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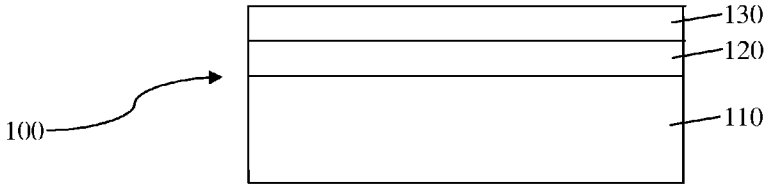


FIG. 1

(57) Abstract: Provided are coated substrates having a polymer substrate, an interfacial coating on the substrate, and an inorganic barrier coating on the interfacial coating. The interfacial coating is prepared by applying a fluorosilicon-modified polymer composition on the polymer substrate and curing the composition, wherein the fluorosilicon-modified polymer composition has a curable polymer composition and a fluorosilicon compound. Electronic packages having an electronic device, a coated substrate overlying the device, and an adhesive coating between and in contact with the coated substrate and the device are also provided. Methods of preparing coated substrates are also provided.

WO 2012/135114 A1

FLUORO SURFACE SEGREGATED MONOLAYER COATING

Field of Invention

[0001] The present invention relates to coated substrates comprising a polymer substrate, an interfacial coating on the substrate, and an inorganic barrier coating on the interfacial coating, wherein the interfacial coating comprises a curable polymer composition and a fluorosilicon compound. The present invention also relates to electronic packages and methods of preparing the coated substrates.

Background

[0002] Barrier coatings play an important role in a wide range of applications including electronic packaging, food packaging, and surface treatment, by protecting sensitive materials from air, moisture, and environmental contaminants. In particular, barrier coatings are frequently applied to electronic devices to protect sensitive electrical contacts from various gases and liquids in the environment. As a result, such coatings increase the reliability and useful lifespan of many consumer products.

[0003] Barrier coatings comprising a single layer of an inorganic material, such as a metal oxide or nitride are known in the art. However, such coatings are often too brittle for use on materials having high thermal expansion, such as polymer substrates. Stresses develop in the barrier layer due to differences in the coefficients of thermal expansion between the substrate and the coating. Thermally induced stresses can cause cracking of the barrier coating, thereby reducing the effectiveness of the coating and reliability of the device.

[0004] One approach to reducing crack formation in barrier coatings is to deposit an organic coating adjacent to the barrier coating. These multilayer coatings typically comprise alternating layers of inorganic and polymer materials. However, prior art organic coatings are limited with regard to low surface energy polymer substrates in that such organic coatings, generally, do not have the requisite surface energies to flow, coat, and adhere to low surface energy polymer substrates.

[0005] Thus, there is continued need for barrier coatings having superior resistance to air, moisture, and environmental elements, particularly water vapor and oxygen.

Summary

[0006] In one embodiment, a coated substrate comprising a polymer substrate, an interfacial coating on the substrate, and an inorganic barrier coating on the interfacial coating

is disclosed. The interfacial coating is prepared by applying a fluorosilicon-modified polymer composition on the polymer substrate and curing the composition. The fluorosilicon-modified polymer composition comprises a curable polymer composition and a fluorosilicon compound.

[0007] In another embodiment, an electronic package comprising an electronic device, a coated substrate overlying the device, and an adhesive coating between an in contact with the coated substrate and the device is disclosed. The coated substrate comprises a polymer substrate, an interfacial coating on the substrate, and an inorganic barrier coating on the interfacial coating. The interfacial coating is prepared by applying a fluorosilicon-modified polymer composition comprising a curable polymer composition and a fluorosilicon compound on the polymer substrate, and curing the composition.

[0008] In another embodiment, a method of preparing a coated substrate is disclosed. The method comprises forming an interfacial coating on a polymer substrate and forming an inorganic barrier on the interfacial coating. The interfacial coating is prepared by applying a fluorosilicon-modified polymer composition comprising a curable polymer composition and a fluorosilicon compound on the substrate, and curing the composition, and forming an inorganic barrier coating on the interfacial coating.

[0009] These and other features and advantages of these and other various embodiments according to the present invention will become more apparent in view of the drawings, detailed description, and claims provided that follow hereafter.

Brief Description

[0010] FIG. 1 depicts a cross-sectional view of a coated substrate according to an embodiment of the present invention;

[0011] FIG. 2 depicts a cross-sectional view of a coated substrate, further comprising an additional inorganic barrier coating on an interfacial coating according to an embodiment of the present invention;

[0012] FIG. 3 depicts a cross-sectional view of a coated substrate, further comprising at least two alternating inorganic barrier and interfacial coatings on an interfacial coating according to an embodiment of the present invention;

[0013] FIG. 4 depicts a cross-sectional view of a coated substrate, further comprising an additional interfacial coating on an inorganic barrier coating according to an embodiment of the present invention;

[0014] FIG. 5 depicts a cross-sectional view of an electronic package according to an embodiment of the present invention; and

[0015] FIG. 6 depicts a cross-sectional view of an electronic package, wherein the electronic package comprises a second interfacial coating on a second inorganic barrier coating in a region over at least an electronic device, and a third inorganic barrier coating on the second interfacial coating and any portion of the second inorganic barrier coating not covered by the second interfacial coating according to an embodiment of the present invention.

[0016] Skilled artisans appreciate that elements in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the elements in the figures may be exaggerated relative to other elements, as well as conventional parts removed, to help to improve understanding of the various embodiments of the present invention.

Detailed Description

[0017] Embodiments of the present invention relate to a coated substrate, an electronic package, and a method of preparing a coated substrate. As shown in FIG. 1, in one embodiment, a coated substrate 100 comprising a polymer substrate 110, an interfacial coating 120 on the substrate 110, and an inorganic barrier coating 130 on the interfacial coating 120 is provided. The interfacial coating 120 is prepared by applying a fluorosilicon-modified polymer composition on the polymer substrate 110 and curing the composition. The fluorosilicon-modified polymer composition comprises a curable polymer composition and a fluorosilicon compound. As used herein, the term "on" refers to a position of direct contact. For example, where the interfacial coating 120 is prepared by applying a fluorosilicon-modified polymer composition on the polymer substrate 110, the fluorosilicon-modified polymer composition and the polymer substrate 110 are in direct contact.

[0018] In one aspect, the coated substrate 100 comprises a polymer substrate 110. The polymer substrate 110 can be any rigid or flexible material having a planar, complex, or irregular contour. The substrate 110 can be transparent or nontransparent to light in the visible region (~400 to ~700 nm) of the electromagnetic spectrum.

[0019] Examples of polymer substrates 110 include, but are not limited to, polyolefins such as polyethylene, polypropylene, polystyrene, polyethylene terephthalate (PET), polyoxymethylene, polyvinylnapthalene, polyetheretherketone, polyamethylstyrene, and polyethylene naphthalate; chlorocarbon polymers such as polyvinyladyne chloride; fluorocarbon polymers such as polytetrafluoroethylene and polyvinylfluoride; polyamides such as Nylon and polyphthalamide; polyimides; polyesters such as poly(methyl methacrylate); epoxy resins; polyethers; polycarbonates; polysulfones; and polyether sulfones. In one particular aspect, the polymer substrate 110 is a fluorocarbon polymer. In a further aspect, the polymer substrate 110 is polytetrafluoroethylene and/or polyvinylfluoride, and combinations thereof.

[0020] In another aspect, the coated substrate 100 comprises an interfacial coating 120 on the substrate 110. The interfacial coating 120 is prepared by applying a fluorosilicon-modified polymer composition comprising a curable polymer composition and a fluorosilicon compound on the polymer substrate 110, and curing the composition. The interfacial coating 120 can be a single layer coating comprising one layer of a cured product of a silicone resin, or a multiple layer coating comprising two or more layers of at least two different cured products of silicone resins, where directly adjacent layers comprise different cured products (i.e., cured products have a different composition and/or property). The multiple layer coating typically comprises from 2 to 7 layers, alternatively from 2 to 5 layers, alternatively from 2 to 3 layers.

[0021] The single layer interfacial coating typically has a thickness of from 0.03 to 30 μm, alternatively from 0.1 to 10 μm, alternatively from 0.1 to 1.5 μm. The multiple layer interfacial coating typically has a thickness of from 0.06 to 30 μm, alternatively from 0.2 to 10 μm, alternatively 0.2 to 3 μm. When the thickness of the interfacial coating 120 is less than 0.03 μm, the coating 120 may become discontinuous. When the thickness of the interfacial coating 120 is greater than 30 μm, the coating 120 may exhibit reduced adhesion and/or cracking.

[0022] In some embodiments, the interfacial coating 120 typically exhibits high transparency. For example, the interfacial coating 120 typically has a percent transmittance of at least 90%, alternatively at least 92%, alternatively at least 94%, for light in the visible region (~400 to ~700 nm) of the electromagnetic spectrum.

[0023] The curable polymer composition can be any curable composition. In one aspect, the curable polymer composition typically contains a thermosetting polymer and additional ingredients, such as an organic solvent, cross-linking agent, and/or catalyst. The thermosetting polymer can be a homopolymer or a copolymer. Moreover, the thermosetting polymer can be a silicone polymer or an organic polymer. As used herein and below, the term "thermosetting polymer" refers to a cured (i.e., cross-linked) polymer that does not convert to a fluid state on heating.

[0024] Examples of curable polymer compositions comprising thermosetting polymers include, but are not limited to curable silicone compositions and curable organic compositions. The curable silicone composition can be any curable silicone composition comprising at least one silicone resin. Examples of curable silicone compositions include, but are not limited to, hydrosilylation-curable silicone compositions; condensation-curable silicone compositions; radiation-curable silicone compositions; and peroxide-curable silicone compositions. Examples of curable organic compositions include, but are not limited to, curable polyolefin compositions such as polyethylene and polypropylene compositions; curable polyamide compositions; curable epoxy resin compositions; curable amino resin compositions; curable polyurethane compositions; curable polyimide compositions; curable polyester compositions; and curable acrylic resin compositions. In one particular aspect, the curable organic composition has a water vapor transmission rate of less than 1×10^{-1} grams/m^2.

[0025] The silicone resin of the curable silicone composition can contain T siloxane units, T and Q siloxane units, or T and/or Q siloxane units in combination with M and/or D siloxane units. For example, the silicone resin can be a T resin, a TQ resin, an MT resin, a DT resin, an MDT resin, an MQ resin, a DQ resin, an MDQ resin, an MTQ resin, a DTQ resin, or an MDTQ resin.

[0026] The silicone resin typically contains silicon-bonded reactive groups capable of reacting in the presence or absence of a catalyst to form a cured product of the silicone resin. Examples of silicon-bonded reactive groups include, but are not limited to, -H, alkenyl, alkynyl, -OH, a hydrolysable group, alkenyl ether, acryloyloxyalkyl, substituted acryloyloxyalkyl, and an epoxy-substituted organic group.

[0027] The silicone resin typically has a weight-average molecular weight (M_W) of from 500 to 1,000,000, alternatively from 1,000 to 100,000, alternatively from 1,000 to 50,000,

alternatively from 1,000 to 20,000, alternatively from 1,000 to 10,000, where the molecular weight is determined by gel permeation chromatography employing a refractive index detector and polystyrene standards.

[0028] Hydrosilylation-curable silicone compositions typically comprise a silicone resin having an average of at least two silicon-bonded alkenyl groups or silicon-bonded hydrogen atoms per molecule; an organosilicon compound in an amount sufficient to cure the silicone resin, wherein the organosilicon compound has an average of at least two silicon-bonded hydrogen atoms or silicon-bonded alkenyl groups per molecule capable of reacting with the silicon-bonded alkenyl groups or silicon-bonded hydrogen atoms in the silicone resin; and a catalytic amount of a hydrosilylation catalyst. Examples of suitable hydrosilylation-curable silicone compositions comprising a silicon resin include those described in PCT Pub. No. WO 2007/145711 and PCT Pub. No. WO 2008/103226, the contents of which are hereby incorporated by reference.

[0029] In one aspect, the hydrosilylation-curable silicone composition comprises (A) a silicone resin having the formula $(R^1R^2_2SiO_{1/2})_w(R^2_2SiO_{2/2})_x(R^2SiO_{3/2})_y(SiO_{4/2})_z$ (I), wherein each R^1 is independently C_1 to C_{10} hydrocarbyl or C_1 to C_{10} halogen-substituted hydrocarbyl, both free of aliphatic unsaturation, each R^2 is independently R^1 or alkenyl, w is from 0 to 0.95, x is from 0 to 0.95, y is from 0 to 1, z is from 0 to 0.9, y+z is from 0.1 to 1, and w+x+y+z=1, provided the silicone resin has an average of at least two silicon-bonded alkenyl groups per molecule; (B) an organosilicon compound having an average of at least two silicon-bonded hydrogen atoms per molecule in an amount sufficient to cure the silicone resin; and (C) a catalytic amount of a hydrosilylation catalyst.

[0030] Component (A) is at least one silicone resin having the formula $(R^1R^2_2SiO_{1/2})_w(R^2_2SiO_{2/2})_x(R^2SiO_{3/2})_y(SiO_{4/2})_z$ (I), wherein each R^1 is independently C_1 to C_{10} hydrocarbyl or C_1 to C_{10} halogen-substituted hydrocarbyl, both free of aliphatic unsaturation, each R^2 is independently R^1 or alkenyl, w is from 0 to 0.95, x is from 0 to 0.95, y is from 0 to 1, z is from 0 to 0.9, y+z is from 0.1 to 1, and w+x+y+z=1, provided the silicone resin has an average of at least two silicon-bonded alkenyl groups per molecule.

[0031] The hydrocarbyl and halogen-substituted hydrocarbyl groups represented by R^1 are free of aliphatic unsaturation and typically have from 1 to 10 carbon atoms, alternatively from 1 to 6 carbon atoms. Acyclic hydrocarbyl and halogen-substituted hydrocarbyl groups

containing at least 3 carbon atoms can have a branched or unbranched structure. Examples of hydrocarbyl groups represented by R^1 include, but are not limited to, alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, octyl, nonyl, and decyl; cycloalkyl, such as cyclopentyl, cyclohexyl, and methylcyclohexyl; aryl, such as phenyl and naphthyl; alkaryl, such as tolyl and xylyl; and aralkyl, such as benzyl and phenethyl. Examples of halogen-substituted hydrocarbyl groups represented by R^1 include, but are not limited to, 3,3,3-trifluoropropyl, 3-chloropropyl, chlorophenyl, dichlorophenyl, 2,2,2-trifluoroethyl, 2,2,3,3-tetrafluoropropyl, and 2,2,3,3,4,4,5,5-octafluoropentyl.

[0032] The alkenyl groups represented by R^2, which may be the same or different, typically have from 2 to about 10 carbon atoms, alternatively from 2 to 6 carbon atoms, and are exemplified by, but not limited to, vinyl, allyl, butenyl, hexenyl, and octenyl.

[0033] In the formula (I) of the silicone resin, the subscripts w, x, y, and z are mole fractions. The subscript w typically has a value of from 0 to 0.95, alternatively from 0 to 0.8, alternatively from 0 to 0.2; the subscript x typically has a value of from 0 to 0.95, alternatively from 0 to 0.8, alternatively from 0 to 0.5; the subscript y typically has a value of from 0 to 1, alternatively from 0.3 to 1, alternatively from 0.5 to 1; the subscript z typically has a value of from 0 to 0.9, alternatively from 0 to 0.5, alternatively from 0 to 0.1; and the sum y+z typically has value of from 0.1 to 1, alternatively from 0.2 to 1, alternatively from 0.5 to 1, alternatively 0.8 to 1.

[0034] Typically at least 50 mol%, alternatively at least 65 mol%, alternatively at least 80 mol%, of the groups R^2 in the silicone resin are alkenyl. The term "mol% of the groups R^2 in the silicone resin are alkenyl" is defined as the ratio of the number of moles of silicon-bonded alkenyl groups in the silicone resin to the total number of moles of the groups R^2 in the resin, multiplied by 100.

[0035] The silicone resin typically contains less than 10% (w/w), alternatively less than 5% (w/w), alternatively less than 2% (w/w), of silicon-bonded hydroxy groups, as determined by ^{29}Si NMR.

[0036] Examples of silicone resins suitable for use as component (A) include, but are not limited to, resins having the following formulae:

$(Vi_2MeSiO_{1/2})_{0.25}(PhSiO_{3/2})_{0.75}$, $(ViMe_2SiO_{1/2})_{0.25}(PhSiO_{3/2})_{0.75}$, $(ViMe_2SiO_{1/2})_{0.25}(MeSiO_{3/2})_{0.25}(PhSiO_{3/2})_{0.50}$, $(ViMe_2SiO_{1/2})_{0.15}(PhSiO_{3/2})_{0.75}(SiO_{4/2})_{0.1}$, and $(Vi_2MeSiO_{1/2})_{0.15}(ViMe_2SiO_{1/2})_{0.1}(PhSiO_{3/2})_{0.75}$, where Me is methyl, Vi is vinyl, Ph is phenyl, and the numerical subscripts outside the parenthesis denote mole fractions. Also, in the preceding formulae, the sequence of units is unspecified.

[0037] Component (A) can be a single silicone resin or a mixture comprising two or more different silicone resins, each as described above.

[0038] Methods of preparing silicone resins containing silicon-bonded alkenyl groups are well known in the art; many of these resins are commercially available. These resins are typically prepared by cohydrolyzing the appropriate mixture of chlorosilane precursors in an organic solvent, such as toluene. For example, a silicone resin consisting essentially of $R^1R^2_2SiO_{1/2}$ units and $R^2SiO_{3/2}$ units can be prepared by cohydrolyzing a compound having the formula $R^1R^2_2SiCl$ and a compound having the formula R^2SiCl_3 in toluene, where R^1 and R^2 are as defined and exemplified above. The aqueous hydrochloric acid and silicone hydrolyzate are separated and the hydrolyzate is washed with water to remove residual acid and heated in the presence of a mild condensation catalyst to "body" the resin to the requisite viscosity. If desired, the resin can be further treated with a condensation catalyst in an organic solvent to reduce the content of silicon-bonded hydroxy groups. Alternatively, silanes containing hydrolysable groups other than chloro, such –Br, -I, $-OCH_3$, $-OC(O)CH_3$, $-N(CH_3)_2$, $NHCOCH_3$, and $–SCH_3$, can be utilized as starting materials in the cohydrolysis reaction. The properties of the resin products depend on the types of silanes, the mole ratio of silanes, the degree of condensation, and the processing conditions.

[0039] Component (B) is at least one organosilicon compound having an average of at least two silicon-bonded hydrogen atoms per molecule in an amount sufficient to cure the silicone resin of component (A).

[0040] The organosilicon compound has an average of at least two silicon-bonded hydrogen atoms per molecule, alternatively at least three silicon-bonded hydrogen atoms per molecule. It is generally understood that cross-linking occurs when the sum of the average number of alkenyl groups per molecule in component (A) and the average number of silicon-bonded hydrogen atoms per molecule in component (B) is greater than four.

[0041] The organosilicon compound can be an organohydrogensilane or an organohydrogensiloxane. The organohydrogensilane can be a monosilane, disilane, trisilane, or polysilane. Similarly, the organohydrogensiloxane can be a disiloxane, trisiloxane, or polysiloxane. The structure of the organosilicon compound can be linear, branched, cyclic, or resinous. Cyclosilanes and cyclosiloxanes typically have from 3 to 12 silicon atoms, alternatively from 3 to 10 silicon atoms, alternatively from 3 to 4 silicon atoms. In acyclic polysilanes and polysiloxanes, the silicon-bonded hydrogen atoms can be located at terminal, pendant, or at both terminal and pendant positions.

[0042] Examples of organohydrogensilanes include, but are not limited to, diphenylsilane, 2-chloroethylsilane, bis[(p-dimethylsilyl)phenyl]ether, 1,4-dimethyldisilylethane, 1,4-bis(dimethylsilyl)benzene, 1,3,5-tris(dimethylsilyl)benzene, 1,3,5-trimethyl-1,3,5-trisilane, poly(methylsilylene)phenylene, and poly(methylsilylene)methylene.

[0043] Examples of organohydrogensiloxanes include, but are not limited to, 1,1,3,3-tetramethyldisiloxane, 1,1,3,3-tetraphenyldisiloxane, phenyltris(dimethylsiloxy)silane, 1,3,5-trimethylcyclotrisiloxane, a trimethylsiloxy-terminated poly(methylhydrogensiloxane), a trimethylsiloxy-terminated poly(dimethylsiloxane/methylhydrogensiloxane), a dimethylhydrogensiloxy-terminated poly(methylhydrogensiloxane), and a resin consisting essentially of $HMe_2SiO_{1/2}$ units, $Me_3SiO_{1/2}$ units, and $SiO_{4/2}$ units, wherein Me is methyl.

[0044] Component (C) of the hydrosilylation-curable silicone composition is at least one hydrosilylation catalyst that promotes the addition reaction of component (A) with component (B). The hydrosilylation catalyst can be any of the well-known hydrosilylation catalysts comprising a platinum group metal, a compound containing a platinum group metal, or a microencapsulated platinum group metal-containing catalyst. Platinum group metals include platinum, rhodium, ruthenium, palladium, osmium and iridium. Preferably, the platinum group metal is platinum, based on its high activity in hydrosilylation reactions.

[0045] Preferred hydrosilylation catalysts include the complexes of chloroplatinic acid and certain vinyl-containing organosiloxanes disclosed by Willing in U.S. Pat. No. 3,419,593, which is hereby incorporated by reference. A preferred catalyst of this type is the reaction product of chloroplatinic acid and 1,3-diethenyl-1,1,3,3-tetramethyldisiloxane.

[0046] The hydrosilylation catalyst can also be a microencapsulated platinum group metal-containing catalyst comprising a platinum group metal encapsulated in a thermoplastic resin. Compositions containing microencapsulated hydrosilylation catalysts are stable for extended

periods of time, typically several months or longer, under ambient conditions, yet cure relatively rapidly at temperatures above the melting or softening point of the thermoplastic resin(s). Microencapsulated hydrosilylation catalysts and methods of preparing them are well known in the art, as exemplified in U.S. Pat. No. 4,766,176 and the references cited therein; and U.S. Pat. No. 5,017,654.

[0047] Component (C) can be a single hydrosilylation catalyst or a mixture comprising two or more different catalysts that differ in at least one property, such as structure, form, platinum group metal, complexing ligand, and thermoplastic resin.

[0048] The concentration of component (C) is sufficient to catalyze the addition reaction of component (A) with component (B). Typically, the concentration of component (C) is sufficient to provide from 0.1 to 1000 ppm of a platinum group metal, preferably from 1 to 500 ppm of a platinum group metal, and more preferably from 5 to 150 ppm of a platinum group metal, based on the combined weight of components (A) and (B). The rate of cure is very slow below 0.1 ppm of platinum group metal. The use of more than 1000 ppm of platinum group metal results in no appreciable increase in cure rate, and is therefore uneconomical.

[0049] In another aspect, the hydrosilylaton-curable silicone composition comprises (A') a silicone resin having the formula $(R^1R^3_2SiO_{1/2})_w(R^3_2SiO_{2/2})_x(R^3SiO_{3/2})_y(SiO_{4/2})_z$ (II), wherein each R^1 is independently C_1 to C_{10} hydrocarbyl or C_1 to C_{10} halogen-substituted hydrocarbyl, both free of aliphatic unsaturation, each R^3 is independently R^1 or –H, w is from 0 to 0.95, x is from 0 to 0.95, y is from 0 to 1, z is from 0 to 0.9, y+z is from 0.1 to 1, and w+x+y+z=1, provided the silicone resin has an average of at least two silicon-bonded hydrogen atoms per molecule; (B') an organosilicon compound having an average of at least two silicon-bonded alkenyl groups per molecule in an amount sufficient to cure the silicone resin; and (C) a catalytic amount of a hydrosilylation catalyst.

[0050] Component (A') is at least one silicone resin having the formula $(R^1R^3_2SiO_{1/2})_w(R^3_2SiO_{2/2})_x(R^3SiO_{3/2})_y(SiO_{4/2})_z$ (II), wherein each R^1 is independently C_1 to C_{10} hydrocarbyl or C_1 to C_{10} halogen-substituted hydrocarbyl, both free of aliphatic unsaturation, each R^3 is independently R^1 or –H, w is from 0 to 0.95, x is from 0 to 0.95, y is from 0 to 1, z is from 0 to 0.9, y+z is from 0.1 to 1, and w+x+y+z=1, provided the silicone resin has an average of at least two silicon-bonded hydrogen atoms per molecule. In the

formula (II), R^1, w, x, y, z, and y+z are as described and exemplified above for the silicone resin having the formula (I).

[0051] Typically at least 50 mol%, alternatively at least 65 mol%, alternatively at least 80 mol%, of the groups R^3 in the silicone resin are hydrogen. The term "mol% of the groups R^3 in the silicone resin are hydrogen" is defined as the ratio of the number of moles of silicon-bonded hydrogen atoms in the silicone resin to the total number of moles of the groups R^3 in the resin, multiplied by 100.

[0052] The silicone resin typically contains less than 10% (w/w), alternatively less than 5% (w/w), alternatively less than 2% (w/w), of silicon-bonded hydroxy groups, as determined by ^{29}Si NMR.

[0053] Examples of silicone resins suitable for use as component (A') include, but are not limited to, resins having the following formulae:

$(HMe_2SiO_{1/2})_{0.25}(PhSiO_{3/2})_{0.75}$, $(HMeSiO_{2/2})_{0.3}(PhSiO_{3/2})_{0.6}(MeSiO_{3/2})_{0.1}$, and $(Me_3SiO_{1/2})_{0.1}(H_2SiO_{2/2})_{0.1}(MeSiO_{3/2})_{0.4}(PhSiO_{3/2})_{0.4}$, where Me is methyl, Ph is phenyl, and the numerical subscripts outside the parenthesis denote mole fractions. Also, in the preceding formulae, the sequence of units is unspecified.

[0054] Component (A') can be a single silicone resin or a mixture comprising two or more different silicone resins, each as described above.

[0055] Methods of preparing silicone resins containing silicon-bonded hydrogen atoms are well known in the art; many of these resins are commercially available. Silicone resins are typically prepared by cohydrolyzing the appropriate mixture of chlorosilane precursors in an organic solvent, such as toluene. For example, a silicone resin consisting essentially of $R^1R^3_2SiO_{1/2}$ units and $R^3SiO_{3/2}$ units can be prepared by cohydrolyzing a compound having the formula $R^1R^3_2SiCl$ and a compound having the formula R^3SiCl_3 in toluene, where R^1 and R^3 are as described and exemplified above. The aqueous hydrochloric acid and silicone hydrolyzate are separated and the hydrolyzate is washed with water to remove residual acid and heated in the presence of a mild non-basic condensation catalyst to "body" the resin to the requisite viscosity. If desired, the resin can be further treated with a non-basic condensation catalyst in an organic solvent to reduce the content of silicon-bonded hydroxy groups. Alternatively, silanes containing hydrolysable groups other than chloro, such –Br, -I,

$-OCH_3$, $-OC(O)CH_3$, $-N(CH_3)_2$, $NHCOCH_3$, and $-SCH_3$, can be utilized as starting materials in the cohydrolysis reaction. The properties of the resin products depend on the types of silanes, the mole ratio of silanes, the degree of condensation, and the processing conditions.

[0056] Component (B') is at least one organosilicon compound having an average of at least two silicon-bonded alkenyl groups per molecule in an amount sufficient to cure the silicone resin of component (A').

[0057] The organosilicon compound contains an average of at least two silicon-bonded alkenyl groups per molecule, alternatively at least three silicon-bonded alkenyl groups per molecule. It is generally understood that cross-linking occurs when the sum of the average number of silicon-bonded hydrogen atoms per molecule in component (A') and the average number of silicon-bonded alkenyl groups per molecule in component (B') is greater than four.

[0058] The organosilicon compound can be an organosilane or an organosiloxane. The organosilane can be a monosilane, disilane, trisilane, or polysilane. Similarly, the organosiloxane can be a disiloxane, trisiloxane, or polysiloxane. The structure of the organosilicon compound can be linear, branched, cyclic, or resinous. Cyclosilanes and cyclosiloxanes typically have from 3 to 12 silicon atoms, alternatively from 3 to 10 silicon atoms, alternatively from 3 to 5 silicon atoms. In acyclic polysilanes and polysiloxanes, the silicon-bonded alkenyl groups can be located at terminal, pendant, or at both terminal and pendant positions.

[0059] Examples of organosilanes suitable for use as component (B') include, but are not limited to, silanes having the following formulae: Vi_4Si, $PhSiVi_3$, $MeSiVi_3$, $PhMeSiVi_2$, Ph_2SiVi_2, and $PhSi(CH_2CH=CH_2)_3$, where Me is methyl, Ph is phenyl, and Vi is vinyl.

[0060] Examples of organosiloxanes suitable for use as component (B') include, but are not limited to, siloxanes having the following formulae: $PhSi(OSiMe_2Vi)_3$, $Si(OSiMe_2Vi)_4$, $MeSi(OSiMe_2Vi)_3$, and $Ph_2Si(OSiMe_2Vi)_2$, where Me is methyl, Ph is phenyl, and Vi is vinyl.

[0061] Component (B') can be a single organosilicon compound or a mixture comprising two or more different organosilicon compounds, each as described above. For example, component (B') can be a single organosilane, a mixture of two different organosilanes, a

single organosiloxane, a mixture of two different organosiloxanes, or a mixture of an organosilane and an organosiloxane.

[0062] The concentration of component (B') is sufficient to cure (cross-link) the silicone resin of component (A'). The exact amount of component (B') depends on the desired extent of cure, which generally increases as the ratio of the number of moles of silicon-bonded alkenyl groups in component (B') to the number of moles of silicon-bonded hydrogen atoms in component (A') increases. The concentration of component (B') is typically sufficient to provide from 0.4 to 2 moles of silicon-bonded alkenyl groups, alternatively from 0.8 to 1.5 moles of silicon-bonded alkenyl groups, alternatively from 0.9 to 1.1 moles of silicon-bonded alkenyl groups, per mole of silicon-bonded hydrogen atoms in component (A').

[0063] Methods of preparing organosilanes and organosiloxanes containing silicon-bonded alkenyl groups are well known in the art; many of these compounds are commercially available.

[0064] Component (C) is as described and exemplified above.

[0065] The hydrosilylation-curable silicone composition can comprise additional ingredients, provided the ingredient does not prevent the silicone composition from curing to form the first interfacial coating 110, described above, of the electronic package 200. Examples of additional ingredients include, but are not limited to, hydrosilylation catalyst inhibitors, such as 3-methyl-3-penten-1-yne, 3,5-dimethyl-3-hexen-1-yne, 3,5-dimethyl-1-hexyn-3-ol, 1-ethynyl-1-cyclohexanol, 2-phenyl-3-butyn-2-ol, vinylcyclosiloxanes, and triphenylphosphine; adhesion promoters, such as the adhesion promoters taught in U.S. Patent Nos. 4,087,585 and 5,194,649; dyes; pigments; anti-oxidants; heat stabilizers; UV stabilizers; flame retardants; flow control additives; and diluents, such as organic solvents and reactive diluents.

[0066] Condensation-curable silicone compositions typically comprise a silicone resin having an average of at least two silicon-bonded hydrogen atoms, hydroxy groups, or hydrolysable groups per molecule and, optionally, a cross-linking agent having silicon-bonded hydrolysable groups and/or a condensation catalyst. Examples of suitable condensation-curable silicone compositions comprising a silicone resin include those described in PCT Pub. No. WO 2007/145711, the contents of which are hereby incorporated by reference.

[0067] In one aspect, the condensation-curable silicone composition comprises a silicone resin having the formula $(R^4R^5_2SiO_{1/2})_w(R^5_2SiO_{2/2})_x(R^5SiO_{3/2})_y(SiO_{4/2})_z$ (III), wherein each R^4 is independently C_1 to C_{10} hydrocarbyl or C_1 to C_{10} halogen-substituted hydrocarbyl, each R^5 is independently R^4, -H, -OH, or a hydrolysable group, w is from 0 to 0.95, x is from 0 to 0.95, y is from 0 to 1, z is from 0 to 0.9, y+z is from 0.1 to 1, and w+x+y+z=1, provided the silicone resin has an average of at least two silicon-bonded hydrogen atoms, hydroxy groups, or hydrolysable groups per molecule. In the formula (III), w, x, y, z, and y+z are as described and exemplified above for the silicone resin having the formula (I).

[0068] The hydrocarbyl and halogen-substituted hydrocarbyl groups represented by R^4 typically have from 1 to 10 carbon atoms, alternatively from 1 to 6 carbon atoms, alternatively from 1 to 4 carbon atoms. Acyclic hydrocarbyl and halogen-substituted hydrocarbyl groups containing at least 3 carbon atoms can have a branched or unbranched structure. Examples of hydrocarbyl groups include, but are not limited to, alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, octyl, nonyl, and decyl; cycloalkyl, such as cyclopentyl, cyclohexyl, and methylcyclohexyl; aryl, such as phenyl and naphthyl; alkaryl, such as tolyl and xylyl; aralkyl, such as benzyl and phenethyl; alkenyl, such as vinyl, allyl, and propenyl; arylalkenyl, such as styryl and cinnamyl; and alkynyl, such as ethynyl and propynyl. Examples of halogen-substituted hydrocarbyl groups include, but are not limited to, 3,3,3-trifluoropropyl, 3-chloropropyl, chlorophenyl, dichlorophenyl, 2,2,2-trifluoroethyl, 2,2,3,3-tetrafluoropropyl, and 2,2,3,3,4,4,5,5-octafluoropentyl.

[0069] As used herein the term "hydrolysable group" means the silicon-bonded group reacts with water in either the presence or absence of a catalyst at any temperature from room temperature (~23 ± 2 °C) to 100 °C within several minutes, for example thirty minutes, to form a silanol (Si-OH) group. Examples of hydrolysable groups represented by R^5 include, but are not limited to, -Cl, -Br, $-OR^6$, $-OCH_2CH_2OR^6$, $CH_3C(=O)O$-, Et(Me)C=N-O-, $CH_3C(=O)N(CH_3)$-, and $-ONH_2$, wherein R^6 is C_1 to C_8 hydrocarbyl or C_1 to C_8 halogen-substituted hydrocarbyl.

[0070] The hydrocarbyl and halogen-substituted hydrocarbyl groups represented by R^6 typically have from 1 to 8 carbon atoms, alternatively from 3 to 6 carbon atoms. Acyclic hydrocarbyl and halogen-substituted hydrocarbyl groups containing at least 3 carbon atoms can have a branched or unbranched structure. Examples of hydrocarbyl include, but are not limited to, unbranched and branched alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 1-ethylpropyl, 2-methylbutyl, 3-methylbutyl, 1,2-dimethylpropyl, 2,2-dimethylpropyl, hexyl, heptyl, and octyl; cycloalkyl, such as cyclopentyl, cyclohexyl, and methylcyclohexyl; phenyl; alkaryl, such as tolyl and xylyl; aralkyl, such as benzyl and phenethyl; alkenyl, such as vinyl, allyl, and propenyl; arylalkenyl, such as styryl; and alkynyl, such as ethynyl and propynyl. Examples of halogen-substituted hydrocarbyl groups include, but are not limited to, 3,3,3-trifluoropropyl, 3- chloropropyl, chlorophenyl, and dichlorophenyl.

[0071] Typically, at least 10 mol%, alternatively at least 50 mol%, alternatively at least 80 mol% of the groups R^5 in the silicone resin are hydrogen, hydroxy, or a hydrolysable group. The term "mol% of the groups R^5 in the silicone resin are in the silicone resin are hydrogen, hydroxy, or a hydrolysable group" is defined as the ratio of the number of moles of silicon-bonded hydrogen, hydroxy, or a hydrolysable groups in the silicone resin to the total number of moles of the groups R^5 in the resin, multiplied by 100.

[0072] Examples of silicone resins having the formula (III) include, but are not limited to, resins having the following formulae:

$(MeSiO_{3/2})_n$, $(PhSiO_{3/2})_n$, $(Me_3SiO_{1/2})_{0.8}(SiO_{4/2})_{0.2}$, $(MeSiO_{3/2})_{0.67}(PhSiO_{3/2})_{0.33}$, $(MeSiO_{3/2})_{0.45}(PhSiO_{3/2})_{0.40}(Ph_2SiO_{2/2})_{0.1}(PhMeSiO_{2/2})_{0.05}$, $(PhSiO_{3/2})_{0.4}(MeSiO_{3/2})_{0.45}(PhSiO_{3/2})_{0.1}(PhMeSiO_{2/2})_{0.05}$, and $(PhSiO_{3/2})_{0.4}(MeSiO_{3/2})_{0.1}(PhMeSiO_{2/2})_{0.5}$, where Me is methyl, Ph is phenyl, the numerical subscripts outside the parenthesis denote mole fractions, and the subscript n has a value such that the silicone resin has a weight-average molecular weight of from 500 to 1,000,000. Also, in the preceding formulae, the sequence of units is unspecified.

[0073] The condensation-curable silicone composition can comprise a single silicone resin or a mixture comprising two or more different silicone resins, each as described above.

[0074] The condensation-curable silicone composition can comprise additional ingredients, provided the ingredient does not prevent the silicone resin from curing to form the first

interfacial coating 110, described above, of the electronic package 200. Examples of additional ingredients include, but are not limited to, adhesion promoters; dyes; pigments; anti-oxidants; heat stabilizers; UV stabilizers; flame retardants; flow control additives; organic solvents, cross-linking agents, and condensation catalysts.

[0075] For example the condensation-curable silicone composition may further comprise a cross-linking agent and/or a condensation catalyst. The cross-linking agent can have the formula $R^6_qSiX_{4-q}$, wherein R^6 is C_1 to C_8 hydrocarbyl or C_1 to C_8 halogen-substituted hydrocarbyl, X is a hydrolysable group, and q is 0 or 1. The hydrocarbyl and halogen-substituted hydrocarbyl groups represented by R^6 are as described and exemplified above. Also, the hydrolysable groups represented by X are as described and exemplified above for R^5.

[0076] Examples of cross-linking agents include, but are not limited to, alkoxysilanes such as $MeSi(OCH_3)_3$, $CH_3Si(OCH_2CH_3)_3$, $CH_3Si(OCH_2CH_2CH_3)_3$, $CH_3Si[O(CH_2)_3CH_3]_3$, $CH_3CH_2Si(OCH_2CH_3)_3$, $C_6H_5Si(OCH_3)_3$, $C_6H_5CH_2Si(OCH_3)_3$, $C_6H_5Si(OCH_2CH_3)_3$, $CH_2=CHSi(OCH_3)_3$, $CH_2=CHCH_2Si(OCH_3)_3$, $CF_3CH_2CH_2Si(OCH_3)_3$, $CH_3Si(OCH_2CH_2OCH_3)_3$, $CF_3CH_2CH_2Si(OCH_2CH_2OCH_3)_3$, $CH_2=CHSi(OCH_2CH_2OCH_3)_3$, $CH_2=CHCH_2Si(OCH_2CH_2OCH_3)_3$, $C_6H_5Si(OCH_2CH_2OCH_3)_3$, $Si(OCH_3)_4$, $Si(OC_2H_5)_4$, and $Si(OC_3H_7)_4$; organoacetoxysilanes such as $CH_3Si(OCOCH_3)_3$, $CH_3CH_2Si(OCOCH_3)_3$, and $CH_2=CHSi(OCOCH_3)_3$; organoiminooxysilanes such as $CH_3Si[O\text{-}N=C(CH_3)CH_2CH_3]_3$, $Si[O\text{-}N=C(CH_3)CH_2CH_3]_4$, and $CH_2=CHSi[O\text{-}N=C(CH_3)CH_2CH_3]_3$; organoacetamidosilanes such as $CH_3Si[NHC(=O)CH_3]_3$ and $C_6H_5Si[NHC(=O)CH_3]_3$; amino silanes such as $CH_3Si[NH(s\text{-}C_4H_9)]_3$ and $CH_3Si(NHC_6H_{11})_3$; and organoaminooxysilanes.

[0077] The cross-linking agent can be a single silane or a mixture of two or more different silanes, each as described above. Also, methods of preparing tri- and tetra-functional silanes are well known in the art; many of these silanes are commercially available.

[0078] When present, the concentration of the cross-linking agent in the silicone composition is sufficient to cure (cross-link) the silicone resin. The exact amount of the cross-linking agent depends on the desired extent of cure, which generally increases as the

ratio of the number of moles of silicon-bonded hydrolysable groups in the cross-linking agent to the number of moles of silicon-bonded hydrogen atoms, hydroxy groups, or hydrolysable groups in the silicone resin increases. Typically, the concentration of the cross-linking agent is sufficient to provide from 0.2 to 4 moles of silicon-bonded hydrolysable groups per mole of silicon-bonded hydrogen atoms, hydroxy groups, or hydrolysable groups in the silicone resin. The optimum amount of the cross-linking agent can be readily determined by routine experimentation.

[0079] As stated above, the condensation-curable silicone composition can further comprise at least one condensation catalyst. The condensation catalyst can be any condensation catalyst typically used to promote condensation of silicon-bonded hydroxy (silanol) groups to form Si-O-Si linkages. Examples of condensation catalysts include, but are not limited to, amines; and complexes of lead, tin, zinc, and iron with carboxylic acids. In particular, the condensation catalyst can be selected from tin(II) and tin(IV) compounds such as tin dilaurate, tin dioctoate, and tetrabutyl tin; and titanium compounds such as titanium tetrabutoxide.

[0080] When present, the concentration of the condensation catalyst is typically from 0.1 to 10% (w/w), alternatively from 0.5 to 5% (w/w), alternatively from 1 to 3% (w/w), based on the total weight of the silicone resin.

[0081] Radiation-curable silicone compositions typically comprise a silicone resin having an average of at least two silicon-bonded radiation-sensitive groups per molecule and, optionally, a photoinitiator. Examples of suitable radiation-curable silicone compositions comprising a silicone resin include those described in PCT Pub. No. WO 2007/145711, the contents of which are hereby incorporated by reference.

[0082] In one aspect, the radiation-curable silicone composition comprises a cured product of a silicone resin having the formula $(R^7R^8_2SiO_{1/2})_w(R^8_2SiO_{2/2})_x(R^8SiO_{3/2})_y(SiO_{4/2})_z$ (IV), wherein each R^7 is independently C_1 to C_{10} hydrocarbyl, C_1 to C_{10} halogen-substituted hydrocarbyl, or $-OR^6$, wherein R^6 is C_1 to C_8 hydrocarbyl or C_1 to C_8 halogen-substituted hydrocarbyl, each R^8 is independently R^7, -H, or a radiation-sensitive group, w is from 0 to 0.95, x is from 0 to 0.95, y is from 0 to 1, z is from 0 to 0.9, y+z is from 0.1 to 1, and w+x+y+z=1, provided the silicone resin has an average of at least two silicon-bonded radiation-sensitive groups per molecule. In the formula (IV), R^6, w, x, y, z, and y+z are as

described and exemplified above. Also, the hydrocarbyl and halogen-substituted hydrocarbyl groups represented by R^7 are as described and exemplified above for R^4.

[0083] Examples of radiation-sensitive groups represented by R^8 include, but are not limited to, acryloyloxyalkyl, substituted acryloyloxyalkyl, an alkenyl ether group, alkenyl, and an epoxy-substituted organic group. As used herein, the term "radiation-sensitive group" means the group forms a reactive species, for example a free radical or cation, in the presence of a free radical or cationic photoinitiator when exposed to radiation having a wavelength of from 150 to 800 nm.

[0084] Examples of acryloyloxyalkyl groups represented by R^8 include, but are not limited to, acryloyloxymethyl, 2-acryloyloxyethyl, 3-acryloyloxyypropyl, and 4-acryloyloxybutyl.

[0085] Examples of substituted acryloyloxyalkyl groups represented by R^8 include, but are not limited to, methacryloyloxymethyl, 2-methacryloyloxyethyl, and 3-methacryloyloxylpropyl.

[0086] Examples of alkenyl ether groups represented by R^8 include, but are not limited to, a vinyl ether group having the formula and -O-R^9-O-CH=CH_2, wherein R^9 is C_1 to C_{10} hydrocarbylene or C_1 to C_{10} halogen-substituted hydrocarbylene.

[0087] The hydrocarbylene groups represented by R^9 typically have from 1 to 10 carbon atoms, alternatively from 1 to 6 carbon atoms, alternatively from 1 to 4 carbon atoms. Examples of hydrocarbylene groups include, but are not limited to, alkylene such as methylene, ethylene, propane-1,3-diyl, 2-methylpropane-1,3-diyl, butane-1,4-diyl, butane-1,3-diyl, pentane-1,5,-diyl, pentane-1,4-diyl, hexane-1,6-diyl, octane-1,8-diyl, and decane-1,10-diyl; cycloalkylene such as cyclohexane-1,4-diyl; arylene such as phenylene. Examples of halogen-substituted hydrocarbylene groups include, but are not limited to, divalent hydrocarbon groups wherein one or more hydrogen atoms have been replaced by halogen, such as fluorine, chlorine, and bromine, such as –$CH_2CH_2CF_2CF_2CH_2CH_2$-.

[0088] Examples of alkenyl groups represented by R^8 include, but are not limited to, vinyl, allyl, propenyl, butenyl, and hexenyl.

[0089] As used herein, the term "epoxy-substituted organic group" refers to a monovalent organic group in which an oxygen atom, the epoxy substituent, is directly attached to two adjacent carbon atoms of a carbon chain or ring system. Examples of epoxy-substituted

organic groups represented by R^8 include, but are not limited to, 2,3-epoxypropyl, 3,4-epoxybutyl, 4,5-epoxypentyl, 2-glycidoxyethyl, 3-glycidoxypropyl, 4-glycidoxybutyl, 2-(3,4-epoxycylohexyl)ethyl, 3-(3,4-epoxycylohexyl)propyl, 2-(3,4-epoxy-3-methylcylohexyl)-2-methylethyl, 2-(2,3-epoxycylopentyl)ethyl, and 3-(2,3 epoxycylopentyl)propyl.

[0090] The silicone resin typically contains an average of at least two silicon-bonded radiation-sensitive groups per molecule. Generally, at least 50 mol%, alternatively at least 65 mol%, alternatively at least 80 mol% of the groups R^8 in the silicone resin are radiation-sensitive groups. The term "mol% of the groups R^8 in the silicone resin are radiation-sensitive groups" is defined as the ratio of the number of moles of silicon-bonded radiation-sensitive groups in the silicone resin to the total number of moles of the groups R^8 in the resin, multiplied by 100.

[0091] Examples of silicone resins having the formula (IV) include, but are not limited to, resins having the following formulae:

$(MeSiO_{3/2})_{0.25}(CH_2=C(CH_3)COO(CH_2)_3SiO_{3/2})_{0.75}$,

$(MeSiO_{3/2})_{0.5}(CH_2=C(CH_3)COO(CH_2)_3SiO_{3/2})_{0.5}$,

$(MeSiO_{3/2})_{0.67}(CH_2=C(CH_3)COO(CH_2)_3SiO_{3/2})_{0.33}$,

$(PhSiO_{3/2})_{0.25}(CH_2=C(CH_3)COO(CH_2)_3SiO_{3/2})_{0.75}$,

$(PhSiO_{3/2})_{0.5}(CH_2=C(CH_3)COO(CH_2)_3SiO_{3/2})_{0.5}$,

$(PhSiO_{3/2})_{0.67}(CH_2=C(CH_3)COO(CH_2)_3SiO_{3/2})_{0.33}$,

$(MeSiO_{3/2})_{0.25}(CH_2=C(CH_3)COO(CH_2)_3SiO_{3/2})_{0.72}(Me_3SiO_{1/2})_{0.03}$,

$(MeSiO_{3/2})_{0.5}(CH_2=C(CH_3)COO(CH_2)_3SiO_{3/2})_{0.47}(Me_3SiO_{1/2})_{0.03}$,

$(MeSiO_{3/2})_{0.67}(CH_2=C(CH_3)COO(CH_2)_3SiO_{3/2})_{0.30}(Me_3SiO_{1/2})_{0.03}$,

$(MeSiO_{3/2})_{0.67}(CH_2=CHCOO(CH_2)_3SiO_{3/2})_{0.33}$,

$(PhSiO_{3/2})_{0.67}(CH_2=CHCOO(CH_2)_3SiO_{3/2})_{0.33}$,

$(MeSiO_{3/2})_{0.33}(CH_2\text{-}CHCH_2OCH_2CH_2CH_2SiO_{3/2})_{0.67}$,

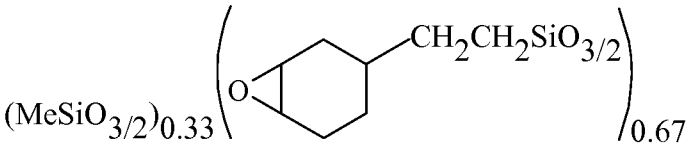
$(MeSiO_{3/2})_{0.67}(CH_2\text{-}CHCH_2OCH_2CH_2CH_2SiO_{3/2})_{0.33}$,

$(MeSiO_{3/2})_{0.6}(CH_2\text{-}CHCH_2OCH_2CH_2CH_2SiO_{3/2})_{0.3}(SiO_{4/2})_{0.1}$,

$(HSiO_{3/2})_{0.6}(CH_2\text{-}CHCH_2OCH_2CH_2CH_2SiO_{3/2})_{0.4}$

$(HSiO_{3/2})_{0.5}(CH_2\text{-}CHCH_2OCH_2CH_2CH_2SiO_{3/2})_{0.5}$

$(HSiO_{3/2})_{0.23}(MeSiO_{3/2})_{0.4}(CH_2\text{-}CHCH_2OCH_2CH_2CH_2SiO_{3/2})_{0.37}$



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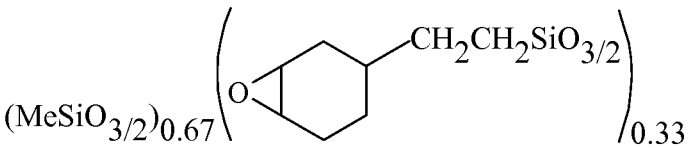

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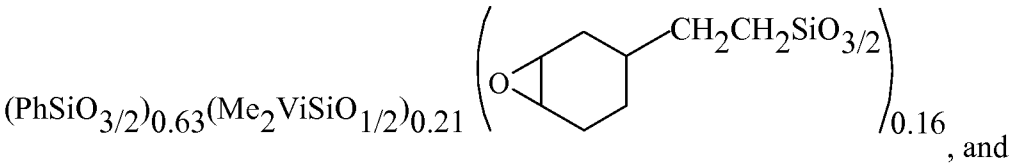

, and

$(MeSiO_{3/2})_{0.485}(HSiO_{3/2})_{0.485}(ViSiO_{3/2})_{0.03}$,

where Me is methyl, Ph is phenyl, Vi is vinyl, and the numerical subscripts outside the parenthesis denote mole fractions. Also, in the preceding formulae, the sequence of units is unspecified.

[0092] Methods of preparing silicone resins having silicon-bonded radiation-sensitive groups are known in the art. For example, silicone resins containing silicon-bonded acryloyloxyalkyl or substituted acryloyloxyalkyl groups can be prepared by co-hydrolyzing an acryloyloxyalkyl- or substituted-acryloyloxyalkylalkoxysilane and an alkoxysilane in the presence of an acidic or basic catalyst, as exemplified in U.S. Patent No. 5,738,976 and U.S. Patent No. 5,959,038. Alternatively, such resins can be produced by co-hydrolyzing an

acryloyloxyalkyl- or substituted-acryloyloxayalkylchlorosilane and at least one chlorosilane, as taught in U.S. Patent No. 4,568,566.

[0093] Silicone resins containing silicon-bonded alkenyl ether groups can be prepared by reacting an alkoxysilane with water in the presence of an acidic condensation catalyst and subsequently treating the reaction mixture with a hydroxy-substituted vinyl ether and a transesterification catalyst, as described in U.S. Patent No. 5,861,467. In brief this method comprises the steps of (I) reacting (a) a silane having the formula $R_xSi(OR^1)_{4-x}$, (b) water, and (c) an acidic condensation catalyst; (II) removing alcohol from the mixture of step (I), (III) neutralizing the mixture of step (II), (IV) adding a vinyl ether compound having the formula $HO\text{-}R^2\text{-}O\text{-}CH{=}CH_2$, (V) adding a transesterification catalyst to the mixture of step (IV); and (VI) removing volatiles from the mixture of step (V); wherein R is a monovalent hydrocarbon or halohydrocarbon radical having from 1 to 20 carbon atoms, R^1 is a monovalent alkyl radical having from 1 to 8 carbon atoms, R^2 is a divalent hydrocarbon or halohydrocarbon radical having from 1 to 20 carbon atoms, and x has a value of from 0 to 3, with the proviso that the molar ratio of water to alkoxy radicals is less than 0.5.

[0094] Alternatively, silicone resins containing alkenyl ether groups can be prepared by reacting an alkoxysilane, water, and a hydroxy-substituted vinyl ether compound in the presence of a non-acidic condensation catalyst, and then treating the reaction mixture with a transesterification catalyst, as described in U.S. Patent No. 5,824,761. Briefly, this method comprises (I) reacting (a) a silane having the formula $R_xSi(OR^1)_{4-x}$, (b) water, (c) a non-acidic condensation catalyst selected from amine carboxylates, heavy metal carboxylates, isocyanates, silanolates, phenoxides, mercaptides, CaO, BaO, LiOH, BuLi, amines, and ammonium hydroxides, and (d) a vinyl ether compound having the formula $HO\text{-}R^2\text{-}O\text{-}CH{=}CH_2$; (II) removing alcohol from the mixture of (I); (III) neutralizing the mixture of (II); (IV) adding a transesterification catalyst to the mixture of (III); and (V) removing volatiles from the mixture of (IV); wherein R is a monovalent hydrocarbon or halohydrocarbon radical having from 1 to 20 carbon atoms, R^1 is a monovalent alkyl radical having from 1 to 8 carbon atoms, R^2 is a divalent hydrocarbon or halohydrocarbon radical having from 1 to 20 carbon atoms, and x has a value of from 0 to 3, with the proviso that the molar ratio of water to alkoxy radicals is less than 0.5.

[0095] Silicone resins containing silicon-bonded alkenyl groups can be prepared as described above for the silicone resin having the formula (I).

[0096] Silicone resins containing silicon-bonded epoxy-substituted organic groups can be prepared by cohydrolyzing an epoxy-functional alkoxysilane and an alkoxysilane in the presence of an organotitanate catalyst, as described in U.S. Patent No. 5,468,826. Alternatively, silicone resins containing silicon-bonded epoxy-substituted organic groups can be prepared by reacting a silicone resin containing silicon-bonded hydrogen atoms with an epoxy-functional alkene in the presence of a hydrosilylation catalyst, as described in U.S. Patent Nos. 6,831,145; 5,310,843; 5,530,075; 5,283,309; 5,468,827; 5,486,588; and 5,358,983.

[0097] The radiation-curable silicone composition can comprise additional ingredients, provided those ingredients do not prevent the silicone resin from curing to form the first interfacial coating 110, described above, of the electronic package 200. Examples of additional ingredients include, but are not limited to, adhesion promoters; dyes; pigments; anti-oxidants; heat stabilizers; flame retardants; flow control additives; fillers, including extending and reinforcing fillers; organic solvents; cross-linking agents; and photoinitiators.

[0098] For example, the radiation-curable silicone composition can further comprise at least one photoinitiator. The photoinitiator can be a cationic or free radical photoinitiator, depending on the nature of the radiation-sensitive groups in the silicone resin. For example, when the resin contains alkenyl ether or epoxy-substituted organic groups, the silicone composition can further comprise at least one cationic photoinitiator. The cationic photoinitiator can be any cationic photoinitiator capable of initiating cure (cross-linking) of the silicone resin upon exposure to radiation having a wavelength of from 150 to 800 nm. Examples of cationic photoinitiators include, but are not limited to, onium salts, diaryliodonium salts of sulfonic acids, triarylsulfonium salts of sulfonic acids, diaryliodonium salts of boronic acids, and triarylsulfonium salts of boronic acids.

[0099] Suitable onium salts include salts having a formula selected from $R^{10}{}_2\ I^+\ MX_z^-$, $R^{10}{}_3\ S^+\ MX_z^-$, $R^{10}{}_3\ Se^+\ MX_z^-$, $R^{10}{}_4\ P^+\ MX_z^-$, and $R^{10}{}_4\ N^+\ MX_z^-$, wherein each R^{10} is independently hydrocarbyl or substituted hydrocarbyl having from 1 to 30 carbon atoms; M is an element selected from transition metals, rare earth metals, lanthanide metals, metalloids, phosphorus, and sulfur; X is a halogen (e.g., chloro, bromo, iodo), and z has a value such that the product z (charge on X + oxidation number of M) = -1. Examples of substituents on the

hydrocarbyl group include, but are not limited to, C_1 to C_8 alkoxy, C_1 to C_{16} alkyl, nitro, chloro, bromo, cyano, carboxyl, mercapto, and heterocyclic aromatic groups, such as pyridyl, thiophenyl, and pyranyl. Examples of metals represented by M include, but are not limited to, transition metals, such as Fe, Ti, Zr, Sc, V, Cr, and Mn; lanthanide metals, such as Pr, and Nd; other metals, such as Cs, Sb, Sn, Bi, Al, Ga, and In; metalloids, such as B, and As; and P. The formula MX_Z^- represents a non-basic, non-nucleophilic anion. Examples of anions having the formula MX_Z^- include, but are not limited to, BF_4^-, PF_6^-, AsF_6^-, $SbF_6^=$, $SbCl_6^-$, and $SnCl_6^-$.

[0100] Examples of onium salts include, but are not limited to, bis-diaryliodonium salts, such as bis(dodecyl phenyl)iodonium hexafluoroarsenate, bis(dodecylphenyl)iodonium hexafluoroantimonate, and dialkylphenyliodonium hexafluoroantimonate.

[0101] Examples of diaryliodonium salts of sulfonic acids include, but are not limited to, diaryliodonium salts of perfluoroalkylsulfonic acids, such as diaryliodonium salts of perfluorobutanesulfonic acid, diaryliodonium salts of perfluoroethanesulfonic acid, diaryliodonium salts of perfluorooctanesulfonic acid, and diaryliodonium salts of trifluoromethanesulfonic acid; and diaryliodonium salts of aryl sulfonic acids, such as diaryliodonium salts of para-toluenesulfonic acid, diaryliodonium salts of dodecylbenzenesulfonic acid, diaryliodonium salts of benzenesulfonic acid, and diaryliodonium salts of 3-nitrobenzenesulfonic acid.

[0102] Examples of triarylsulfonium salts of sulfonic acids include, but are not limited to, triarylsulfonium salts of perfluoroalkylsulfonic acids, such as triarylsulfonium salts of perfluorobutanesulfonic acid, triarylsulfonium salts of perfluoroethanesulfonic acid, triarylsulfonium salts of perfluorooctanesulfonic acid, and triarylsulfonium salts of trifluoromethanesulfonic acid; and triarylsulfonium salts of aryl sulfonic acids, such as triarylsulfonium salts of para-toluenesulfonic acid, triarylsulfonium salts of dodecylbenzenesulfonic acid, triarylsulfonium salts of benzenesulfonic acid, and triarylsulfonium salts of 3-nitrobenzenesulfonic acid.

[0103] Examples of diaryliodonium salts of boronic acids include, but are not limited to, diaryliodonium salts of perhaloarylboronic acids. Examples of triarylsulfonium salts of boronic acids include, but are not limited to, triarylsulfonium salts of perhaloarylboronic acid.

Diaryliodonium salts of boronic acids and triarylsulfonium salts of boronic acids are well known in the art, as exemplified in European Patent Application No. EP 0562922.

[0104] The cationic photoinitiator can be a single cationic photoinitiator or a mixture comprising two or more different cationic photoinitiators, each as described above. The concentration of the cationic photoinitiator is typically from 0.01 to 20% (w/w), alternatively from 0.1 to 20% (w/w), alternatively from 0.1 to 5%, based on the weight of the silicone resin.

[0105] When the silicone resin contains acryoyloxyalkyl, substituted acryloyloxyalkyl, or alkenyl groups, the silicone composition can further comprise at least one free radical photoinitiator. The free radical photoinitiator can be any free radical photoinitiator capable of initiating cure (cross-linking) of the silicone resin upon exposure to radiation having a wavelength of from 150 to 800 nm.

[0106] Examples of free radical photoinitiators include, but are not limited to, benzophenone; 4,4'-bis(dimethylamino)benzophenone; halogenated benzophenones; acetophenone; α-hydroxyacetophenone; chloro acetophenones, such as dichloroacetophenones and trichloroacetophenones; dialkoxyacetophenones, such as 2,2-diethoxyacetophenone; α-hydoxyalkylphenones, such as 2-hydroxy-2-methyl-1-phenyl-1-propanone and 1-hydroxycyclohexyl phenyl ketone; α-aminoalkylphenones, such as 2-methyl-4'-(methylthio)-2-morpholiniopropiophenone; benzoin; benzoin ethers, such as benzoin methyl ether, benzoin ethyl ether, and benzoin isobutyl ether; benzil ketals, such as 2,2-dimethoxy-2-phenylacetophenone; acylphosphinoxides, such as diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide; xanthone derivatives; thioxanthone derivatives; fluorenone derivatives; methyl phenyl glyoxylate; acetonaphthone; anthraquninone derivatives; sufonyl chlorides of aromatic compounds; and *O*-acyl α-oximinoketones, such as 1-phenyl-1,2-propanedione-2-(*O*-ethoxycarbonyl)oxime.

[0107] The free radical photoinitiator can also be a polysilane, such as the phenylmethylpolysilanes described by West in U.S. Pat. No. 4,260,780, which is hereby incorporated by reference; the aminated methylpolysilanes described by Baney et al. in U.S. Pat. No. 4,314,956, which is hereby incorporated by reference; the methylpolysilanes of Peterson et al. in U.S. Pat. No. 4,276,424, which is hereby incorporated by reference; and the polysilastyrene described by West et al. in U.S. Pat. No. 4,324,901, which is hereby incorporated by reference.

[0108] The free radical photoinitiator can be a single free radical photoinitiator or a mixture comprising two or more different free radical photoinitiators. The concentration of the free radical photoinitiator is typically from 0.1 to 20% (w/w), alternatively from 1 to 10% (w/w), based on the weight of the silicone resin.

[0109] The peroxide-curable silicone composition typically comprises a silicone resin having silicon-bonded unsaturated groups and an organic peroxide. Examples of suitable peroxide-curable silicone compositions comprising a silicone resin include those described in PCT Pub. No. WO 2007/145711, the contents of which are hereby incorporated by reference.

[0110] In one aspect, the peroxide-curable silicone composition comprises a silicone resin having the formula $(R^1R^{11}{}_2SiO_{1/2})_w(R^{11}{}_2SiO_{2/2})_x(R^{11}SiO_{3/2})_y(SiO_{4/2})_z$ (V), wherein each R^1 is independently C_1 to C_{10} hydrocarbyl or C_1 to C_{10} halogen-substituted hydrocarbyl, both free of aliphatic unsaturation; each R^{11} is independently R^1, alkenyl, alkynyl, acryloxyalkyl, or substituted acryloxyalkyl; w is from 0 to 0.95, x is from 0 to 0.95, y is from 0 to 1, z is from 0 to 0.9, y+z is from 0.1 to 1, and w+x+y+z=1; and an organic peroxide. In the formula (V), R^1, w, x, y, z, and y+z are as described and exemplified above for the silicone resin having the formula (I).

[0111] The alkenyl groups represented by R^{11}, which may be the same or different, typically have from 2 to about 10 carbon atoms, alternatively from 2 to 6 carbon atoms, and are exemplified by, but not limited to, vinyl, allyl, butenyl, hexenyl, and octenyl.

[0112] The alkynyl groups represented by R^{11}, which may be the same or different, typically have from 2 to about 10 carbon atoms, alternatively from 2 to 6 carbon atoms, and are exemplified by, but not limited to, ethynyl, propynyl, butynyl, hexynyl, and octynyl.

[0113] In one aspect of the silicone resin, the resin contains an average of at least one alkenyl group or alkynyl group per molecule.

[0114] The silicone resin typically contains less than 10% (w/w), alternatively less than 5% (w/w), alternatively less than 2% (w/w), of silicon-bonded hydroxy groups, as determined by ^{29}Si NMR.

[0115] Examples of silicone resins having the formula (V) include, but are not limited to, resins having the following formulae:

$(Vi_2MeSiO_{1/2})_{0.25}(PhSiO_{3/2})_{0.75}$, $(ViMe_2SiO_{1/2})_{0.25}(PhSiO_{3/2})_{0.75}$, $(ViMe_2SiO_{1/2})_{0.25}(MeSiO_{3/2})_{0.25}(PhSiO_{3/2})_{0.50}$, $(ViMe_2SiO_{1/2})_{0.15}(PhSiO_{3/2})_{0.75}(SiO_{4/2})_{0.1}$, and $(Vi_2MeSiO_{1/2})_{0.15}(ViMe_2SiO_{1/2})_{0.1}(PhSiO_{3/2})_{0.75}$, where Me is methyl, Vi is vinyl, Ph is phenyl, and the numerical subscripts outside the parenthesis denote mole fractions. Also, in the preceding formulae, the sequence of units is unspecified.

[0116] The silicone resin can be a single silicone resin or a mixture comprising two or more different silicone resins, each as described above.

[0117] Methods of preparing silicone resins having silicon-bonded alkenyl groups or silicon-bonded alkynyl groups are well known in the art; many of these resins are commercially available. These resins are typically prepared by cohydrolyzing the appropriate mixture of chlorosilane precursors in an organic solvent, such as toluene. For example, a silicone resin consisting essentially of $R^1R^{11}{}_2SiO_{1/2}$ units and $R^{11}SiO_{3/2}$ units can be prepared by cohydrolyzing a compound having the formula $R^1R^{11}{}_2SiCl$ and a compound having the formula $R^{11}SiCl_3$ in toluene, where R^1 and R^{11} are as defined and exemplified above. The aqueous hydrochloric acid and silicone hydrolyzate are separated and the hydrolyzate is washed with water to remove residual acid and heated in the presence of a mild condensation catalyst to "body" the resin to the requisite viscosity. If desired, the resin can be further treated with a condensation catalyst in an organic solvent to reduce the content of silicon-bonded hydroxy groups. Alternatively, silanes containing hydrolysable groups other than chloro, such –Br, -I, $-OCH_3$, $-OC(O)CH_3$, $-N(CH_3)_2$, $-NHCOCH_3$, and $–SCH_3$, can be utilized as starting materials in the cohydrolysis reaction. The properties of the resin products depend on the types of silanes, the mole ratio of silanes, the degree of condensation, and the processing conditions.

[0118] Examples of organic peroxides include, diaroyl peroxides such as dibenzoyl peroxide, di-p-chlorobenzoyl peroxide, and bis-2,4-dichlorobenzoyl peroxide; dialkyl peroxides such as di-t-butyl peroxide and 2,5-dimethyl-2,5-di-(t-butylperoxy)hexane; diaralkyl peroxides such as dicumyl peroxide; alkyl aralkyl peroxides such as t-butyl cumyl peroxide and 1,4-bis(t-butylperoxyisopropyl)benzene; and alkyl aroyl peroxides such as t-butyl perbenzoate, t-butyl peracetate, and t-butyl peroctoate.

[0119] The organic peroxide can be a single peroxide or a mixture comprising two or more different organic peroxides. The concentration of the organic peroxide is typically from 0.1 to 5% (w/w), alternatively from 0.2 to 2% (w/w), based on the weight of the silicone resin.

[0120] The peroxide-curable silicone composition of the present invention can comprise additional ingredients, provided those ingredients do not prevent the silicone resin of the silicone composition from curing to form the first interfacial coating 110, described above, of the electronic package 200. Examples of additional ingredients include, but are not limited to, silicone rubbers; polyunsaturated compounds; free radical initiators; organic solvents; UV stabilizers; sensitizers; dyes; flame retardants; antioxidants; fillers, such as reinforcing fillers, extending fillers, and conductive fillers; and adhesion promoters.

[0121] In one aspect, the interfacial coating 120 is prepared by applying a fluorosilicon-modified polymer composition comprising a curable polymer composition and a fluorosilicon compound on the polymer substrate 110, and curing the composition. The fluorosilicon compound can be any compound containing at least one silicon atom, an average of at least one silicon-bonded alkoxy group or silicon-bonded hydroxyl group per molecule, and an average of at least one monovalent fluorocarbon group per molecule, wherein the compound has a molecular weight of from 100 to 5000, alternatively from 100 to 4500, alternatively from 100 to 4000, alternatively from 100 to 3000, alternatively from 100 to 2500, and alternatively from 100 to 1000. The fluorosilicon compound can be a silane, disilane, polysilane, siloxane, disiloxane, or polysiloxane. Moreover, the fluorosilicon compound can be a single fluorosilicon compound or a mixture comprising two or more different fluorosilicon compounds. Examples of fluorosilicon compounds include, but are not limited to, fluoro-containing alkoxysilanes, fluoro-containing alkoxysilicates, and fluoro-containing sol-gels.

[0122] In one particular aspect, the fluorosilicon compound can be a fluoro-containing alkoxysilane. In this particular aspect, the fluoro-containing alkoxysilane has the formula $(RfQ^1)_ySi(OR^{12})_{4-y}$ (VI), wherein R^{12} is a C_1 to C_4 alkyl, Rf is a C_1 to C_8 monovalent fluorocarbon group, Q^1 is a C_1 to C_8 divalent hydrocarbon group, and y is 1, 2, or 3.

[0123] The alkyl groups represented by R^{12} can have a branched or unbranched structure. Examples of the alkyl groups represented by R^{12} include, but are not limited to methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, and 1,1-dimethylethyl.

[0124] Fluorocarbon groups result from replacing one or more hydrogen atoms of a hydrocarbon molecule with an equal number of fluorine atoms. The fluorocarbon groups represented by Rf can have a branched, unbranched, or cyclic structure. Examples of the monovalent fluorocarbon groups represented by Rf include, but are not limited to C_1 to C_8 monovalent fluorocarbons wherein about 25% to about 100% of the hydrogen atoms have been replaced with an equal number of fluorine atoms. Examples of the fluorocarbon groups represented by Rf include, but are not limited to $-CH_2CF_3$, $-CH_2CH_2CF_3$, $-CH_2CH_2CH_2CF(CF_3)_2$, perfluoromethyl, perfluoroethyl, perfluorovinyl ($-CF=CF_2$), perfluoroallyl ($-CF_2-CF=CF_2$), perfluoropropyl, perfluoro-1-methylethyl (isopropyl), perfluorobutyl, perfluoro-1-methylpropyl, perfluoro-2-methylpropyl, perfluoro-1,1-dimethylethyl (*tert*-butyl), perfluoropentyl, perfluoro-1-methylbutyl, perfluoro-1-ethylpropyl, perfluoro-2-methylbutyl, perfluoro-3-methylbutyl, perfluoro-1,2-dimethylpropyl, perfluoro-2,2-dimethylpropyl, perfluorohexyl, perfluoroheptyl, perfluorooctyl, perfluorocyclopentyl, perfluorocyclohexyl, and perfluorobenzyl.

[0125] Examples of divalent hydrocarbon groups represented by Q^1 can have a linear, branched, or cyclic structure, and combinations thereof, wherein neighboring carbon atoms may be joined by a single bond, a double bond, or a triple bond. Thus, the divalent hydrocarbon groups represented by Q^1 can include both saturated divalent hydrocarbons and unsaturated divalent hydrocarbons. Examples of divalent hydrocarbon groups represented by Q^1 include, but are not limited to methanediyl (methylene, $-CH_2-$), ethane-1,2-diyl (ethylene, $-CH_2-CH_2-$), vinylene ($-CH=CH-$), propane-1,3-diyl ($-CH_2-CH_2-CH_2-$), propane-1,2-diyl ($-CH_2-CH^{\bullet}-CH_3$), butandiyl, pentandiyl, hexandiyl, heptandiyl, octandiyl, cyclopentane-1,2-diyl, cyclopentane-1,3-diyl, cyclohexane-1,2-diyl, cyclohexane-1,3-diyl, cyclohexane-1,4-diyl, benzene-1,2-diyl, benzene-1,3-diyl, benzene-1,4-diyl (1,4-phenylene), and toluenediyl.

[0126] Examples of fluoro-containing alkoxysilanes represented by formula (VI) include, but are not limited to $F_3CCF_2CF_2CF_2CH_2CH_2Si(OCH_3)_3$, $F_3CCH_2CH_2Si(OCH_3)_3$, $(CF_3)_2CFCH_2CH_2CH_2Si(OCH_3)_3$, and $F_3CCF_2CF_2CF_2CH_2CH_2Si(OCH_3)_3$.

[0127] In another aspect, the fluorosilicon compound can be a fluoro-containing alkoxysilicate. In this particular aspect, the fluoro-containing alkoxysilicate has the formula $[SiO_{4/2}]_x[(R^{13}O)_aSiO_{(4-a)/2}]_y[(RfO)_bSiO_{(4-b)/2}]_z$ (VII), wherein R^{13} is a C_1 to C_4 alkyl or hydrogen, Rf is a C_1 to C_8 monovalent fluorocarbon group, a is from 1 to 3, b is from 1 to 3, x is from 2 to 500, y is from 1 to 50, and z is from 1 to 5.

[0128] The alkyl groups represented by R^{13} can have a branched or unbranched structure. Examples of the alkyl groups represented by R^{13} include, but are not limited to methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, and 1,1-dimethylethyl.

[0129] The fluorocarbon groups represented by Rf can have a branched, unbranched, or cyclic structure. Examples of the monovalent fluorocarbon groups represented by Rf are as described and exemplified above.

[0130] The fluoro-containing alkoxysilicate can also be a copolymer prepared by reacting an organopolysiloxane resin as described, for example, by Daudt et al. in U.S. Patent No. 2,672,182, with a fluoro-containing alkoxysilicate having the formula (VII) as described and exemplified above.

[0131] The fluorosilicon compound alkoxysilicate can also be a fluoro-containing sol-gel comprising a reaction product formed from the cohydrolysis and co-condensation of at least one alkoxy-functional organometallic compound of the general formula $M^1(OR^{14})_4$ (A) and at least one alkoxysilane compound having formula (VI) (B), with a predetermined quantity of water (C), and a siloxane polymerization catalyst (D).

[0132] In one aspect, component (A) has the general formula $M^1(OR^{14})_4$ wherein M^1 is a metal or metalloid, and R^{14} is a C_1 to C_4 alkyl. Examples of metals or metalloids represented by $M^1$of component (A) include, but are not limited to Si and Ti. The alkyl groups represented by R^{14} can have a branched or unbranched structure. Examples of the alkyl groups represented by R^{14} include, but are not limited to methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, and 1,1-dimethylethyl.

[0133] Examples of alkoxy-functional organometallic compounds of component (A) include, but are not limited to, tetraethoxysilane and tetrabutyltitanate.

[0134] In another aspect, component (B) has the general formula (VI) as described and exemplified above.

[0135] In another aspect, component (C) is a predetermined quantity of water sufficient to cause co-polymerization and co-condensation without gelling component (B) or causing a precipitate to form. In one particular aspect, the cohydrolysis and co-condensation are carried out by first blending component (A) with component (B) and thereafter adding component (C) to the blend.

[0136] The siloxane polymerization catalyst can be any catalyst typically used in the hydrolysis and condensation of alkoxysilanes. Examples of siloxane polymerization catalysts include but are not limited to H_2SO_4, $HClO_4$, trifluoromethane sulfonic acid, acrylic acid, KOH, NaOH, and amine-containing compounds.

[0137] In one particular aspect, a fluorosilicon-modified polymer composition is prepared by blending a curable polymer composition and a fluorosilicon compound together. In a further aspect, the fluorosilicon-modified polymer composition is prepared by blending the curable polymer composition and the fluorosilicon compound together such that the curable polymer composition and the fluorosilicon compound form a mixture. In another aspect, the curable polymer composition and the fluorosilicon compound are blended together at a weight ratio of from 100/15 to 100/0.01 curable polymer composition to fluorosilicon compound. In a further aspect, the curable polymer composition and the fluorosilicon compound are blended together at a weight ratio of from 100/5 to 100/0.1 curable polymer composition to fluorosilicon compound. In yet a further aspect, the curable polymer composition and the fluorosilicon compound are blended together at a weight ratio of 100/0.5 curable polymer composition to fluorosilicon compound.

[0138] In another aspect, the weight percentage of fluorosilicon compound in the fluorosilicon-modified polymer composition is from about 10.0 to about 0.001, alternatively from about 10.0 to about 0.01, and alternatively from about 5.0 to about 0.1. In another aspect, the concentration of the fluorosilicon compound in the fluorosilicon-modified polymer composition is from about 0.1% to about 10% by weight, alternatively from about 0.1% to about 8.0% by weight, and alternatively from about 0.4% to about 5.0% by weight.

[0139] In one particular aspect, the interfacial coating 120 is prepared by applying a fluorosilicon-modified polymer composition on the polymer substrate 110, and curing the composition. The fluorosilicon-modified polymer composition can be applied on the polymer substrate 110 using conventional printing methods, such as ink jet printing, screen printing, stencil printing, flexography, lithography, gravure printing, soft lithography, xerography, imprinting (embossing), microdispensing, friction transfer printing, laser transfer printing, and thermal transfer printing. The particular method selected will depend on several factors, including the rheology of the silicone composition, the desired thickness of the coating, application temperature, and desired resolution.

[0140] The interfacial coating 120 can be cured by exposing the interfacial coating 120 to ambient temperature, elevated temperature, moisture, or radiation, depending on the type of curable silicone composition applied on the polymer substrate 110. For example, when the curable silicone composition applied on the polymer substrate 110 is a hydrosilylation-curable silicone composition, the silicon resin can be cured by heating the resin to a temperature of from room temperature (~23 ± 2 °C) to 250 °C, alternatively from room temperature to 200 °C, alternatively from room temperature to 150 °C, at atmospheric pressure. The resin is heated for a length of time sufficient to cure (cross-link) the silicone resin. For example, the resin is typically heated at a temperature of from 150 to 200 °C for a time of from 0.1 to 3 h.

[0141] In one aspect, the interfacial coating 120 is prepared by applying a fluorosilicon-modified polymer composition comprising a curable polymer composition and a fluorosilicon compound on the polymer substrate 110, and curing the composition.

[0142] When the silicone composition applied on the polymer substrate 110 is a condensation-curable silicone composition, the conditions for curing the silicone resin depend on the nature of the silicon-bonded groups in the resin. For example, when the silicone resin contains silicon-bonded hydroxy groups, the silicone resin can be cured (i.e., cross-linked) by heating. For example, the silicone resin can typically be cured by heating at a temperature of from 50 to 250 °C, for a period of from 1 to 50 h. When the condensation-curable silicone composition comprises a condensation catalyst, the silicone resin can typically be cured at a lower temperature, e.g., from room temperature (~23 ± 2 °C) to 200 °C.

[0143] When the silicone resin contains silicon-bonded hydrogen atoms, the silicone resin can be cured by exposing the film to moisture or oxygen at a temperature of from 100 to 450 °C for a period of from 0.1 to 20 h. When the condensation-curable silicone composition contains a condensation catalyst, the silicone resin can typically be cured at a lower temperature, e.g., from room temperature (~23 ± 2 °C) to 400 °C.

[0144] Further, when the silicone resin contains silicon-bonded hydrolysable groups, the silicone resin can be cured by exposing the film to moisture at a temperature of from room temperature (~23 ± 2 °C) to 250 °C, alternatively from 100 to 200 °C, for a period of from 1 to 100 h. For example, the silicone resin can typically be cured by exposing the film to a relative humidity of 30% at a temperature of from about room temperature (~23 ± 2 °C) to

150 °C, for a period of from 0.5 to 72 h. Cure can be accelerated by application of heat, exposure to high humidity, and/or addition of a condensation catalyst to the composition.

[0145] When the silicone composition applied on the first polymer substrate 110 is a radiation-curable silicone composition, the silicone resin can be cured by exposing the film to an electron beam. Typically, the accelerating voltage is from about 0.1 to 100 keV, the vacuum is from about 10 to 10-3 Pa, the electron current is from about 0.0001 to 1 ampere, and the power varies from about 0.1 watt to 1 kilowatt. The dose is typically from about 100 microcoulomb/cm^2 to 100 coulomb/cm^2, alternatively from about 1 to 10 coulombs/cm^2. Depending on the voltage, the time of exposure is typically from about 10 seconds to 1 hour.

[0146] Also, when the silicone composition further comprises a cationic or free radical photoinitiator, described above, the silicone resin can be cured by exposing the film to radiation having a wavelength of from 150 to 800 nm, alternatively from 200 to 400 nm, at a dosage sufficient to cure (cross-link) the silicone resin. The light source is typically a medium pressure mercury-arc lamp. The dose of radiation is typically from 30 to 1,000 mJ/cm^2, alternatively from 50 to 500 mJ/cm^2. Moreover, the film can be externally heated during or after exposure to radiation to enhance the rate and/or extent of cure.

[0147] When the silicone composition applied on the polymer substrate 110 is a peroxide-curable silicone composition, the silicone resin can be cured by heating the film at a temperature of from room temperature (~23 ± 2 °C) to 180 °C, for a period of from 0.05 to 1 h.

[0148] In another aspect, the coated substrate 100 comprises an inorganic barrier coating 130 on the interfacial coating 120. In one particular aspect, the inorganic barrier coating 130 can be any barrier coating comprising an inorganic material having a low permeability to water vapor (moisture). The inorganic material can be an electrical conductor, nonconductor, or semiconductor.

[0149] The inorganic barrier coating 130 may be transparent or nontransparent to light in the visible region (~400 to ~700 nm) of the electromagnetic spectrum. A transparent inorganic barrier coating 130 typically has a percent transmittance of at least 30%, alternatively at least 60%, alternatively at least 80%, for light in the visible region of the electromagnetic spectrum.

[0150] Examples of inorganic materials include, but are not limited to, metals such as aluminum, calcium, magnesium, nickel, and gold; metal alloys such as aluminum magnesium alloy, silver magnesium alloy, lithium aluminum alloy, indium magnesium alloy, and aluminum calcium alloy; oxides such as silicon dioxide, aluminum oxide, titanium(II) oxide, titanium(III) oxide, barium oxide, beryllium oxide, magnesium oxide, tin(II) oxide, tin(IV) oxide, indium(III) oxide, lead(II) oxide, lead(IV) oxide, zinc oxide, tantalum(V) oxide, yttrium(III) oxide, phosphorus pentoxide, boric oxide, zirconium(IV) oxide, and calcium oxide; mixed oxides such as indium tin oxide (ITO), indium zinc oxide (IZO), and indium cerium oxide; nitrides such as silicon nitride, titanium nitride, aluminum nitride, indium(III) nitride, and gallium nitride; mixed nitrides such as aluminum silicon nitride; oxynitrides such as silicon oxynitride, aluminum oxynitride, and boron oxynitride; carbides such as silicon carbide, aluminum carbide, boron carbide, and calcium carbide; oxycarbides such as silicon oxycarbide; mixed oxynitrides such as aluminum silicon oxynitrides and titanium silicon oxynitrides; fluorides such as magnesium fluoride and calcium fluoride; and carbide nitrides such as silicon carbide nitride.

[0151] Methods of forming inorganic barrier coatings 130 are well known in the art. For example inorganic barrier coatings 130 can be deposited using chemical vapor deposition techniques, such as thermal chemical vapor deposition, plasma enhanced chemical vapor deposition, photochemical vapor deposition, electron cyclotron resonance, inductively coupled plasma, magnetically confined plasma, and jet vapor deposition; and physical vapor deposition techniques, such as RF sputtering, atomic layer deposition, and DC magnetron sputtering.

[0152] As shown in FIG. 1, the inorganic barrier coating 130 can be a single layer coating comprising an inorganic material. Alternatively, as shown in FIG. 2, the inorganic barrier coating 130 can be a multiple layer coating comprising two 130, 140, or more layers of at least two different inorganic materials, where directly adjacent layers comprise different inorganic materials (i.e., inorganic materials have a different composition and/or property). When the layer of inorganic material in a single layer coating comprises two or more elements (e.g. TiN), the layer can be a gradient layer, where the composition of the layer changes with thickness. Similarly, when at least one layer of inorganic material in a multiple layer coating comprises two or more elements, the layer can be a gradient layer. The multiple layer coating typically comprises from 2 to 7 layers, alternatively from 2 to 5 layers, alternatively from 2 to 3 layers.

[0153] The single layer inorganic barrier coating 130 typically has a thickness of from 0.03 to 3 μm, alternatively from 0.1 to 1 μm, alternatively from 0.2 to 0.8 μm. The multiple layer inorganic barrier coating 130, 140 typically has a thickness of from 0.06 to 5 μm, alternatively from 0.1 to 3 μm, alternatively from 0.2 to 2.5 μm. When the thickness of the inorganic barrier coating 130 is less than 0.03 μm, the permeability of the coating to moisture may be too high for some applications. When the thickness of the inorganic barrier coating 130 is greater than 5 μm, the inorganic barrier coating 130 may be susceptible to cracking.

[0154] As shown in FIG. 3, in one particular aspect, the coated substrate 100 can further comprise at least two (three shown) alternating inorganic barrier 150 and interfacial 160 coatings on the inorganic barrier coating 130, wherein each alternating interfacial coating 160 comprises a cured product of a polymer composition comprising a curable polymer composition and a fluorosilicon compound. The alternating inorganic barrier 150 and alternating interfacial 160 coatings are as described above for the inorganic barrier 130 and interfacial 120 coatings of the first aspect of the coated substrate 100.

[0155] As shown in FIG. 4, in another aspect, the coated substrate 100 can further comprise an additional interfacial coating 170 on the inorganic barrier coating 130, wherein the additional interfacial coating 170 comprises a cured product of a polymer composition comprising a curable polymer composition and a fluorosilicon compound. The additional interfacial coating 170 is as described above.

[0156] In another aspect, as shown in FIG. 5, the present invention relates to an electronic package 200. In one particular aspect, the electronic package 200 comprises an electronic device 210, a coated substrate 100 overlying the device 210, and an adhesive coating 220 between and in contact with the coated substrate 100 and the device 210. As used herein, the term "overlying" refers to a position of indirect contact and/or a position of direct contact. For example, in one particular aspect wherein the electronic package 200 comprises an electronic device 210, a coated substrate 100 overlying the device 210, and an adhesive coating 220 between and in contact with the coated substrate 100, the electronic device 210 and the coated substrate 100 are in indirect contact.

[0157] In this particular aspect, the coated substrate 100 may be used as a lid and/or a cap to protect sensitive electronic devices 210 from moisture and other environmental contaminants. The coated substrate 100 is as described above, and generally comprises a polymer substrate 110, an interfacial coating 120 on the substrate 110, and an inorganic

barrier coating 130 on the interfacial coating 120, wherein the interfacial coating 120 is prepared by applying a fluorosilicon-modified polymer composition and a fluorosilicon on the polymer substrate 110 and curing the composition.

[0158] In one aspect, the electronic package 200 comprises an electronic device 210 comprising electrical contacts (not shown). In one particular aspect, the electronic device 210 can be a discrete device or an integrated circuit. The electronic device 210 has electrical contacts for receiving and transmitting electrical signals. In the case of integrated circuits, the electrical contacts or bond pads (i.e., I/O terminals) are usually located on the periphery of the device. The number of bond pads per integrated circuit can range from about 4 to about 2,000, depending on the complexity of the circuit. The bond pads are made of an electrically conductive metal, typically aluminum, copper, or alloys thereof.

[0159] Examples of discrete devices include, but are not limited to, diodes, such as PIN diodes, voltage reference diodes, varactor diodes, Avalanche diodes, DIACs, Gunn diodes, Snap diodes, IMPATT diodes, tunnel diodes, Zener diodes, normal (p-n) diodes, and Shottky diodes; transistors, such as bipolar transistors, including, insulated gate bipolar transistors (IGBTs) and Darlington transistors, and field-effect transistors (FETs), including metal oxide semiconductor FETs (MOSFETs), junction FETs (JFETs), metal-semiconductor FETs (MESFETs), organic FETs, high electron mobility transistors (HEMTs), and thin film transistors (TFTs), including organic field effect transistors; thyristors, for example, DIACs, TRIACs, silicon controlled rectifiers (SCRs), distributed buffer-gate turn-off (DB-GTO) thyristors, gate turn-off (GTO) thyristors, MOFSET controlled thyristors (MCTs), modified anode-gate turn-off (MA-GTO) thyristors, static induction thyristors (SIThs), and field controlled thyristors (FCThs); varistors; resistors; condensers; capacitors; thermistors; and optoelectronic devices, such as photodiodes, solar cells (for example CIGS solar cells and organic photovoltaic cells), phototransistors, photomultipliers, integrated optical circuit (IOC) elements, light-dependent resistors, laser diodes, light-emitting diodes (LEDs), and organic light-emitting diodes (OLEDs), including small-molecule OLEDs (SM-OLEDs) and polymer light-emitting diodes (PLEDs).

[0160] Examples of integrated circuits include, but are not limited to, monolithic integrated circuits, such as memory ICs, including RAM (random-access memory), including DRAM and SRAM, and ROM (read-only memory); logic circuits; analog integrated circuits; hybrid integrated circuits, including thin-film hybrid ICs and thick-film hybrid ICs; thin film batteries; solar cells, and fuel cells.

[0161] In another aspect, the electronic package 200 comprises a coated substrate 100 overlying the electronic device 210. In one particular aspect, the coated substrate 100 is as described and exemplified above. More particularly, the coated substrate 100 comprises a polymer substrate 110, an interfacial coating 120 on the substrate 110, wherein the interfacial coating 120 is prepared by applying a fluorosilicon-modified polymer composition comprising a curable polymer composition and a fluorosilicon compound on the polymer substrate 110, and curing the composition, and an inorganic barrier coating 130 on the interfacial coating 120.

[0162] The inorganic barrier coating 130 is on the interfacial coating 120 and the interfacial coating 120 is on the polymer substrate 110 in a region over the electronic device 210. Typically, the region over the electronic device 210 is slightly greater than the dimensions of the device 210. For example, the region over the electronic device 210 is typically from 105 to 110% greater, alternatively from 110 to 120 % greater than the dimensions of the device 210.

[0163] In another aspect, the electronic package 200 comprises an adhesive coating 220 between and in contact with the coated substrate 100 and the device 210. In one aspect, the adhesive coating 220 typically has a thickness of from 0.001 to 625, more typically from 0.1 to 375, most typically from 25 to 250 μm. The adhesive coating 220 is formed from an adhesive composition. For example, the adhesive composition may comprise a multi-functional acrylate and an initiating agent. Typically, the adhesive composition is free from organosilicon compounds, such as those in the barrier composition described above.

[0164] The multi-functional acrylate of the adhesive composition is typically selected from the group of aliphatic urethane acrylates, aromatic urethane acrylates, epoxy-functional acrylates, isobutylene acrylates, and combinations thereof. In certain aspects, the multi-functional acrylate is the aliphatic is the aliphatic urethane acrylate, such as aliphatic urethane diacrylate. When the multi-functional acrylate is typically what is referred to in the art as a "pre-polymer." Pre-polymers are typically oligomers which are formed by reacting two or more components such that the pre-polymers have excess functional groups which remain unreacted in the pre-polymers. It is to be appreciated that the multi-functional acrylate may be a monomer or may be a polymer. In addition, the multi-functional acrylate may comprise a blend of different types of multi-functional acrylates. The blend of multi-functional acrylates may comprise any combination of multi-functional acrylates which are monomeric, oligomeric, and/or polymeric. When the multi-functional acrylate is the aliphatic urethane

acrylate, the aliphatic urethane acrylate is typically formed by reacting an isocyanate and a polyol such that the aliphatic urethane acrylate formed therefrom has at least two functional groups selected from acryloxy functional groups, methacryloxy functional groups, and combinations thereof. At least one of the isocyanate and the polyol has at least one acryloxy functional group and/or methacryloxy functional groups, and combinations thereof. At least one of the isocyanate and the polyol has at least one acryloxy functional group and/or methacryloxy functional group, which remains in the aliphatic urethane acrylate formed from reacting the isocyanate and the polyol. As designated by the term "aliphatic," the aliphatic urethane acrylate is free from aromatic groups. An example of a multi-functional acrylate suitable for the purposes of the present invention is Ebecryl® 230, commercially available from Cytec Industries, Inc. of West Paterson, NJ. Another example of a multi-functional acrylate suitable for the purposes of the present invention is pentaerythritol tetraacrylate.

[0165] As set forth above, the adhesive composition further comprises an initiating agent. The initiating agent may be any initiating agent known in the art. In certain aspects, the initiating agent comprises a photoinitiating agent. Photoinitiating agents are known in the art and undergo a photoreaction upon the absorption of light, which is typically in the ultraviolet spectrum, i.e., from 300 to 400 nm. The photoreaction generally forms reactive species, which may initiate or catalyze further chemical reactions. Typically, the photoreaction initiates a polymerization or polycondensation reaction. Therefore, when the adhesive composition of the present invention includes the photoinitiating agent, the adhesive flexible barrier film may be cured by applying ultraviolet radiation to the adhesive layer formed therefrom.

[0166] As shown in FIG. 5, in one particular aspect, the electronic package 200 comprises an electronic device 210, a coated substrate 100 overlying the device 210, and an adhesive coating 220 between and in contact with the coated substrate 100 and the device 210. In this particular aspect, the coated substrate 100 overlies the device 210 such that the polymer substrate 110 is on the adhesive coating 220, the interfacial coating 120 is on the substrate 110 and the inorganic barrier coating 130 is on the interfacial coating 120.

[0167] In another aspect, as shown in FIG. 6, the electronic package 200 comprises an electronic device 210, a coated substrate 100 overlying the device 210, and an adhesive coating 220 between and in contact with the coated substrate 100 and the device 210. In this particular aspect, the coated substrate 100 overlies the device 210 such that the inorganic

barrier coating 130 is on the adhesive coating 220, the interfacial coating 120 is on the inorganic barrier coating 130, and the polymer substrate 110 is on the interfacial coating 120.

[0168] In another aspect, the electronic package 200 comprises an electronic device 210, a coated substrate 100 overlying the device 210, and an adhesive coating 220 between and in contact with the coated substrate 100. In this particular aspect, the inorganic barrier coating 130 can be a multiple layer coating comprising two 130, 140, or more layers of at least two different inorganic materials, where directly adjacent layers comprise different inorganic materials (i.e., inorganic materials have a different composition and/or property). In yet another aspect, the coated substrate 100 can further comprise at least two (three shown) alternating inorganic barrier 150 and interfacial 160 coatings on the inorganic barrier coating 130, wherein each alternating interfacial coating 160 comprises a cured product of a polymer composition comprising a curable polymer composition and a fluorosilicon compound. In yet still another aspect, the coated substrate 100 can further comprise an additional interfacial coating 170 on the inorganic barrier coating 130, wherein the additional interfacial coating 170 comprises a cured product of a polymer composition comprising a curable polymer composition and a fluorosilicon compound.

[0169] In another embodiment, a method of preparing a coated substrate 100 is provided. The method comprises forming an interfacial coating 120 on a polymer substrate 110, wherein the interfacial coating 120 is prepared by applying a fluorosilicon-modified polymer composition comprising a curable polymer composition and a fluorosilicon compound on the substrate 110, and curing the composition, and forming an inorganic barrier coating 130 on the interfacial coating 120.

[0170] The method of preparing the coated substrate 100 of the present invention can be carried out using conventional equipment and techniques, and readily available silicone compositions. For example inorganic barrier coatings 130 can be deposited using chemical vapor deposition techniques and physical vapor deposition techniques. Moreover, interfacial coatings 120 can be formed using conventional methods of applying and curing silicone compositions. Also, the methods of the present invention are scaleable to high throughput manufacturing processes.

[0171] In one aspect, the method comprises forming an interfacial coating 120 on a polymer substrate 110. The polymer substrate 110 is as described and exemplified above. In another aspect, the method comprises forming an interfacial coating 120 on a polymer

substrate 110 wherein the interfacial coating 120 is prepared by applying a fluorosilicon-modified polymer composition comprising a curable polymer composition and a fluorosilicon compound on the substrate 110, and curing the composition. The interfacial coating 120 is prepared as described and exemplified above. In another aspect, the coated substrate 100 is prepared by forming an inorganic barrier coating 130 on the interfacial coating 120. The inorganic barrier coating 130 is as described and exemplified above.

Examples

[0172] The following examples are presented to better illustrate various embodiments of the coated substrate of the present invention, but are not to be considered as limiting the invention, which is delineated in the appended claims. The following methods and materials were employed in the examples:

Example 1

[0173] *Urethane Acrylate Interfacial Coating on Ethylene Tetrafluorine Films.* Aliphatic urethane acrylate coatings mixed with fluorosilicon compounds were prepared. More particularly, an acrylate oligomer with hydroxyl functionality sold under the name CN3100, supplied by Sartomer Company (Exton, PA), was mixed with fluorosilicon compounds. The aliphatic urethane acrylate coatings were prepared by mixing CN3100 with $F_3CCF_2CF_2CF_2CH_2CH_2Si(OMe)_3$ sold under the name Dow Corning® B-3958, supplied by Dow Corning Corporation (Midland, MI), and/or $F_3CCH_2CH_2Si(OMe)_3$ sold under the name Dow Corning® Z-9030, supplied by Dow Corning Corporation (Midland, MI). A photoinitiating agent sold under the name Darocur™ CN-2022, supplied by Ciba Specialty Chemicals (Tarrytown, NY), was added. Darocur™ CN-2022 is a highly efficient liquid curing agent used to initiate radical polymerization, comprising Irgacure™ 819 and 80% Darocur™ 1173. A control sample comprising aliphatic urethane acrylate coatings without the addition of fluorosilicon compounds was also prepared. More particularly, a control sample comprising CN3100 without the addition of fluorosilicon compounds was prepared.

[0174] The formulations, i.e. Dow Corning® B-3958, Dow Corning® Z-9030, Darocur™ CN-2022, and/or CN3100, and combinations thereof, were applied to ethylene tetrafluoroethylene ("ETFE") film using a #12 Meyer ™ rod. The formulations were cured with approximately 1000 mJ/cm^2 energy. The surface energy, surface uniformity, adhesion, and wetting of the formulations were tested.

[0175] The surface energy was determined via Video Contact Angle Analysis. More specifically, the surface energy was determined by measuring the contact angle between the cured formulations applied to ETFE film and water and methylene iodide dispensed onto the cured formulations. The contact angle was determined using a VCA Optima Goniometer supplied from AST Products, Inc. (Billerica, MA). The VCA Optima Goniometer captured static or dynamic images of the droplet and determined tangent lines for the basis of the contact angle measurement. The data and images were stored in a computer. The data and images were analyzed using VCA Optima XE software for Windows™.

[0176] The surface uniformity was evaluated qualitatively. More particularly, the surface uniformity was visually determined by observing the appearance of the cured formulations applied to the ETFE film.

[0177] Adhesion was also evaluated qualitatively using a finger rub test to determine rub resistance. More particularly, adhesion was evaluated by rubbing the middle finger over the cured formulations applied to the ETFE film 10 times to build up abrasion. The visual appearance of the cured formulation was then evaluated. Specifically, the visual appearance of the cured formulations was evaluated to determine if the cured formulations peeled off of the ETFE film.

[0178] The coating wetting was also evaluated qualitatively. More particularly, the coating wetting was determined before and after curing by making visual observations regarding the appearance of the formulations applied to the ETFE film.

[0179] The results are shown in Table I below. The ETFE film has a dynamic surface energy of approximately 18.6 dynes/cm^2. For wetting to occur, the dynamic surface having a high surface energy must be covered by a liquid having a surface energy that is close to or lower than the dynamic surface.

[0180] *Results*. As shown in Table I, the addition of the fluorosilicon compounds reduced the surface energy of the cured coating by as much as 14 dynes/cm^2. Further, the fluorosilicon compound improved the surface uniformity, adhesion and coating wetting properties, such that the cured coating remained adhered to the ETFE film reducing the surface flaws in the interfacial layer coating. Additionally, the fluorosilicon compound improved the strength of the interfacial coating by increasing resistance to abrasion and peeling of the coating.

Table I

	Control	1	2	1A	7	8
CN3100 (g)	10.0	10.0	10.0	10.0	10.0	10.0
Darocur™ CN-2022 (g)	0.5	0.5	0.5	0.5	0.5	0.5
Dow Corning® B-3958 (g)		0.1	0.5	1.0		
Dow Corning® Z-9030 (g)					0.1	0.5
Surface Energy (dynes/cm^2)	35.6	37.6	21.8		31.2	28.7
Surface Uniformity	Poor, severe shrinkage	Uniform spreading, beaded up over the surface	Uniform spreading, beaded up over the surface	Excellent, slight haze	Poor, severe shrinkage	Small discontinuities
Adhesion	Very Poor, easily peeled off, severe delamination	Good adhesion, peeled with moderate pressure	Poor adhesion, peeled off with moderate pressure	Excellent	Poor adhesion, peeled off with moderate pressure	Good adhesion, peeled with moderate pressure
Coating Wetting	Poor	Uniform spreading,	Uniform spreading,	Excellent	Poor	Excellent wetting

Example 2

[0181] *Methacrylate Interfacial Coating on ETFE*. Methacrylate coatings mixed with fluoro-containing compounds were prepared. More particularly, methacrylate coatings comprising $(phenylSiO_{3/2})_{0.67}(methacrylateSiO_{3/2})_{0.33}$ sold under the name Dow Corning® WL-7154, supplied by Dow Corning Corporation (Midland, MI), mixed with Dow Corning® B-3958 or Dow Corning® Z-9030 were prepared. A control sample comprising Dow Corning® WL-7154 without the addition of Dow Corning® B-3958 and Dow Corning® Z-9030 was also prepared. The formulations, i.e. Dow Corning® B-3958, Dow Corning® Z-

9030, and/or Dow Corning® WL-7154, and combinations thereof, were applied to ETFE film using a #12 Meyer™ rod. The formulations were cured with approximately 1000 mJ/cm^2 energy. The surface energy, surface uniformity, adhesion and wetting of the formulations were tested as described previously. The results are shown in Table II below.

[0182] *Results*. As shown in Table II, the addition of the fluorosilicon compounds improved the surface uniformity, adhesion, and coating wetting properties, such that the cured coating remained adhered to the ETFE film reducing the surface flaws in the interfacial layer coating.

Table II

	Control	**3**	**4**	**2A**	**9**	**10**
Dow Corning® WL-7154 (g)	10.0	10.0	10.0	10.0	10.0	10.0
Dow Corning® B-3958 (g)		0.1	0.5	1.0		
Dow Corning® Z-9030 (g)					0.1	0.5
Surface Energy (dynes/cm^2)		24	20.2		25.4	23.5
Surface Uniformity	Poor, severe shrinkage			Clear coating, uniform	Coating delaminaltion	Coating delaminaltion
Adhesion	Very poor adhesion, easily peeled off with light finger pressure	Coating delamination, no adhesion	Coating delamination, no adhesion	Excellent	No adhesion	No adhesion
Coating Wetting	Poor			Excellent		

Example 3

[0183] *Epoxy and Methacrylate Interfacial Coating on ETFE*. Epoxy coatings and methacrylate coatings mixed with fluoro-containing compounds were prepared. More particularly, epoxy coatings comprising $(phenylSiO_{3/2})_{0.67}(epoxySiO_{3/2})_{0.33}$ sold under the name Dow Corning® PHEEP, supplied by Dow Corning Corporation (Midland, MI), and methacrylate coatings comprising propylene glycol monomethylether acetate ("PGMEA") were prepared. The Dow Corning® PHEEP and PGMEA were combined and mixed with Dow Corning® B-3958 or Dow Corning® Z-9030. A photoinitiating agent comprising a solution of 50% of triarylsulfonium hexafluoroantimonate salts in propylene carbonate, sold under the name Pfaltz & Bauer T17775, supplied by Pfaltz & Bauer (Waterbury, CT), was added. A control sample comprising Dow Corning® PHEEP and PGMEA without the addition of Dow Corning® B-3958 and Dow Corning® Z-9030 was also prepared. The formulations, i.e. Dow Corning® PHEEP, PGMEA, Dow Corning® B-3958, Dow Corning® Z-9030 and/or Dow Corning® WL-7154, and combinations thereof, were applied to ETFE film using a #12 Meyer™ rod. The formulations were cured with approximately 1000 mJ/cm^2 energy. The surface energy, surface uniformity, adhesion and wetting of the formulations were tested as described previously. The results are shown in Table III below.

[0184] *Results*. As shown in Table III, the addition of the fluorosilicon compounds improved the surface uniformity, adhesion, and coating wetting properties, such that the cured interfacial coating remained adhered to the ETFE film reducing the surface flaws in the interfacial layer coating.

Table III

	Control	**5**	**6**	**11**	**12**
Dow Corning® PHEEP (g)	10.0	10.0	10.0	10.0	10.0
PGMEA (g)	2.0	2.0	2.0	2.0	2.0
Pfaltz & Bauer T17775 catalyst (g)	0.1	0.1	0.1	0.1	0.1
Dow Corning® B-3958 (g)		0.1	0.5		

Dow Corning® Z-9030 (g)				0.1	0.5
Surface Energy (dynes/cm^2)		26.4	24.6	31.4	29.6
Surface Uniformity	Poor, severe shrinkage	Poor, but uniform	Coating spread evenly, but eventually beaded up	Excellent	Excellent surface uniformity
Adhesion	Very poor adhesion, easily peeled off with light finger pressure	Poor adhesion, easily peeled off with light finger pressure	Good adhesion, easily peeled off with light finger pressure	Poor adhesion, easily peeled off with light finger pressure	Excellent, but some signs of delamination upon aging
Coating Wetting	Poor	Good	Coating remain spread evenly, but eventually bead up	Uniform, no coating defects	Excellent surface uniformity

Example 4

[0185] *Interfacial Coating on ETFE.* Aliphatic urethane acrylate coatings, mixed with fluoro-containing compounds were prepared. More particularly, low viscosity oligomers featuring high elongation, good chemical resistance, and hydroxyl functionalities, CN3100 and methacrylate coatings, Dow Corning® WL-7154, mixed with fluoro-containing compounds were prepared. More particularly, aliphatic urethane acrylate coatings and methacrylate coatings were mixed with a fluoro-containing alkoxysilicate sold under the name Dow Corning® DC-2607, supplied by Dow Corning Corporation (Midland, MI). Control samples comprising CN3100 or Dow Corning® WL-7154 without the addition of Dow Corning® DC-2607 were also prepared. The formulations, i.e. CN3100 , Dow Corning® WL-7154, and/or Dow Corning® DC-2607 and combinations thereof, were applied to ETFE film using a #12 Meyer™ rod. The formulations were cured with approximately 1000 mJ/cm^2 energy. The surface energy, surface uniformity, adhesion and coating wetting of the formulations was tested as described previously. The results are shown in Table IV below.

[0186] *Results*. As shown in Table IV, the addition of the fluoro-containing alkoxysilicate to both the aliphatic urethane coating significantly improved the surface uniformity, adhesion, and coating wetting properties such that the cured coating to remain adhered to the ETFE film reducing the surface flaws in the interfacial coating. Additionally, the strength of the interfacial coating was improved by increasing the resistance to abrasion and peeling.

Table IV

	5	**3**	**6**	**5**
CN-3100 (g)	20	20		
Darocur™ CN-2022 (g)	1	1		
Dow Corning® WL-7154 (g)			20	20
Dow Corning® DC-2607 (g)		1		1
Surface Uniformity	Poor, severe shrinkage	Clear, uniform	Poor, severe shrinkage	Clear, uniform
Adhesion	Very poor, easily peeled off, severe delamination	Excellent	Very poor adhesion, easily peeled off with light finger pressure	Excellent
Coating Wetting	Poor	Excellent	Poor	Excellent

[0187] For the purposes of describing and defining the present invention it is noted that the terms "about" and "substantially" are utilized herein to represent the inherent degree of uncertainty that may be attributed to any quantitative comparison, value, measurement, or other representation. The terms "about" and "substantially" are also utilized herein to represent the degree by which a quantitative representation may vary from a stated reference without resulting in a change in the basic function of the subject matter at issue.

[0188] The above description and drawings are only to be considered illustrative of exemplary embodiments, which achieve the features and advantages of the present invention. Modification and substitutions the features and steps described can be made without departing from the intent and scope of the present invention. Accordingly, the invention is

not to be considered as being limited by the foregoing description and drawings, but is only limited by the scope of the appended claims.

Claims

1. A coated substrate, comprising:

a polymer substrate;

an interfacial coating on the substrate, wherein the interfacial coating is prepared by applying a fluorosilicon-modified polymer composition comprising a curable polymer composition and a fluorosilicon compound on the polymer substrate, and curing the composition; and

an inorganic barrier coating on the interfacial coating.

2. The coated substrate according to claim 1, wherein the polymer substrate is selected from a polyolefin, a chlorocarbon polymer, a fluorocarbon polymer, a polyamide, a polyimide, a polyester, an epoxy resin, a polyether, a polycarbonate, a polysulfone, and a polyether sulfone.

3. The coated substrate according to claim 1, wherein the polymer substrate is a fluorocarbon polymer.

4. The coated substrate according to claim 1, wherein the curable polymer composition is a curable silicone composition selected from a hydrosilylation-curable composition, a condensation-curable silicone composition, a radiation-curable silicone composition and a peroxide-curable silicone composition or a curable organic composition selected from a curable polyolefin composition, a curable polyamide composition, a curable epoxy resin composition, a curable amino resin composition, a curable polyurethane composition, a curable polyimide composition, a curable polyester composition, and a curable acrylic resin composition.

5. The coated substrate according to claim 1, wherein the fluorosilicon compound comprises a fluoro-containing alkoxysilane having the formula:

$$(RfQ^1)_ySi(OR^{12})_{4-y},$$

wherein Rf is a C_1 to C_8 monovalent fluorocarbon group,

Q^1 is a C_1 to C_8 divalent hydrocarbon group,

R^{12} is a C_1 to C_4 divalent hydrocarbon group, and

y is 1, 2, or 3.

6. The coated substrate according to claim 1, wherein the fluorosilicon compound comprises a fluoro-containing alkoxysilicate having the formula:

$$[SiO_{4/2}]_x[(R^{13}O)_aSiO_{(4-a)/2}]_y[(RfO)_bSiO_{(4-b)/2}]_z,$$

wherein R^{13} is a C_1 to C_4 alkyl or hydrogen,

Rf is a C_1 to C_8 monovalent fluorocarbon group,

a is from 1 to 3,

b is from 1 to 3,

x is from 2 to 500,

y is from 1 to 50, and

z is from 1 to 5.

7. The coated substrate according to claim 6, wherein the fluoro-containing alkoxysilicate comprises a copolymer prepared by reacting an organopolysiloxane resin with the fluoro-containing alkoxysilicate.

8. The coated substrate according to claim 1, wherein the fluorosilicon compound comprises a reaction product formed from the cohydrolysis and co-condensation of at least one alkoxy-functional organometallic compound, and at least one alkoxysilane with a predetermined quantity of water and a siloxane polymerization catalyst.

9. The coated substrate according to claim 1, wherein the inorganic barrier coating comprises a single layer coating of an inorganic material or multiple layer coating comprising at least two layers of at least two different inorganic materials.

10. An electronic package comprising:

an electronic device;

a coated substrate overlying the device, wherein the coated substrate comprises a polymer substrate, an interfacial coating on the substrate, wherein the interfacial coating is prepared by applying a fluorosilicon-modified polymer composition comprising a curable polymer composition and a fluorosilicon compound on the polymer substrate and curing the composition, and an inorganic barrier coating on the interfacial coating; and

an adhesive coating between and in contact with the coated substrate and the device.

11. The electronic package according to claim 10, wherein the electronic device is a discrete device selected from a diode, a transistor, a thyristor, a varistor, a resistor, a condenser, a capacitor, a thermistor, and an optoelectronic device or an integrated circuit selected from a monolithic integrated circuit, a logic circuit, an analog integrated circuit, a hybrid integrated circuit, a thin film battery, a solar cell, and a fuel cell.

12. The electronic package according to claim 10, wherein the fluorosilicon compound comprises a fluoro-containing alkoxysilane having the formula:

$$(RfQ^1)_ySi(OR^{12})_{4-y},$$

wherein Rf is a C_1 to C_8 monovalent fluorocarbon group,

Q^1 is a C_1 to C_8 divalent hydrocarbon group,

R^{12} is a C_1 to C_4 divalent hydrocarbon group, and

y is 1, 2, or 3.

13. The electronic package according to claim 10, wherein the fluorosilicon compound comprises a fluoro-containing alkoxysilicate having the formula:

$$[SiO_{4/2}]_x[(R^{13}O)_aSiO_{(4-a)/2}]_y[(RfO)_bSiO_{(4-b)/2}]_z,$$

wherein R^{13} is a C_1 to C_4 alkyl or hydrogen,

Rf is a C_1 to C_8 monovalent fluorocarbon group,

a is from 1 to 3,

b is from 1 to 3,

x is from 2 to 500,

y is from 1 to 50, and

z is from 1 to 5.

14. The electronic package according to claim 10, wherein the fluorosilicon compound comprises a reaction product formed from the cohydrolysis and co-condensation of at least one alkoxy-functional organometallic compound, and at least one alkoxysilane with a predetermined quantity of water and a siloxane polymerization catalyst.

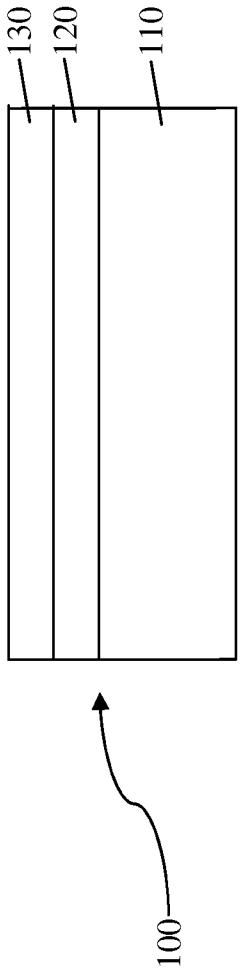

FIG. 1

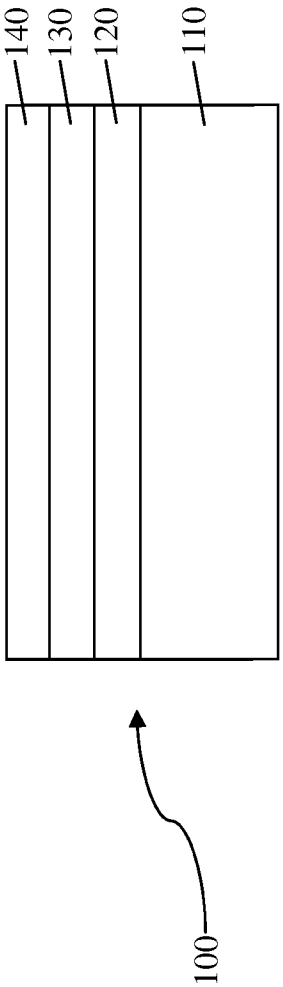

FIG. 2

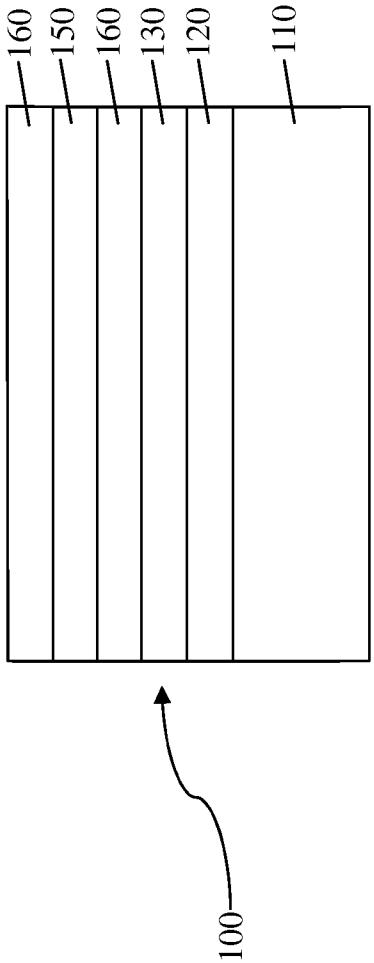

FIG. 3

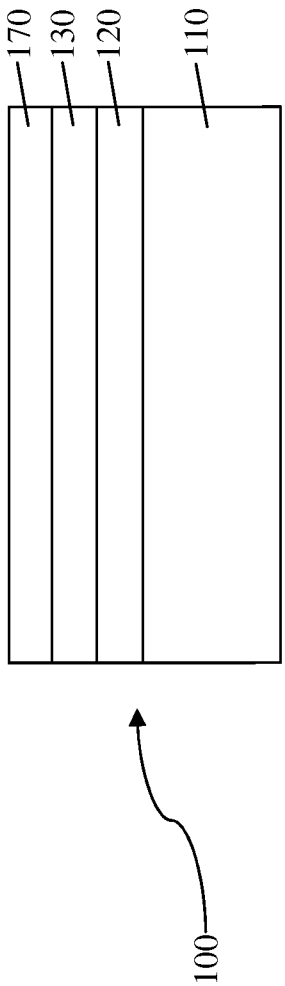

FIG. 4

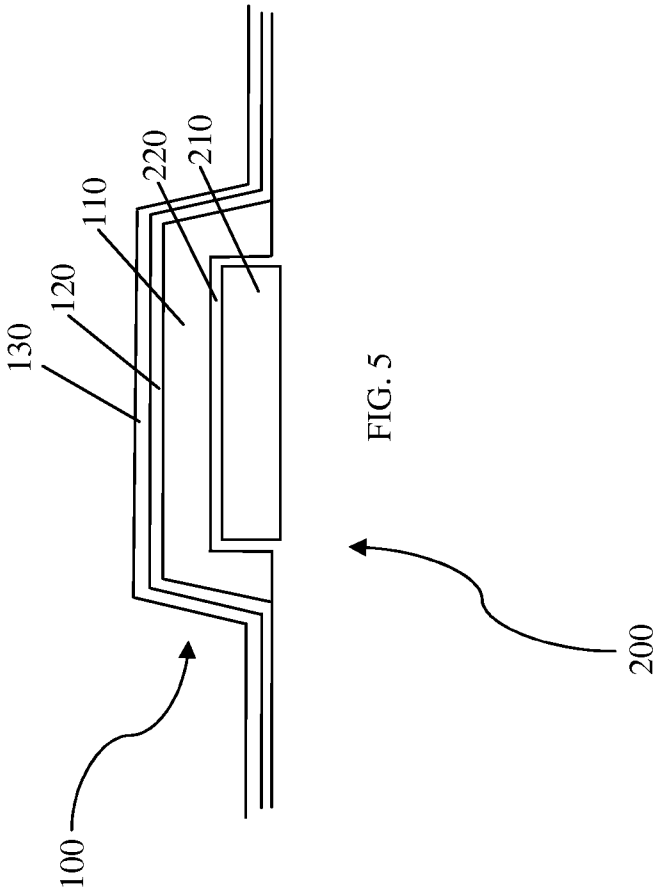

FIG. 5

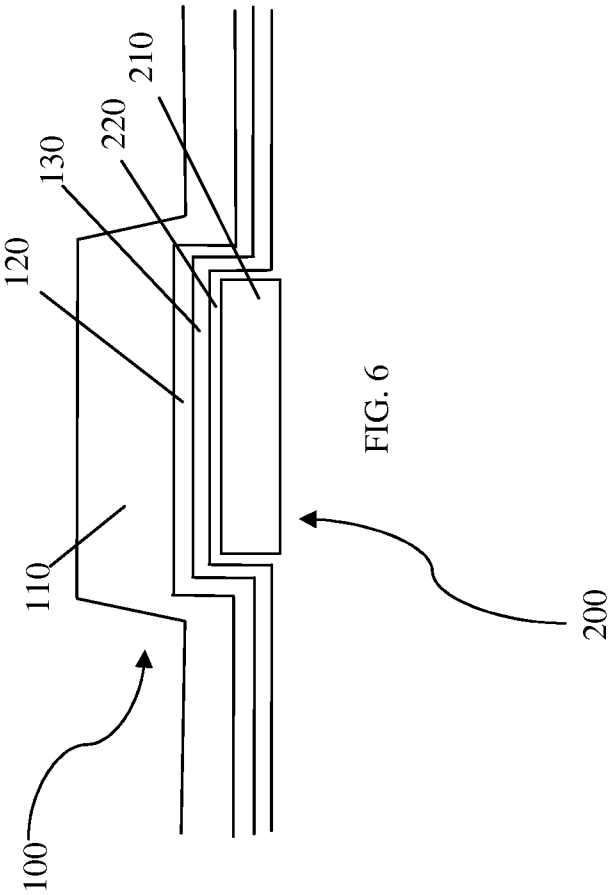

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/030557

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08J7/04
ADD.

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)
C08J

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/168545 A1 (SAWAI YUICHI [JP] ET AL) 14 November 2002 (2002-11-14) example 1	1-14
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 July 2012	20/07/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Andriollo, Giovanni

2

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/030557

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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2

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International application No
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