | A.<br>Mildew<br>Resistance | B.<br>Flame<br>Retardancy | C.<br>Water Repellency | D.<br>Stain<br>Release |
|-----------------------------------------|----------------------------|---------------------------|------------------------|------------------------|
| Example 49*                             | Pass                       | Pass                      | 100                    | Pass                   |
| Comparison<br>Resin Water<br>Repellent* | Fail                       | Fail                      | 100                    | Pass                   |

\* Samples of Ex. 49 and the Comparison were also applied to a 70 Denier polyamide 66 woven fabric. Ex. 49 was noted to impart a better feel, of hand, to the fabric. The Comparison resulted in a fabric feel that was more stiff and less supple.

## CLAIMS

1. A composition comprising

5 (A) 100 parts by weight of at least one organosiloxane copolymer having a general formula (I)  $R^1_nSiO_{(4-n)/2}$ , where each  $R^1$  is independently chosen from a hydrogen atom or a monovalent hydrocarbon group comprising 1 to 10 carbon atoms, provided greater than 80 mole percent of  $R^1$  are methyl groups,  $n$  is a value from 0.8 to 1.5, greater than 50 mole percent of the copolymer comprises  $R^1SiO_{3/2}$  units, and having a hydroxyl content from 0.2  
10 to 5 weight percent;

(B) 10 to 120 parts by weight of at least one polyorganosiloxane having a general formula (II)  $R^2R^3_2SiO(R^3_2SiO_{2/2})_a(R^3SiO_{3/2})_bSiR^3_2R^2$  where each  $R^2$  is an independently chosen hydrogen atom, monovalent hydrocarbon group comprising 1 to 10 carbon atoms, hydroxy group, or alkoxy group, each  $R^3$  is independently chosen from a  
15 hydrogen atom or a monovalent hydrocarbon group comprising 1 to 10 carbon atoms,  $a$  is an integer from 2 to 2000, and  $b$  is chosen such that  $b/(a+b)$  is from 0 to 0.05; and

(C) 10 to 150 parts by weight of at least one metal alkoxide.

2. The composition of claim 1 where each  $R^1$  is independently chosen from alkyl groups  
20 comprising 1 to about 8 carbon atoms and  $n$  is a value from 1 to 1.5.

3. The composition of claim 1 where each  $R^1$  is methyl,  $n$  is a value from 1 to 1.3, greater than 70 mole percent of the organosiloxane copolymer comprises  $R^1SiO_{3/2}$  units, and the organosiloxane copolymer comprises essentially no  $SiO_{4/2}$  units.

25 4. The composition of any of claims 1 to 3 where each  $R^2$  of component (B) is an independently chosen alkyl group comprising 1 to 8 carbon atoms.

5. The composition of any of claims 1 to 3 where each  $R^2$  is methyl.

6. The composition of any of claims 1 to 5 where the metal alkoxide has the formula  $M(OR^4)_4$ , where M is titanium or zirconium and each  $R^4$  is independently chosen from alkyl groups comprising 1 to 12 carbon atoms or hydroxylated alkyl groups comprising 1 to 12 carbon atoms and containing less than 4 hydroxyl groups.

5

7. The composition of any of claims 1 to 5 where the metal alkoxide has the formula  $M(OR^4)_4$ , where M is titanium and each  $R^4$  is an alkyl group comprising 6 to 12 carbon atoms.

10 8. The composition of any of claims 1 to 7 comprising 50 to 140 parts of component (C) per 100 parts of component (A).

9. The composition of any of claims 1 to 8 where the amount of Component C in the composition is equal to or greater than the amount of Component B.

15

10. The composition of any of claims 1 to 9 further comprising (D) at least one carrier chosen from water, organic solvents, and silicone compounds.

11. The composition of any of claims 1 to 9 further comprising (D) 10 to 400 parts by weight per 100 parts by weight of component (A) of at least one carrier chosen from water, organic solvents, and silicone compounds

20

12. The composition of any of claims 1 to 10 comprising 40 to 200 parts by weight of component (D) per 100 parts by weight of component (A).

25

13. A method of preparing a composition of any of claims 1 to 12 comprising mixing the components described therein.

14. A method for treating substrates comprising applying the composition of any of claims 1 to 12 to a substrate.

30

15. The method for treating substrates of claim 14 where the substrate is chosen from leather, wood, textile fabrics, fibers, and masonry.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/19372

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D183/04 C08L83/04 D06M15/643

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 C09D C08L D06M C09K C04B

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 1 085 066 A (GEN ELECTRIC)<br>21 March 2001 (2001-03-21)<br>claims 1-10<br>page 2, line 50 -page 3, line 20<br>page 3, line 21 - line 44<br>page 4, line 29 - line 32  | 1-7                   |
| A          | US 4 404 348 A (FAU ALAIN ET AL)<br>13 September 1983 (1983-09-13)<br>claim 1                                                                                             | 1                     |
| A          | PATENT ABSTRACTS OF JAPAN<br>vol. 1996, no. 03,<br>29 March 1996 (1996-03-29)<br>& JP 07 305053 A (TOSHIBA SILICONE CO<br>LTD), 21 November 1995 (1995-11-21)<br>abstract | 1                     |
|            | ---<br>-/--                                                                                                                                                               |                       |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

\* Special categories of cited documents:

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

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

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

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

8 October 2003

Date of mailing of the international search report

15/10/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Depijper, R

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/19372

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                  | Relevant to claim No. |
|------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A          | <p>PATENT ABSTRACTS OF JAPAN<br/>vol. 018, no. 578 (C-1269),<br/>7 November 1994 (1994-11-07)<br/>&amp; JP 06 212114 A (UBE IND LTD),<br/>2 August 1994 (1994-08-02)<br/>abstract<br/>&amp; DATABASE WPI<br/>Derwent Publications Ltd., London, GB;<br/>AN 1994-283503<br/>abstract</p> <p style="text-align: center;">---</p>                      | 1                     |
| A          | <p>PATENT ABSTRACTS OF JAPAN<br/>vol. 2000, no. 10,<br/>17 November 2000 (2000-11-17)<br/>&amp; JP 2000 186279 A (SHIN ETSU CHEM CO<br/>LTD;KONISHI CO LTD),<br/>4 July 2000 (2000-07-04)<br/>abstract<br/>&amp; DATABASE WPI<br/>Derwent Publications Ltd., London, GB;<br/>AN 2000-567699<br/>abstract</p> <p style="text-align: center;">---</p> | 1                     |
| A          | <p>US 4 399 247 A (ONA ISAO ET AL)<br/>16 August 1983 (1983-08-16)<br/>claim 1<br/>column 6, line 14<br/>column 6, line 22 - line 32</p> <p style="text-align: center;">---</p>                                                                                                                                                                     | 1                     |
| A          | <p>GB 834 376 A (GEN ELECTRIC)<br/>4 May 1960 (1960-05-04)<br/>claims 1,6,8</p> <p style="text-align: center;">-----</p>                                                                                                                                                                                                                            | 1                     |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/US 03/19372

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s)                                                                                                                                                             | Publication<br>date                                                                                                                                    |
|-------------------------------------------|---|---------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------|
| EP 1085066                                | A | 21-03-2001          | US 6245431 B1<br>EP 1085066 A2<br>JP 2001115092 A                                                                                                                                      | 12-06-2001<br>21-03-2001<br>24-04-2001                                                                                                                 |
| US 4404348                                | A | 13-09-1983          | FR 2511384 A1<br>BR 8204713 A<br>CA 1186841 A1<br>DE 3272724 D1<br>EP 0074913 A1<br>ES 8403151 A1<br>FI 822796 A<br>JP 1326555 C<br>JP 58037054 A<br>JP 60054990 B<br>NO 822721 A , B, | 18-02-1983<br>02-08-1983<br>07-05-1985<br>25-09-1986<br>23-03-1983<br>01-06-1984<br>13-02-1983<br>16-07-1986<br>04-03-1983<br>03-12-1985<br>14-02-1983 |
| JP 07305053                               | A | 21-11-1995          | NONE                                                                                                                                                                                   |                                                                                                                                                        |
| JP 06212114                               | A | 02-08-1994          | NONE                                                                                                                                                                                   |                                                                                                                                                        |
| JP 2000186279                             | A | 04-07-2000          | NONE                                                                                                                                                                                   |                                                                                                                                                        |
| US 4399247                                | A | 16-08-1983          | JP 1364015 C<br>JP 58001749 A<br>JP 61029623 B                                                                                                                                         | 09-02-1987<br>07-01-1983<br>08-07-1986                                                                                                                 |
| GB 834376                                 | A | 04-05-1960          | NONE                                                                                                                                                                                   |                                                                                                                                                        |