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(71) Applicants: **DOW CORNING CORPORATION** [US/US]; 2200 West Salzburg Road, Midland, MI 48686-0994 (US). **DOW CORNING TAIWAN INC.**; 10F, No. 246, Sec. 1, Nei Hu Road, Nei Hu District, Taipei, 11493 (TW).

(72) Inventors: **CURTIS, James**; 3615 Collingwood Ct., Midland, MI 48642 (US). **KROUPA, Laurie, Nolta**; 182 Tinley Park Circle, Delaware, OH 43015 (US). **MALCZEWSKI, Regina, Marie**; 4210 Linden Dr., Midland, MI 48640 (US). **PAN, Do-lung**; 5f, No. 58-2, Jyr-shinn 2nd Rd., Chungli, Taoyuan Hsien (TW). **PERZ, Susan**; 445 Old Orchard Dr., Essexville, MI 47832 (US). **SCHMIDT, Randall, Gene**; 813 Honeysuckle Cr., Midland, MI 48642 (US). **XU, Shengqing**; 3815 Aspen Way, Midland, MI 48642 (US).

(74) Agents: **GARETTO, Janet, M.** et al.; Nixon Peabody LLP, 300 S. Riverside Plaza, 16th Floor, Chicago, IL 60606 (US).

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(54) Title: SILVER-LOADED SILICONE PARTICLES AND THEIR SILVER-CONTAINING POLYMER COMPOSITES

(57) Abstract: Provided in various embodiments are methods of loading solid microparticles and nanoparticles of silver, including silver-based compounds, in and/or on silicone particles to modify the silicone particles. The silver-loaded microparticles and silver-loaded nanoparticles can be dispersed into a formulation of one or more polymers, polymer blends, and/or polymer composites. Once dispersed, the silver-loaded microparticles and silver-loaded nanoparticles and their silver-containing polymer composites can be used in antimicrobial and other applications.

SILVER-LOADED SILICONE PARTICLES AND THEIR SILVER-CONTAINING POLYMER COMPOSITES

FIELD OF THE INVENTION

[0001] The invention relates to methods of loading solid microparticles and nanoparticles of silver, including silver-based compounds, on silicone particles to surface modify the silicone particles. The silver-loaded microparticles and silver-loaded nanoparticles can be dispersed or loaded into one or more polymers, polymer blends, and/or polymer composites. Once dispersed or loaded, the silver-loaded microparticles and silver-loaded nanoparticles and their silver-containing polymer composites can be used in antimicrobial and other applications.

BACKGROUND OF THE INVENTION

[0002] While techniques for loading by coating of silver onto or into inorganic particles such as glass or ceramic and polymer particles such as polystyrene and melamine are known, the loading of silver into silicones (such as silicone elastomers and gels) is much more difficult due to the large differences in density between these materials and their poor miscibility. The use of silicones as silver carriers is desirable as silicones provide numerous advantages such as lower toxicity, higher biocompatibility, higher thermal stability, lower density, and higher elastomeric properties when compared to traditional silver-carriers (inorganic particles such as glass or ceramic and polymer particles such as polystyrene and melamine). The inventive methods described herein improve the dispersion of silver, including silver-based compounds, into polymers including liquid polymers, solid polymers and polymer gels, thereby decreasing the required amount of silver while providing the same level of antimicrobial behavior and other advantageous properties as would be exhibited by larger amounts of silver.

[0003] Another issue with prior techniques of loading silver into polymers is the precipitation of the silver into a liquid polymer matrix during storage. The inventive methods described herein provide a longer shelf life once the silver-loaded microparticles and silver-loaded nanoparticles are dispersed or loaded into a liquid polymer, polymer emulsion, polymer dispersion, polymer suspension or their solid(s) by curing and/or drying. This provides a commercial advantage for the resulting polymer dispersion containing the silver-loaded microparticles and silver-loaded nanoparticles as the products can remain on the shelf longer without precipitation, while still providing effective antimicrobial behavior and other advantageous properties.

[0004] Therefore, what is needed in the art are improved methods for loading solid microparticles and nanoparticles of silver and silver-based compounds onto silicone particles and dispersing or loading the silver-loaded microparticles and the silver-loaded nanoparticles into a formulation of one or more polymers, polymer blends, and/or polymer composites including liquid polymers, polymer emulsions, polymer dispersions, polymer suspensions or their solid(s). This invention answers that need.

SUMMARY OF THE INVENTION

[0005] The present disclosure relates to methods of loading solid microparticles and nanoparticles of silver on silicone particles to surface modify the silicone particles. The silver-loaded microparticles and silver-loaded nanoparticles can be dispersed or loaded into one or more polymers, polymer blends, and/or polymer composites.

[0006] A silver-containing polymer composite having stability against coagulation of silver may be formed by providing silicone particles and silver-containing particles; mixing the silicone particles with the silver-containing particles to form silver-loaded silicone particles; and dispersing the silver-loaded silicone particles into a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites to form a silver-containing polymer composite having stability against coagulation of silver. The mixing may be by wet blending or dry blending.

[0007] In another embodiment, a silver-containing polymer composite having stability against coagulation of silver may be formed by providing silicone particles, a reagent solution containing silver-containing compounds, and a reactive agent; treating the silicone particles with the reagent solution followed by the reactive agent to form modified silicone particles; isolating the modified silicone particles; treating the modified silicone particles with the reagent solution to form silver-loaded silicone particles; and dispersing the silver-loaded silicone particles into a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites to form a silver-containing polymer composite having stability against coagulation of silver.

[0008] In a still further embodiment, a silver-containing polymer composite having stability against coagulation of silver may be formed by providing silicone particles containing an excessive number of -SiH groups; mixing the silicone particles with a dispersion or an emulsion containing silver-containing particles or a solution containing silver-containing particles to form silver-loaded silicone particles; isolating the silver-loaded silicone particles; and dispersing the silver-loaded silicone particles into a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites to form a silver-containing polymer composite having stability against coagulation of silver.

[0009] In yet another embodiment, a silver-containing polymer composite having stability against coagulation of silver may be formed by providing silicone particles and silver-containing particles; depositing the silver-containing particles onto the silicone particles using physical doping conditions to form silver-loaded silicone particles; and dispersing the silver-loaded silicone particles into a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites to form a silver-containing polymer composite having stability against coagulation of silver.

[0010] In the various methods of the present disclosure, the silicone particles comprise siloxy units of ($RR^1R^2SiO_{1/2}$), ($R^1R^2SiO_{2/2}$), ($RSiO_{3/2}$), or ($SiO_{4/2}$) where R, R^1, R^2 is independently selected from a hydrogen atom and a monovalent organic group. Also in the various methods, the silver-containing particles are solid microparticles or nanoparticles of silver or silver compounds.

[0011] The silver-containing polymer composite of the present disclosure has stability against coagulation of silver solid and comprises silver-loaded silicone particles having a loading content of silver in the range of from about 0.1 to about 70 wt.% of the total amount of the silver-loaded silicone particles. The silver-loaded silicone particles are loaded in a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites in the range of from about 0.01 to about 50 wt. % of the formulation of polymers.

[0012] Additional aspects of the invention will be apparent to those of ordinary skill in the art in view of the detailed description of various embodiments, a brief description of which is provided below.

DETAILED DESCRIPTION

[0013] The invention relates to methods of loading solid microparticles and nanoparticles of silver, including silver-based compounds, onto silicone particles. The loading includes both coating the silver onto the surface of the silicone particles and burying the silver inside the silicone particles. The silicone particles are surface-modified via the methods described herein. The loading by coating can be accomplished using a variety of techniques such as dry solid blending, wet blending, electroless deposition, chemical reactions including chemical reduction, physical deposition such as physical vapor deposition, sol-gel reaction, film deposition, chemical deposition such as chemical vapor deposition. The silver-loaded microparticles and silver-loaded nanoparticles can be dispersed or loaded into polymers to form a silver silicone matrix in the form of a silver-containing polymer composite. The silver-containing polymer composite may be liquid or solid. The silver-loaded microparticles and silver-loaded nanoparticles that are dispersed or loaded into the polymers are also referred to herein as silver-loaded microparticles and silver-loaded nanoparticles. The silver-loaded microparticles or silver-loaded nanoparticles can be dispersed or loaded alone into the polymers or they can be dispersed or loaded with one or more optional antimicrobial agents into the polymers. It is contemplated that the silver-loaded microparticles and silver-loaded nanoparticles described herein may also be further treated for other functions by physical and/or chemical processes such as surface treatment, heat treatments, calcinations, light treatments, radiation, etc.

[0014] The silver-containing polymer composite containing the silver-loaded microparticles and the silver-loaded nanoparticles can be used in antimicrobial and other applications. The methods described herein provide a more uniform dispersion of the silver-loaded microparticles and silver-loaded nanoparticles and better stability against precipitation of the silver-loaded microparticles and silver-loaded nanoparticles into the silicone matrix. The methods described herein may also be used to provide additional functions such as viscosity control, synergistic microbial control and the like.

SILICONE PARTICLES

[0015] In the inventive methods described herein, silicone particles are provided. The silicone particles may be elastomeric silicone particles. The silicone particles contemplated for use in the inventive concepts described herein are silicone particles comprising siloxy units of ($RR^1R^2SiO_{1/2}$), ($R^1R^2SiO_{2/2}$), ($RSiO_{3/2}$), and/or ($SiO_{4/2}$) where R, R^1, R^2 is independently selected from hydrogen atom and a monovalent organic group including a metal-containing organic group. The silicone particles are prepared from silicones with functional groups by chemical reactions and polymerization via any process in bulk (solid, liquid, gas), solution, dispersion, or emulsion. The particle size of the silicone particles may range from about 0.1 to about 3000 microns (μm) in average diameter. In some embodiments, the silicone particles contemplated for use in the inventive concepts described herein may range from about 1 to about 500 microns (μm) in average diameter. In still further embodiments, the silicone particles contemplated for use in the inventive concepts described herein may range from about 0.5 to about 100 microns (μm) in average diameter.

[0016] The silicone particles may be hydrophobic or hydrophilic. The silicone particles may be solid particles, porous particles, hollow particles, and/or core-shell particles with silicone as the core and/or the shell.

[0017] The surface of the silicone particles contemplated for use in the inventive concepts described herein may be electrically charged (positive or negative) or non-charged/neutral. In some embodiments, it is desired that the silicone particles be positively charged.

[0018] The silicone particles may also comprise silicones reacted with other chemical compounds.

[0019] The silicone particles for use in the inventive concepts described herein facilitate the controlled delivery of a substance such as an antimicrobial. The silicone elastomeric particles are generally available as a dry powder but may also be available in an aqueous suspension.

[0020] A family of silicone elastomeric particles known as E-powders is produced by Dow Corning Toray Silicone Co., Ltd. Examples of suitable silicones that can be used herein are those described in U.S. Pat. Nos. 4,370,160, 4,742,142, 4,743,670, 5,387,624, 5,492,945, 5,945,471, 5,948,469, 5,969,039 and 7,393,582, which are hereby incorporated by reference in their entirety. These silicone elastomeric particles are prepared by various methods such as by curing liquid silicones into a wet emulsion or dispersion followed by drying, “in situ” particle formation by curing the liquid and forming into droplets, or “in situ” particle formation during liquid spraying and then curing, etc.

[0021] In U.S. Pat. No. 4,370,160, microparticles, such as microspheres and microcapsules, comprising a solid organopolysiloxane are prepared by irradiating a dispersion of discrete entities with UV light. The discrete entities are dispersed in a UV-transparent fluid continuous phase and are sphere-like particles of a UV-curable, liquid organopolysiloxane composition, or such a liquid organopolysiloxane composition containing a material to be encapsulated. In U.S. Pat. No. 4,742,142, powdered, cured silicone rubber in the form of microfine particles is prepared by emulsifying a curable liquid silicone rubber composition in a mixture of water and a surfactant at a temperature of from 0 to 25°C, dispersing the curable composition in water heated to a temperature of at least 25°C and recovering the resultant cured particles. U.S. Pat. No. 4,743,670, cured silicone rubber in the form of a finely divided powder is prepared by dispersing a heat-curable liquid silicone rubber composition in water maintained at a temperature of from 0 to 25°C, dispersing the resultant dispersion in a liquid heated to a temperature of at least 50°C, and recovering the resultant cured powder.

[0022] In U.S. Pat. No. 5,387,624, a powder mixture of cured silicone microparticles and inorganic microparticles is prepared by (i) forming a water-based suspension of a plurality of cured silicone microparticles having an average diameter of 0.1 to 200 micrometers, a plurality of inorganic microparticles having an average particle diameter of 0.1 to 200 micrometers and, optionally, at least one surfactant; and (ii) removing the water from the water-based suspension.

[0023] In U.S. Pat. No. 5,492,945, a cured silicone rubber composition is prepared by (i) preparing a water-based dispersion of a cured silicone powder having an average particle diameter of 0.1 to 200 micrometers and an amorphous silica micropowder that has an average particle diameter not exceeding 1 micrometer and a surface silanol group density of at least 2 silanol groups per 100 square angstroms; (ii) heating the water-based dispersion; and (iii) removing the water from the dispersion. The silica micropowder is immobilized on the surface of the cured silicone powder. In U.S. Pat. No. 5,945,471, a composite powder composition having excellent flowability and water repellency is disclosed, the composition comprising: (A) 100 parts by weight of a cured silicone powder that has an average particle size of 0.1 to 500 micrometers and contains 0.5 to 80 weight percent of a non-crosslinking oil; and (B) 0.1 to 100 parts by weight of a microfine inorganic powder, the inorganic powder being coated on the surface of the cured silicone powder. In U.S. Pat. No. 5,948,469, silicone rubber particulates coated with metal oxide microparticles are prepared, wherein the metal oxide microparticles are derived from a sol. The prepared silicone rubber particulates reduce aggregation of the particulate mass.

[0024] In U.S. Pat. No. 5,969,039, cured silicone powder having a uniform particle size is prepared, in which a platinum-alkenylsilozane complex catalyst is added to a water-based dispersion of a silicone composition. The silicone composition is an organopolysiloxane having at least two silicon-bonded alkenyl groups in each molecule and an organopolysiloxane having at least two silicon-bonded hydrogen atoms in each molecule. The catalyst is added and dispersed in the form of liquid particles with an average particle size in volumetric particle size distribution in water of no more than one micron. In U.S. Pat. No. 7,393,582, composite silicone rubber particles include silicone rubber particles A and silicone rubber particles B, wherein the surface of the particles A is covered with the particles B having sizes smaller than sizes of particles A.

[0025] In the inventive methods described herein, silicone particles as silver carriers are provided. The silicone preparation may be selected from any types of silicone including M, D, T, Q structure into molecular compositions which are known in the art. In some embodiments, the silicone formulation that is used in the methods described herein is a liquid silicone. The silicone formulation may contain siloxy units having the formula ($RR^1R^2SiO_{1/2}$), ($R^1R^2SiO_{2/2}$), ($RSiO_{3/2}$), and/or ($SiO_{4/2}$); R, R^1, R^2 may be independently selected from a hydrogen atom and a monovalent organic group. These units may be alternatively described as organopolysiloxane segments and are known in the art as M, D, T, and Q units, respectively. In one embodiment, the silicone compositions include “M” siloxy units. In another embodiment, the silicone compositions include “D” siloxy units. In still another embodiment, the silicone compositions include “T” siloxy units. In a further embodiment, the silicone compositions include “Q” siloxy units. In even further embodiments, the silicone compositions include “M” and “D” units, “M” and “T” units, “M” and “Q” units, “D” and “T” units, “D” and “Q” units, or “T” and “Q” units.

[0026] The organopolysiloxane units in the silicone components may further include cyclic siloxane ring containing n atoms of silicon with $n \geq 3$ (preferably, $n = 3-6$) including ($R^1R^2SiO_{n/n}$), ($RHSiO_{n/n}$), $(R^1R^2SiO)_n$, or $(RHSiO)_n$ units, or a combination thereof.

[0027] In the formulae above, the monovalent group of R, R^1, R^2 is independently a hydrocarbon or halogenated hydrocarbon group including 1 to 30 carbon atoms. Non-limiting examples include alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, undecyl, and octadecyl groups; an aliphatically unsaturated group such as an alkenyl group. Suitable alkenyl groups contain from 2 carbon to about 6 carbon atoms and may be, but not limited to, vinyl, allyl, and hexenyl; cycloalkyl groups such as cyclohexyl; aryl groups such as phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl; and halogenated hydrocarbon groups such as 3,3,3-trifluoropropyl, 3-chloropropyl, and dichlorophenyl groups. The number of siloxy units may vary. The number and type of siloxy units may affect the molecular weight of the organopolysiloxane segment, and hence the molecular weight of the composition.

[0028] The R, R^1, R^2 groups may also include, but are not limited to, acrylate functional groups such as acryloxyalkyl groups; methacrylate functional groups such as methacryloxyalkyl groups; cyanofunctional groups; monovalent hydrocarbon groups; and combinations thereof. The monovalent hydrocarbon groups may include alkyl groups such as methyl, ethyl, propyl, isopropyl, n-butyl, s-butyl, t-butyl, pentyl, neopentyl, octyl, undecyl, and octadecyl groups; cycloalkyl groups such as cyclohexyl groups; aryl groups such as phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl groups; halogenated hydrocarbon groups such as 3,3,3-trifluoropropyl, 3-chloropropyl, dichiorophenyl, and 6,6,6,5,5,4,4,3,3-nonafluorohexyl groups; and combinations thereof. The cyano-functional groups may include cyanoalkyl groups such as cyanoethyl and cyanopropyl groups, and combinations thereof.

[0029] The R, R^1, R^2 groups may also include alkyloxypoly(oxyalkyene) groups such as propyloxy(polyoxyethylene), propyloxypoly(oxypropylene) and propyloxy-poly(oxypropylene)-co-poly(oxyethylene) groups, halogen substituted alkyloxypoly(oxyalkyene) groups such as perfluoropropyloxy(polyoxyethylene), perfluoropropyloxypoly(oxypropylene) and perfluoropropyloxy-poly(oxypropylene) copoly(oxyethylene) groups, alkenyloxypoly(oxyalkyene) groups such as allyloxypoly(oxyethylene), allyloxypoly(oxypropylene) and allyloxy-poly(oxypropylene) copoly(oxyethylene) groups, alkoxy groups such as methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy and ethylhexyloxy groups, aminoalkyl groups such as 3-aminopropyl, 6-aminohexyl, 11-aminoundecyl, 3-(N-allylamino)propyl, N-(2-aminoethyl)-3-aminopropyl, N-(2-aminoethyl)-3-aminoisobutyl, *p*-aminophenyl, 2-ethylpyridine, and 3-propylpyrrole groups, hindered aminoalkyl groups such as tetramethylpiperidinyl oxypropyl groups, epoxyalkyl groups such as 3-glycidoxypropyl, 2-(3,4,-epoxycyclohexyl)ethyl, and 5,6-epoxyhexyl groups, ester functional groups such as acetoxymethyl and benzoyloxypropyl groups, hydroxyl functional groups such as hydroxy and 2-hydroxyethyl groups, isocyanate and masked isocyanate functional groups such as 3-isocyanatopropyl, tris-3-propylisocyanurate, propyl-t-butylcarbamate, and propylethylcarbamate groups, aldehyde functional groups such as undecanal and butyraldehyde groups, anhydride functional groups such as 3-propyl succinic anhydride and 3-propyl maleic anhydride groups, carbonyl and carboxy functional groups such as 3-carboxypropyl, 2-carboxyethyl, and 10-carboxydecyl groups, functional groups of carboxalkoxy, carboxamido, amidino, nitro, cyano, primary amino, secondary amino, acylamino, alkylthio, sulfoxide, sulfone, metal salts of carboxylic acids such as zinc, sodium, and potassium salts of 3-carboxypropyl and 2-carboxyethyl groups, and combinations thereof. Any metal atoms may be included into the R groups and/or the siloxane chains.

[0030] Non-limiting examples of suitable silicone particles that are commercially available include DOW CORNING® Trefil E-500, Trefil E-506C, Trefil E-506S, Trefil E-506W, Trefil

E-507, Trefil E-508, Trefil E-521, Trefil E-600, Trefil E-601, Trefil E-606, Trefil E-701, and DOW CORNING® 9506 POWDER, available from Dow Corning Corporation in Midland, Michigan.

SILVER AND SILVER COMPOUNDS

[0031] In the inventive methods described herein, silver-containing particles are provided. The silver and silver compounds suitable for use in the inventive concepts as the source of the silver-containing particles described herein include, but are not limited to, silver-containing liquids, solids of silver alloys, silver salts (such as silver citrate hydrate ($AgO_2CCH_2C(OH)(CO_2Ag)CH_2CO_2Ag \cdot xH_2O$)), silver sulfadiazine (silver[(4-aminophenyl)sulfonyl](pyrimidin-2-yl)azanide)), silver-copper alloy, silver-tin alloy, silver carbonate (Ag_2CO_3), silver benzoate ($C_6H_5CO_2Ag$), silver lactate ($CH_3CH(OH)COOAg$), silver chloride ($AgCl$), silver nitrate ($AgNO_3$), silver sulfite (Ag_2SO_3), silver sulfate (Ag_2SO_4), silver-containing inorganic compounds (such as silver-zeolite), silver-containing organic compounds (such as silver sulfadiazine, silver citrate, silver lactate and/or silver acetate), silver-doping polymers (such as synthetic polymers, natural polymers such as sugar, protein, cellulose, and their derivatives), and the dispersion(s) of these silver solids into any liquid. The silver-containing particles may be solid microparticles or nanoparticles of metallic silver. The silver-containing particles may also be solid microparticles or nanoparticles of silver and silver compounds.

[0032] The silver and silver compounds suitable for use in the inventive concepts described herein may have varied particle sizes and shapes (such as spheres and irregular shapes such as ovals, sheets, plates, fibers, needles, bars, rods, chains, dumbbells, cages, rings, dendrimers, core-shell and/or janus comprised of two or more materials, balloons, and the like).

COATING VIA DRY SOLID BLENDING PROCESS

[0033] The silver microparticles and silver-loaded nanoparticles may be loaded by coating onto the silicone(s) by a dry blending process. The silver-containing particles are dry blended such as by mechanical mixing with the silicone particles to form silver-loaded silicone particles. The mechanical mixing may be any suitable type of industrial mixer such as a paddle mixer, a V blender, a ribbon blender, a double cone blender, a high shear mixer, a drum-blender including a dental mixer, a vortex mixer, a roller mixer, or the like. The dry blending process enables the silver-containing particles to be applied, depending on the materials selected, to the surface of and/or between the silicone particles. A liquid or solid dispersion aid may be added to blend the silver-containing solid particles and the silicone particles as the carrier for more uniform dispersion of the silver-containing microparticles or silver-loaded nanoparticles in and/or on the silicone particles.

[0034] The silver microparticles and/or silver-loaded nanoparticles used in the dry blending process are desirably poorly soluble into water, aqueous solutions, or organic solvents. In some embodiments, the solubility of the silver microparticles and/or silver-loaded nanoparticles is less than about 2g/100g water/solvent.

COATING VIA WET BLENDING PROCESS

[0035] The silver microparticles and silver-loaded nanoparticles may be loaded by coating onto the silicone(s) by a wet blending process. The silver-containing particles are wet blended with the silicone particles to form silver-loaded silicone particles. The wet blending may be via any suitable type of industrial mixer including a dental mixer, a vortex mixer, a rotary mixer, a roller mixer or the like. The wet blending process enables the silver-containing particles to be applied, depending on the materials selected, to the surface of and/or between the silicone particles.

[0036] The silver-containing solid microparticles and/or silver-loaded nanoparticles used in the wet blending process are desirably a solution or a dispersion into a liquid medium such as water, aqueous solutions, or organic solvents. In some embodiments, the concentration of the silver or the silver compound is higher than about 0.01 wt.% and, in still further embodiments, higher than about 0.5 wt.%.

COATING VIA ELECTROLESS DEPOSITION PROCESS

[0037] The silver-containing solid microparticles and silver-loaded nanoparticles may be loaded by coating onto the silicone(s) by an electroless deposition process. The electroless deposition is a chemical deposition process that deposits the silver-containing particles onto the silicone particles to form silver-loaded silicone particles. The silicone particles may be pretreated by other chemical and/or physical methods before the silver deposition. The silicone particles may be pre-coated with other metal or chemicals prior to the silver deposition.

[0038] The electroless deposition may be accomplished via any suitable technique including chemical deposition, auto-catalytic deposition, or the like. For example, a reagent solution of silver-containing compounds may be used to treat the silicone particles, followed by one or more reactive agents in the presence of a catalyst or without any catalyst to form the coated layer on the particle surface to obtain the modified silicone particles. The modified silicone particles may be isolated and then treated with a silver-containing solution to form silver-loaded silicone particles.

[0039] The reagent solution may include any silver-containing compounds known in the art. Non-limiting examples of suitable silver-containing compounds include silver-containing liquids, solids of silver salts (such as silver nitrate ($AgNO_3$), silver acetate, silver citrate hydrate ($AgO_2CCH_2C(OH)(CO_2Ag)CH_2CO_2Ag \cdot xH_2O$)), silver sulfadiazine, (silver[(4-aminophenyl)sulfonyl](pyrimidin-2-yl)azanide)), silver carbonate (Ag_2CO_3), silver benzoate ($C_6H_5CO_2Ag$), silver lactate ($CH_3CH(OH)COOAg$), silver sulfite (Ag_2SO_3), silver chloride (AgCl), silver sulfate (Ag_2SO_4)), silver-containing inorganic compounds (such as silver-zeolite), silver-alloys (such as silver-copper alloy, silver-tin alloy), silver-doping polymers (including synthetic polymers, natural polymers such as sugar, protein, cellulose, and their derivatives), and silver-loading inorganic particles (such as silica, $CaCO_3$, $MgSO_4$, etc.). The reactive agent for further reaction with the silver-containing reagent solution can be any kind which may generate a layer of the silver compounds on the silicone particles, thereby forming the modified silicone particles. The reactive agent enables reactions with the silver-containing compounds in the reagent solution to form silver-containing materials on the silicone particles, thereby forming the modified silicone particles. Non-limiting examples of suitable reactive agents include any reducing agent (such as borohydride (BH_4^-), hydrazine, silicon hydride (SiH)-containing compounds), any compound containing anions of Cl^-, SO_4^{2-} which can react with Ag^+ to form insoluble products, and any ligand-providing compound which can react/coordinate with Ag^+ to form stable complexes. In some cases where the Ag^+ ions can be reduced by any physical method such as their exposure to light (visible light, ultraviolet (UV) and infrared (IR)), irradiation, and/or plasma, the reactive agent mentioned as above may be unnecessary for the silver-loading process.

[0040] The electroless deposition process enables the silver-containing particles to be applied, depending on the materials selected, to the surface of the silicone particles and/or between the silicone particles.

COATING VIA CHEMICAL DEPOSITION PROCESS BY CHEMICAL REDUCTION

[0041] The silver microparticles and silver-loaded nanoparticles may be loaded by coating onto the silicone(s) by a chemical reduction process. The chemical reduction process is a chemical deposition process that deposits the silver-containing particles onto the silicone particles to form silver-loaded silicone particles. The silicone particles may be pretreated by other chemical and/or physical methods before the silver deposition. The silicone particles may be pre-coated with other metal or chemicals prior to the silver deposition.

[0042] The chemical reduction deposition may be accomplished via any suitable reduction process by the chemistry or physics of the silver cations or silver atoms introduced by the silver compounds to these silicone particles. Silicone particles having an excessive number of silicon hydride (-SiH) groups as the reduction agent may be mixed and/or reacted with (a) a dispersion or an emulsion containing the silver-containing particles and/or (b) the silver-containing solution to form the silver-loaded silicone particles. A physical reduction process is the silver-containing particles, which were obtained by treatment of silicone particles by silver compounds by mixing and/or reaction, to be exposed on light including visible light and ultraviolet (UV) light and/or by any radiation and/or by heat to produce a layer of silver or silver compounds to form the silver-loaded silicone particles. The silver-loaded silicone particles may be isolated and then further treated.

[0043] The electroless deposition process enables the silver-containing particles to be applied, depending on the materials selected, to the surface of the silicone particles and/or between the silicone particles.

COATING VIA PHYSICAL DEPOSITION PROCESS

[0044] The silver microparticles and silver-loaded nanoparticles may be loaded by coating onto the silicone(s) by a physical deposition process such as physical vapor deposition (PVD). The physical deposition process deposits the silver-containing particles onto the silicone particles to form silver-loaded silicone particles. The silicone particles may be pretreated by other chemical and/or physical methods before the silver deposition. The silicone particles may be pre-coated with other metals or chemicals prior to the silver deposition.

[0045] The physical deposition process may be accomplished via any suitable technique including doping, sputtering, ion plating, evaporation, or the like. The physical deposition process enables the silver-containing particles to be applied, depending on the materials selected, to the surface of the silicone particles and/or between the silicone particles to form silver-loaded silicone particles.

COATING VIA ADDITIONAL MISC. PROCESSES

[0046] The silicone particles may be loaded by coating onto the silicones by further techniques including the sol-gel method, film deposition methods such as the Langmuir-Blodgett film deposition method, and chemical deposition methods such as chemical vapor deposition. With the sol-gel method, a precursor of a silver-containing compound undergoes hydrolysis and polycondensation reactions with and/or in presence of the silicone(s).

[0047] The resulting silver-loaded silicone particles may be used as pesticides, antimicrobial agents (in and/or on the antimicrobial gels, antimicrobial elastomers and antimicrobial wound care devices), electrical conductive fillers and functional additives (such as antistatic additives).

DISPERSING INTO POLYMERS, POLYMER BLENDS, AND/OR POLYMER COMPOSITE(S)

[0048] The silver-loaded microparticles and/or silver-loaded nanoparticles can be dispersed or loaded into a formulation of one or more polymers, polymer blends, and/or polymer composites. The one or more polymers, polymer blends, and/or polymer composites include liquid polymers, polymer emulsions, polymer dispersions, polymer suspensions or their solid(s). The term "polymer blend" as used herein means a polymer-polymer mixture. The term "polymer composite" as used herein means a polymer or polymer blend with filler and/or additive. The silver-loaded microparticles and silver-loaded nanoparticles that are dispersed or loaded into the polymers are also referred to herein as silver-loaded microparticles and silver-loaded nanoparticles.

[0049] The dispersing may be accomplished via any suitable technique including mixing or the like. The mixing may be by mechanical mixing of the silver-loaded microparticles and/or silver-loaded nanoparticles into the polymer, the polymer blend, and/or the polymer composite, by solution mixing of the silver-loaded microparticles and/or silver-loaded nanoparticles and then drying or curing.

[0050] The dispersion of the silver-loaded microparticles and/or silver-loaded nanoparticles (the silver-containing silicone dispersion) into the formulation of one or more polymers, polymer blends, and/or polymer composites described herein is improved by the methods described herein. It is believed that the smaller difference in density between the silver-loaded microparticles and/or silver-loaded nanoparticles and the polymers and/or the enhanced interaction between the dispersed silver-loaded microparticles and/or silver-loaded nanoparticles and the polymer matrices provides improved performance, improved dispersion, and improved stabilization for longer shelf life.

[0051] The loading content of the silver is in the range of from about 0.01 to about 99 wt.% (weight percent) of the total amount of the silver-loaded silicone particles. In alternative embodiments, the loading content of the silver is in the range of from about 0.1 to about 70 wt.% of the total amount of the silver-loaded silicone particles. In still further embodiments, the loading content of the silver is in the range of from about 0.1 to about 50 wt.% of the total amount of the silver-loaded silicone particles. Other metals and non-metals and their compounds may be loaded together with the silver and silver compounds. In other words, the silver and silver compounds may be mixtures in different chemical compositions.

[0052] The silver-loaded silicone particles are loaded in a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites in the range of from about 0.01 to about 70 wt.% of the formulation of polymers. In alternative embodiments, the silver-loaded silicone particles are loaded in a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites in the range of from about 0.01 to about 50 wt.% of the formulation of polymers. In still further embodiments, the silver-loaded silicone particles are loaded in a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites in the range of from about 0.01 to about 30 wt.% of the formulation of polymers.

[0053] The silver-loaded microparticles and silver-loaded nanoparticles can be dispersed alone into the formulation of the one or more polymers, polymer blends, and/or polymer composites. In some embodiments, the silver-loaded microparticles and silver-loaded nanoparticles can be dispersed into the formulation of the one or more polymers, polymer blends, and/or polymer composites contemplated herein with one or more optional additional ingredients. In some embodiments, the silver-loaded microparticles and silver-loaded nanoparticles can be dispersed into the formulation of the one or more polymers, polymer blends, and/or polymer composites contemplated herein with one or more optional antimicrobial agent(s) that either kill or slow the growth of microbes such as, but not limited to, antibacterial agents, antiviral agents, antifungal agents, antialgae agents and antiparisitic agents. These optional antimicrobial agents may selected from any chemical compounds and polymers such as silicones containing silanol (SiOH), silicon hydride (SiH), carbinol ($Si(CH_2)xOH$, where x = 1-18), and phenol; sulfonium compounds; phosphonium compounds; acids such as sorbic acid (vitamin C), citric acid, salicylic acid, fatty acids and derivatives, acetic acid, benzoic acid, tannic acid, gallic acid, octadecenedioic acid, hesperedin, glycyrrhizic acid, glycyrrhetinic acid, n-acyl amino acid, hydroxyproline, niacin (vitamin B_3); aldehydes such as glutaraldehyde; alcohols such as erythritol, p-cymen-5-ol, p-cymen-7-ol, benzyl alcohol, phenol, thymol(2-isopropyl-5-methylphenol); 4-amino-N-(5-methyl-3-isoxazoly) benzenesulfonamide; quaternary ammonium compounds (QACs) such as cetyl pyridinium chloride, Poly (hexamethylene biguanide) hydrochloride (PHMB); quinolone such as 8-hydroxyquinoline; carbendazim such as benzimidazole compounds, 2-benzimidazolecarbamoyl compounds; Isothiazolinone derivatives such as n-butyl-1,2-benzisothiazolin-3-one (BBIT); methylisothiazolinone (MIT), chloromethylisothiazolinone (CMIT), benzisothiazolinone (BIT), octylisothiazolinone (OIT), dichlorooctylisothiazolinone (DCOIT), 2-n-octyl-4-isothiazolin-3-one (OBIT), 4-(1-methyl-1-mesitycyclobutane-3-yl)-2-(2-hydroxy-3-methoxybenzylidenehydrazino) thiazole; hexahydro-1,3,5-tris-hydroxyethyl-s-triazine (HHT); chitosan, chitin; halogen-containing compounds such as chlorothalonil (tetrachloro-isophthalonitrile, CHTL), 2-bromo-2-nitropropane-1,3-diol (BNP), 3-lodo-2-propynl-n-butylcarbamate (IPBC); metal-containing compounds or alloys such copper (Cu), zinc (Zn) such as ZPT (zinc pyrithione), tin (Sn), gold (Au); 7-formyanil-substituted-imino-4-(4-methyl-2-butanone)-8-hydroxyquinoline-5-sulphonic acid complexes of cobalt, nickel or copper; As-containing compounds such as 10, 10'-oxybisphenoxyarsine (OBPA); sodium pyrithione (NaPT); and proteins such as lactoferrin. The silver-loaded microparticles and silver-loaded nanoparticles can be dispersed into the formulation of the one or more polymers, polymer blends, and/or polymer composites in combination with other active agents such as antioxidants, UV absorbing agents and the like.

POLYMERS, POLYMER BLENDS AND POLYMER COMPOSITES

[0054] The polymers, polymer blends, and/or polymer composites into which the silver-loaded microparticles and the silver-loaded nanoparticles may be dispersed may be selected from synthetic polymers, natural polymers, thermoplastic polymers, thermosetting polymers or their modified polymers. Nonlimiting examples of suitable polymers include silicone copolymers such as siloxane copolymer with polyamide, polycarbonate, polyurethane, polyimide, polyester, and/or polyether; vinyl polymers such as polyvinyl chloride (PVC), polystyrene (PS), polyvinyl alcohol (PVA), polyacrylonitrile, polyvinylidene chloride (PVDC), and/or polyacrylamide; polyacrylic polymers such as PMMA, poly(ethyl methacrylate) (PEMA), poly(methyl acrylate) (PMA), and/or poly(butyl acrylate) (PBA); acrylonitrile-methyl acrylate copolymer (AMA), acrylonitrile-butadiene-styrene copolymer (ABS), acrylonitrile-styrene-acrylate copolymer (ASA), styrene-acrylonitrile copolymer (SAN), and/or styrene-maleic anhydride copolymer (SMAH); polyolefins such as polyethylene, (PE), polybutene (PB) and their copolymers, and/or cyclic olefin copolymer (COC); polyamides (PA) such as nylon 6, nylon 12, nylon 66, nylon 610, and/or nylon 612; polycarbonates such as polybutylene terephthalate (PBT), polyethylene terephthalate (PET), polyethylene napthalate (PEN), polycyclohexylenedimethylene terephthalate (PCTG), and/or polycyclohexylenedimethylene ethylene terephthalate (PETG); polyimides (PI); polyethers such as polyoxymethylene (Acetal), poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(butylene oxide), and/or poly(phenyl ether) (PPE); polysulfones such as polyethersulfone (PES); polysulfides such as polyphenylenesulfide (PPS); ethylene-vinyl acetate copolymer (EVA), ethylene-vinyl alcohol copolymer (EVOH), and/or ethylene-acrylic acid copolymer (EAA); fluorinated polymers such as PTFE (polytetrafluoroethylene), FEP (fluorinated ethylene-propylene copolymer), and/or perfluoroalkoxy resin (MFA, PFA); partially fluorinated polymers such as ECTFE (ethylene-chlorotrifluoroethylene copolymer), PCTFE (polychlorotrifluoroethylene), ETFE (ethylene-tetrafluoroethylene copolymer), and PVDF (polyvinylidene fluoride), HTE (hexafluoropropylene, tetrafluoroethylene, ethylene terpolymer), tetrafluoroethylene, hexafluoropropylene, and/or vinylidene luoride terpolymer (THY); parylene including poly(*p*-xylylene); ionic polymers such as quaternary ammonium polymer and acid salt polymer; ionomers such as polymers or copolymers containing acid groups partially neutralized with metal ions such as sodium and/or zinc; liquid crystal polymers (LCP) such as polyester; styrene-butadiene block copolymers (SBS, SEBS); polybutadiene thermoplastic elastomers (TPE); biocompatible polymers such as poly(lactic acid) (PLA), poly(ε-caprolactone) (PCL), and/or polyvinylpyrrolidone (PVP).

[0055] Where the polymer(s) used herein are natural polymers, the polymer may be a natural rubber, a lignin, a polysaccharide and/or a protein. Where the polymer(s) is a polysaccharide, the polysaccharide may be a starch (including amylase and amylopectin), glycogen, a cellulosic polymer (including cellulose acetate (CA), cellulose acetate butyrate (CAB), cellulose propionate (CP), and/or ethyl cellulose), arabinoxylan, detran, glucan, pectin, chitosan, chitin, and/or alginate. Where the polymer(s) is a protein, the protein may be silk, collagen, keratin, gelatin, fibrinogen, elastin, actin, myosin, zein, gluten, and/or casein. Where the polymer(s) used herein is a thermosetting polymer, the polymer may be an epoxy resin, a cyanate resin, a bismaleimide resin, a phenolic resin, a polyester resin, a silicone elastomer, a urethane elastomer, an acrylic elastomer, a polyimide and/or combinations thereof.

[0056] Where a polymer composite is used in the methods described herein, the filler or additive may be hydrophilic or hydrophobic, polar or nonpolar, and solid and/or liquid. The filler or additive may react with the polymer components; alternatively, the fillers or additive may not react with the polymer components. The fillers or additive may be a small molecule or a polymer such as a synthetic polymer and/or a natural product and its derivatives.

[0057] The polymer(s) contemplated for use in the methods described herein may be in various forms including plastics, liquids, gels, solids, pastes, elastomers, solutions, emulsions, dispersions, suspensions, particles, membranes, films, fibers, coatings, fabrics and the like.

POST LOADING AND END USES

[0058] The polymer matrix for the silver-containing polymer composite (*i.e.,* the silver-loaded microparticles and the silver-loaded nanoparticles dispersed in the formulation of the one or more polymers, polymer blends, or polymer composites) can be further processed based on the desired end use(s). For example, the silver silicone matrix can be vulcanized into elastomers, gels, foams, plastics, etc. The methods described herein provide a more uniform dispersion of the silver-loaded microparticles and silver-loaded nanoparticles and better stability against precipitation of the silver-loaded microparticles and silver-loaded nanoparticles into the silver-containing polymer composite.

[0059] The resulting silver-containing polymer composites comprising the silver-loaded silicone particles dispersed or loaded into the polymer matrices have stability against coagulation of silver and may be used in broad applications such as water treatment, food, medicine and healthcare, packaging, coatings, electronics, textiles, construction, and agriculture articles. Illustrative examples include antimicrobial wound care devices include medical devices, wound dressings, multi-layered contact lens materials, drug eluting or delivering medical devices, and wound care materials such as adhesives, transdermal patches, films, multi-layer dressings, and tissue scaffolds. The resulting silver-containing polymer composites comprising the silver-loaded silicone particles dispersed or loaded into the polymer matrices may also be used in moisture-curable construction sealants, agricultural applications such as water conservation for agrarian and civilian distribution systems, delivery and moisture management for personal care applications, cosmetics, silicone-hydrogel hybrid wound care materials, water-swellable materials for water sealing solutions, and reservoir systems.

EXAMPLES

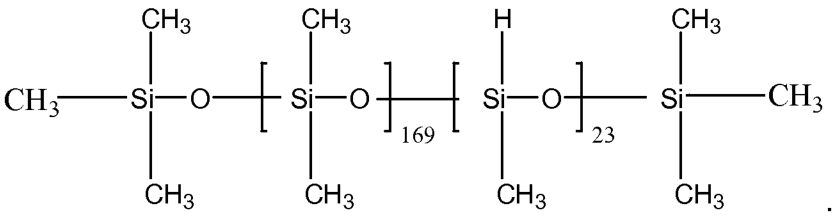
[0060] These examples are intended to illustrate the invention to one of ordinary skill in the art and should not be interpreted as limiting the scope of the invention set forth in the claims. All measurements and experiments were conducted at about 25°C, unless indicated otherwise.

[0061] As used herein,

[0062] “DOW CORNING® Trefil E-521” was obtained from Dow Corning Corporation (Midland, MI). DOW CORNING® Trefil E-521 is a biocompatible cured silicone powder.

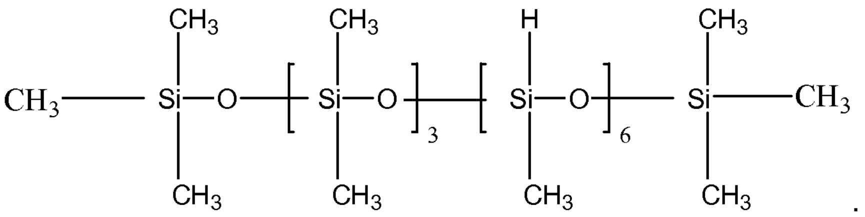
[0063] An “E-48” silicone particle sample was prepared. The E-48 sample was prepared by phase inverse emulsion polymerization as follows. 50.0 g $MD_{169}D'_{23}M$ and 4.61 g of tetra(dimethylvinylsiloxy)silane ($Si[OSi(CH_3)_2CH=CH_2]_4$) were weighed into a polypropylene cup and then ~0.05 g of Kasterdt’s catalyst with 0.51 wt.% Pt added. The mixture was spun for 10 sec. in a rotary mixer (SpeedMixer DAC 150 FVZ, Hauschild, Germany). 1.06 g ARLASOLVE® 200 (70 wt.% dispersion into water) in water was added followed by 2 g of deionized water. The cup was spun at a spinning speed of *ca.* 3540 rpm for 20 sec. The mixture was observed to have inverted into an oil/water (o/w) emulsion. The cup was spun for an additional 20 sec. at maximum speed, after which 2.5 g of additional water was added. The cup was spun for 15 sec. at a speed of *ca.* 2000 rpm. This was followed by adding an additional 6.5 g of dilution water and 15 sec. spinning at *ca.* 2000 rpm. A final addition of water was made such that the total amount of dilution water that had been added was 12 g. The cup was placed at room temperature for 60 hrs. The particles were harvested by filtration, and the resulting filter cake was washed with of water and then allowed to air dry overnight at ambient followed by an additional 2 hrs in a 50°C oven for 2 hrs.

[0064] “$MD_{169}D'_{23}M$” was obtained from Dow Corning Corporation (Midland, MI) and has the chemical formula:



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_{169}-\left[\underset{CH_3}{\overset{H}{Si}}-O\right]_{23}-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3 .$$

[0065] “$MD_3D'_6M$” was obtained from Dow Corning Corporation (Midland, MI) and has the chemical formula:



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_{3}-\left[\underset{CH_3}{\overset{H}{Si}}-O\right]_{6}-\underset{CH_3}{\overset{CH_3}{Si}}-CH_3 .$$

[0066] "SYLGARD® 184" is a two-component silicone elastomer from curing of the liquid mixture of Part A and Part B available as SYLGARD® 184 silicone elastomer kit and was obtained from Dow Corning Corporation (Midland, MI).

[0067] "DOW CORNING® MG-7-9900 SOFT SKIN ADHESIVE Part A" is an organopolysiloxane obtained from Dow Corning in Midland, Michigan.

Example 1: Silver and Silver Compounds Loaded on DOW CORNING® Trefil E-521 by Dry Solid Blending

[0068] 3.33 g of the silver and silver compounds listed below in Table A was mixed with 10.0 g of DOW CORNING® Trefil E-521 in a polypropylene cup by a rotary mixer (SpeedMixer DAC 150 FVZ) for 1 min. at a spinning speed of *ca.* 3540 rpm to load the silver/silver compounds onto the DOW CORNING® Trefil E-521. The particles obtained were characterized by SEM (scanning electron microscopy). The silver particles were observed on the surface of the DOW CORNING® Trefil E-521 particles or between the DOW CORNING® Trefil E-521 particles as noted below.

Table A

Ex. 1, Sample	Silver / Silver Compound	Silver Compound into Mixture (vol.%)	Result*
1	Silver sulfate powder (4.82 µm in mean size)	5.65	Silver dispersed on surface of and among the DOW CORNING® Trefil E-521 particles (referred to herein as 521Ag#1)
2	Silver powder (2-3.5 µm) (Aldrich, #327085, St. Louis, MO)	3.02	Silver dispersed on surface of and among the DOW CORNING® Trefil E-521 particles (referred to herein as 521Ag#2)
3	Silver citrate hydrate (Aldrich, #361259, pink powder)	7.00	Silver dispersed on surface of and among the DOW CORNING® Trefil E-521 particles (referred to herein as 521Ag#3)
4	Silver nanopowder (<100 nm, Aldrich, black powder)	3.02	Silver dispersed on surface of the DOW CORNING® Trefil E-521 particles (referred to herein as 521Ag#4)
5	Silver-copper nanopowder (97.5/2.5 alloy, 70 nm in size) (Aldrich, #576824, black powder)	5.65	Silver dispersed on surface of the DOW CORNING® Trefil E-521 particles (referred to herein as 521Ag#5)

6	Silver sulfadiazine (Aldrich, #481181, white powder)	33.3**	Silver dispersed among the DOW CORNING® Trefil E-521 particles (referred to herein as 521Ag#6)
7	Silver carbonate (Aldrich, #179647, grey powder)	5.10	Silver dispersed on surface of and among the DOW CORNING® Trefil E-521 particles (referred to herein as 521Ag#7)
8	Silver benzoate (Aldrich, #227277, white powder)	33.3**	Silver dispersed on surface of and among the DOW CORNING® Trefil E-521 particles (referred to herein as 521Ag#8)
9	Silver nitrate 10 wt.% on silica gel (Aldrich, #248762, white beads, 230 mesh in size)	6.99***	Silver dispersed on surface of and among the DOW CORNING® Trefil E-521 particles (referred to herein as 521Ag#10B)

* Observation by SEM (scanning electron microscopy)

**Weight percent (wt.%).

***10 wt.% silver nitrate on silica gel into the DOW CORNING® Trefil E-521 mixture

Example 2: Silver Sulfide Loaded on E-48 by Dry Solid Blending

[0069] 3.33g of silver sulfide (Ag_2SO_4) was mixed with 10.0 g of E-48 in a polypropylene cup by a rotary mixer (SpeedMixer DAC 150 FVZ) for 1 min. at a spinning speed of *ca*. 3540 rpm to load the silver/silver compounds onto the E-48. The particles obtained were characterized by SEM, and the presence of silver particles was confirmed. The silver particles were observed as being uniformly dispersed on the surface of the E-48 particles.

Example 3: Silver Loaded on E-48 by Wet Blending

[0070] A silver colloidal dispersion (8.0 g of silver dispersion of 30-35 wt.% nanoparticles in triethylene glycol monomethyl ether, Aldrich, #736465) was mixed with 5.2 g of E-48 in a polypropylene cup by a rotary mixer (SpeedMixer DAC 150 FVZ) for 1 min. at a spinning speed of *ca.* 3540 rpm. The resulting wet mixture was maintained overnight at room temperature. The obtained mixture was then dried at 140°C under reduced pressure followed by spinning with the rotary mixer for 1 min. at a spinning speed of *ca.* 3540 rpm. The obtained silver loaded E-48 dispersion (referred to herein as E-48Ag#2) contained 20 wt.% silver.

Example 4: Silver Nitrate Loaded on DOW CORNING® Trefil E-521 by Wet Blending

[0071] A silver nitrate ($AgNO_3$) aqueous solution (10.15 g into 12.7 g water) was mixed with 30.0 g of DOW CORNING® Trefil E-521 in a polypropylene cup by a dental mixer (SpeedMixer DAC 150 FVZ) for 1 min. at a spinning speed of *ca.* 3540 rpm. The resulting wet mixture was then dried at 140°C under reduced pressure. The resulting grey powder was then mixed into a dental mixer for 1 min. at a spinning speed of *ca.* 3540 rpm. The particles obtained (referred to herein as 521Ag#10-2) were characterized by SEM, and the presence of silver particles was confirmed.

Example 5: Silver Loaded on Polystyrene Microspheres by Wet Blending

[0072] A silver colloidal dispersion (8.0 g, silver dispersion of polystyrene particles from Aldrich, #479322, poly(styrene-co-divinylbenzene) with 1% crosslinking level, 200-400 mesh in size, 5.2 g) was mixed with the polystyrene microspheres in a polypropylene cup by a rotary mixer (SpeedMixer DAC 150 FVZ) for 1 min. at a spinning speed of *ca.* 3540 rpm. The resulting wet mixture was maintained overnight at room temperature. The obtained mixture was then dried at 140°C under reduced pressure (boiling point 198°C, 122°C/10 mmHg for methyltriglycol) followed by spinning with the rotary mixer for 1 min. at a spinning speed of *ca.* 3540 rpm. The particles obtained were characterized by SEM, and the presence of silver particles was confirmed. The obtained silver loaded polystyrene microspheres (referred to herein as PS300Ag#2) contained 20 wt.% silver.

Example 6: Silver Loaded on DOW CORNING® Trefil E-521 by Electroless Deposition

Step 1: Chemical Pretreatment of DOW CORNING® Trefil E-521 Particles

[0073] 50.0 g of DOW CORNING® Trefil E-521 was surface-modified by mixing with 25.0 g sulfuric acid (98% conc.) in 200 ml of isopropanol in a polypropylene cup by a rotary mixer (SpeedMixer DAC 150 FVZ) for 1 min. at a spinning speed of *ca.* 2000 rpm. The resulting wet mixture with was maintained overnight at room temperature. The mixture was then dispersed into 800 mL of deionized water by ultrasonic mixing and then filtered. This dispersion and filtration process was repeated three times.

Step 2: Silver Deposition

[0074] The modified DOW CORNING® Trefil E-521 sample was then surface-metallized using wet electroless plating technology. 10.0 g of the resulting particles were sensitized using 20 mL of an aqueous solution of $SnCl_2$ (0.1 M, Aldrich) for 30 min. in isopropanol (60 mL), which resulted in the adsorption of Sn^{2+} ions on the modified DOW CORNING® Trefil E-521 particle surface. After filtration, the obtained Sn^{2+} ion-sensitized DOW CORNING® Trefil E-521 particles were dipped into an aqueous solution of palladium chloride ($PdCl_2$, 5-10 wt.% Aldrich) with hydrochloric acid (30 mmol) for 10 min. at 60°C. These Pd-modified particles were rinsed repeatedly with deionized water and acetone, and filtered and then immersed in a silver electroless solution (electroless silver, Transene Company, Danvers, MA) overnight. After filtration and washing with deionized water (200 mL) three times, the resulting powder was dried at 80°C followed by spinning with the rotary mixer for 1 min. at a spinning speed of *ca.* 3540 rpm. The presence of Ag was confirmed by SEM.

Example 7: Silver Loading on Silicone Particles by Chemical Reduction

Step 1: Preparation of the Silicone Particles

[0075] 250 g of a methylhydrogen/dimethyl polysiloxane fluid ($MD_{169}D'_{23}M$) and 3.0 g ($MD_3D'_6M$) were weighed into a polypropylene cup. This was followed by 9.36 g of 1,5-hexadiene and 0.5 g of Kasterdt's catalyst with 0.51 wt.% Pt added. The mixture was spun for 10 sec. in a rotary mixer (SpeedMixer DAC 150 FVZ) at a spinning speed of *ca.* 3540 rpm. 3.15 g ARLASOLVE® 200 (70 wt.% dispersion into water, Croda USA, Edison, NJ) in water was added followed by 6.0 g of deionized water (initial water). The cup was spun for 20 sec. at a spinning speed of *ca.* 3540 rpm. The mixture was observed to have inverted into an oil/water (o/w) emulsion. The cup was spun for an additional 20 sec. at maximum speed, after which 10.0 g of dilution water was added. The cup was spun for 15 sec. at a spinning speed of *ca.* 2000 rpm. This was followed by adding an additional 15.0 g of dilution water and 15 sec. spinning at *ca.* 2000 rpm. A final addition of water was made such that the total amount of dilution water that had been added was 35 g. The cup was placed at 50°C for 2 hrs. The particles were harvested by filtration, and the resulting filter cake was washed with deionized water and then allowed to air dry overnight at ambient conditions followed by an additional 2 hrs in a 50°C oven for 2 hrs.

Step 2: Silver Deposition

[0076] 10 g of a 3 wt.% aqueous solution of $AgNO_3$ was added to the emulsion and allowed to remain undisturbed for approximately 24 hrs at room temperature. The color of the emulsion changed from milky white to a very dark black-brown. The treated silicone elastomer particles were harvested by filtration and then washed with deionized water. The particles were dried at ambient temperature overnight followed by an additional 2 hrs in a 50°C oven. The color of the particles was light brown. The presence of Ag was confirmed by X-ray fluorescence and found to be 0.3 wt.%. This product is referred to herein as E#1.

Example 8: Silver Loading on E-48 by Physical Deposition

[0077] Silver loading on solid microparticles of E-48 was realized by physical vapor deposition (PVD) using diode sputtering on a Cressington 208HR High Resolution Sputter Coater. The deposition was performed at room temperature at deposition times ranging from 0 to 130 sec., a total argon pressure of about 4 Pa, an electrode distance of 50 mm, and a current of 40 mA. The silver-target used for metal coating on the E-48 and other types of particles were purchased from Ted Pella, Inc. (Redding, CA). The E-48 sample was put in a Petri dish with a thickness smaller than 1 mm. The dish was then put inside the chamber, and kept moving during metal coating. The coating process was repeated 7 times, 10 nm/each (the thickness of the metal layer was calculated once the weight of metal deposited and the deposition area was known), and mixed the sample each time using a specula. The presence of Ag was confirmed by SEM.

Example 9: Antimicrobial Testing of Silver into Polymer Solids

[0078] 100 g of PEGDMA (polyethylene glycol dimethacrylate with a molecular weight of *ca.* 550, Aldrich), 10 g of DOW CORNING® DC193C (poly(ethylene oxide)-siloxane copolymer, colorless liquid with 260 cSt in viscosity, Dow Corning) fluid, and 1 g of peroxide were mixed into they formed a clear and colorless liquid in a polypropylene cup on a rotary mixer (SpeedMixer DAC 150 FVZ) for 30 sec. at a spinning speed of *ca*. 3540 rpm. The resulting wet mixture was de-aired. The obtained silicone liquid mixture (9.50 g) was poured into a glass dish (100 x 20 mm) and then instantly put into an oven at 150°C for 10-15 min. to be cured into a clear and colorless elastomeric film with a thickness of *ca.* 1.2 mm for antimicrobial test. The antimicrobial testing was in accordance with ASTM E2149-10 described above. A PEO-siloxane copolymer film was formed.

[0079] Other PEO-siloxane copolymer composite films containing silver-loaded E-powder were formed. 20 g of PEGDMA, 2 g of DOW CORNING® DC193C and 0.2 g of peroxide were mixed with the listed amounts of silver, silver compounds, or silver-loaded DOW CORNING® Trefil E-521 in a polypropylene cup on a rotary mixer (DAC 150 FVZ) for 30 sec. at a spinning speed of *ca*. 3540 rpm. The resulting wet mixtures were de-aired. The obtained silicone liquid mixtures (9.50 g) were poured into a glass dish (100 x 20 mm) and then instantly put into an oven at 150°C for 5-10 min. to be cured into a silicone elastomeric film as the PEO-siloxane copolymer composite film containing silver-loaded E-powder with a thickness of *ca.* 1.2 mm for antimicrobial test. The antimicrobial testing was in accordance with ASTM E2149-10. The antimicrobial test results are summarized in Table F below.

Table F

Ex. 9 Sample	**Formulation (weight)**	**Silver resource**	**Silver content (wt%)**	**ASTM 2149 log reduction**	**ZOI**
1	PEO-siloxane 100	None	0	0	none
2	PEO-siloxane 100 521Ag#1 4.0	Silver dispersed on surface of and among the DOW CORNING® Trefil E-521 particles (Ex. 1, Sample 1)	0.333	4.7	zone
3	PEO-siloxane 100 E-48Ag#2 5.0	E-48Ag#2 (Ex. 3)	0.952	4.7	zone
4	PEO-siloxane 100 E#1 10.0	E#1 (Ex. 7)	0.027	0.4	none
5	PEO-siloxane 100 521Ag#5 1.0	Silver-copper nanoparticles used in Ex. 1, Sample 5	0.960	4.8	zone

6	PEO-siloxane 100 521Ag#5 4.0	521Ag#5 (Ex. 1, Sample 5)	0.933	4.8	zone
7	PEO-siloxane 100 521Ag#7 1.0	Silver sulfadiazine used in Ex. 1, Sample 7	0.299	4.8	zone
8	PEO-siloxane 100 521Ag#7 4.0	521Ag# 7 (Ex. 1, Sample 7)	0.290	4.8	zone
9	PEO-siloxane 100 521Ag#10B 10.0	Silver nitrate 10 wt.% on silica gel (Aldrich, #248762, white beads, 230 mesh in size) (Silver used in Ex. 1, Sample 9)	0.577	4.7	zone
10	PEO-siloxane 100 521Ag#10-2 4.0	Ex. 4 (521Ag#10-2)	0.611	4.8	zone

Example 10

[0080] A TPU copolymer film was prepared from a solution of polyurethane elastomer (124.8 g ESTANE® 58238, a polyester thermoplastic polyurethane, TPU, from Noveon, Inc. OH) into tetrahydrofuran (THF, 253.9 g) with a TPU content of 32.95 wt.%. 29.0 g of this solution was poured into a glass dish (100 x 20mm) and exposed in air for 2 days at room temperature. The obtained film was dried at 70°C *in vacuo* overnight to form a transparent elastomeric film as the TPU film with a thickness of *ca.* 1.2 mm for antimicrobial test. The antimicrobial testing was in accordance with ASTM E2149-10.

[0081] Other TPU composite films containing silver-loaded E-powder were formed. 40 g of the above TPU solution was mixed with the listed amounts of silver, silver compounds, or silver-loaded DOW CORNING® Trefil E-521 in a polypropylene cup on a rotary mixer (DAC 150 FVZ) for 30 sec. at a spinning speed of *ca*. 3540 rpm. The resulting dispersions (29.0 g) were poured into a glass dish (100 x 20mm) and exposed in air for 2 days at room temperature. The obtained films were dried at 70C *in vacuo* for overnight to form an elastomeric film as the TPU composite film containing silver-loaded E-powder with a thickness of *ca.* 1.2 mm for antimicrobial test. The antimicrobial testing was in accordance with ASTM E2149-10. The antimicrobial test results are summarized in Table G below.

Table G

Ex. 10 Sample	**Formulation (weight)**	**Silver resource**	**Silver content (wt%)**	**ASTM 2149 log reduction**	**ZOI**
1	TPU 100	None	0	0.2	none

2	TPU 100 Ag#1 1.0	Silver sulfate powder (4.82 μm in mean size) (starting material of Ex. 1, Sample 1)	0.342	4.8	zone
3	TPU 100 521Ag#1 1.0	Silver dispersed on surface of and among the DOW CORNING® Trefil E-521 particles (Ex. 1, Sample 1, 521Ag#1)	0.086	4.5	zone
4	TPU 100 E-48Ag#2 5.0	Ex. 3 (E-48Ag#2)	0.952	4.5	zone
5	TPU 100 521Ag#10-2 4.0	Ex. 4 (521Ag#10-2)	0.611	4.8	zone

[0082] While the invention is susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and described in detail herein. It should be understood, however, that the invention is not intended to be limited to the particular forms disclosed. Rather, the invention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

What is claimed is:

1. A method for forming a silver-containing polymer composite having stability against coagulation of silver comprising:

providing silicone particles and silver-containing particles;

mixing the silicone particles with the silver-containing particles to form silver-loaded silicone particles; and

dispersing the silver-loaded silicone particles into a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites to form a silver-containing polymer composite having stability against coagulation of silver.

2. The method of claim 1 wherein the mixing is by wet blending or dry blending.

3. The method according to claim 1 or claim 2, wherein the silicone particles comprise siloxy units of ($RR^1R^2SiO_{1/2}$), ($R^1R^2SiO_{2/2}$), ($RSiO_{3/2}$), or ($SiO_{4/2}$) where R, R^1, R^2 is independently selected from a hydrogen atom and a monovalent organic group.

4. The method according to any of claims 1-3, wherein the silver-containing particles are solid microparticles or nanoparticles of silver or silver compounds.

5. A method for forming a silver-containing polymer composite having stability against coagulation of silver comprising:

providing silicone particles, a reagent solution containing silver-containing compounds, and a reactive agent;

treating the silicone particles with the reagent solution followed by the reactive agent to form modified silicone particles;

isolating the modified silicone particles;

treating the modified silicone particles with the reagent solution to form silver-loaded silicone particles; and

dispersing the silver-loaded silicone particles into a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites to form a silver-containing polymer composite having stability against coagulation of silver.

6. The method of claim 5, wherein the reactive agent enables reactions with the silver-containing compounds in the reagent solution to form silver-containing materials on the silicone particles.

7. The method according to claim 5 or claim 6, wherein the silicone particles comprise siloxy units of ($RR^1R^2SiO_{1/2}$), ($R^1R^2SiO_{2/2}$), ($RSiO_{3/2}$), or ($SiO_{4/2}$) where R, R^1, R^2 is independently

selected from a hydrogen atom and a monovalent organic group.

8. The method according to any of claims 5-7, wherein the silver-containing particles are solid microparticles or nanoparticles of silver or silver compounds.

9. A method for forming a silver-containing polymer composite having stability against coagulation of silver comprising:

providing silicone particles containing an excessive number of -SiH groups;

mixing the silicone particles with a dispersion or an emulsion containing silver-containing particles or a solution containing silver-containing particles to form silver-loaded silicone particles;

isolating the silver-loaded silicone particles; and

dispersing the silver-loaded silicone particles into a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites to form a silver-containing polymer composite having stability against coagulation of silver.

10. The method according to claim 9, wherein the silicone particles comprise siloxy units of $(RR^1R^2SiO_{1/2})$, $(R^1R^2SiO_{2/2})$, $(RSiO_{3/2})$, or $(SiO_{4/2})$ where R, R^1, R^2 is independently selected from a hydrogen atom and a monovalent organic group.

11. The method according to claim 9 or claim 10, wherein the silver-containing particles are solid microparticles or nanoparticles of silver or silver compounds.

12. A method for forming a silver-containing polymer composite having stability against coagulation of silver comprising:

providing silicone particles and silver-containing particles;

depositing the silver-containing particles onto the silicone particles using physical doping conditions to form silver-loaded silicone particles; and

dispersing the silver-loaded silicone particles into a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites to form a silver-containing polymer composite having stability against coagulation of silver.

13. The method according to claim 12, wherein the silicone particles comprise siloxy units of $(RR^1R^2SiO_{1/2})$, $(R^1R^2SiO_{2/2})$, $(RSiO_{3/2})$, or $(SiO_{4/2})$ where R, R^1, R^2 is independently selected from a hydrogen atom and a monovalent organic group.

14. The method according to claim 12 or claim 13, wherein the silver-containing particles are solid microparticles or nanoparticles of silver or silver compounds.

15. A silver-containing polymer composite having stability against coagulation of silver

comprising:

silver-loaded silicone particles having a loading content of silver in the range of from about 0.1 to about 70 wt.% of the total amount of the silver-loaded silicone particles, wherein the silver-loaded silicone particles are loaded in a formulation of polymers comprising one or more polymers, polymer blends, or polymer composites in the range of from about 0.01 to about 50 wt.% of the formulation of polymers.

16. The silver-containing polymer composite of claim 15, wherein the silver-loaded silicone particles have a loading content of silver in the range of from about 0.1 to about 50 wt.% of the total amount of the silver-loaded silicone particles.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/031201

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K9/08
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)
C08K

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

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

EPO-Internal, PAJ, 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	WO 2009/048169 A1 (DOW CORNING TORAY CO LTD [JP]; HARIMOTO YUKINARI [JP]) 16 April 2009 (2009-04-16)	15,16
A	claims; example 4	1-4

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 24 June 2013	Date of mailing of the international search report 14/10/2013
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Devriese, Karel

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/031201

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-4(completely); 15, 16(partially)

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-4(completely); 15, 16(partially)

   process with "providing silicone particles ...mixing the silicone particles with silver containing particles to form silver -loaded silicone particles"

   \---

2. claims: 5-8(completely); 15, 16(partially)

   process with "providing silicone particles, a reagent solution containing silver-containing compounds, and a reactive agent"

   \---

3. claims: 9-11(completely); 15, 16(partially)

   process with "providing silicone particles containing an excessive number of -SiH groups ..."

   \---

4. claims: 12-14(completely); 15, 16(partially)

   process with "depositing silver containing particles on the silicone particles using physical doping conditions to form silver-loaded silicone particles"

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/031201

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009048169 A1	16-04-2009	CN 101821339 A	01-09-2010
		JP 2009108312 A	21-05-2009
		TW 200925199 A	16-06-2009
		US 2010267885 A1	21-10-2010
		WO 2009048169 A1	16-04-2009