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(54) Title: COMPOSITION AND PRODUCT FOR PROTECTION OF LEATHER AND/OR TEXTILE ARTICLES

(57) Abstract: Composition and product for protecting external surfaces of leather and/or textile articles from multiple environmental factors, e.g., dirt and water. The composition includes (a) a solvent system including at least one linear C2-C6 alcohol solvent; (b) at least one oxide of metal or metalloid nanoparticles; and (c) an organosilicon component including one or more of a silicone oil, silicone wax, or silicone resin. Synergism exists between the nanoparticles and the organosilicon component. Together the nanoparticles and the organosilicon component provide ultimate performance, whereas when the organosilicon component is not present, loss of performance occurs. Preferably, the nanoparticles are present as a core structure with a polymeric coating. Preferably, the composition is contained in a non-aerosol storage and spray dispensing container and applied to an external surface of a finished leather and/or textile article by spraying.

COMPOSITION AND PRODUCT FOR PROTECTION OF LEATHER AND/OR TEXTILE ARTICLES

FIELD OF THE INVENTION

[0001] Composition and product for the protection of external surfaces of leather and/or textile articles from environmental factors, e.g., dirt and water.

BACKGROUND OF THE INVENTION

[0002] A composition and product including such composition is sought which is easy to use and which provides both dirt repellency and water repellency while being safer for the user and the environment than products previously commercially available.

[0003] Compositions containing silicon compounds alone can provide water repellency following application to an external surface of a leather or textile article. Such compositions, however, can also serve to attract dirt rather than repel dirt from such surface.

[0004] Products currently on the commercial market which repel both dirt and water following application to an external surface of a leather or textile article contain perfluorinated chemicals (PFCs) which are not environmentally desirable and which are bio-accumulative in living organisms, including the human body.

[0005] Accordingly, a need is present for an all-in-one or single protector composition and product which provides both water repellency and dirt repellency without using PFCs and which is safer for the user and environment. The

same composition and product provide a further advantage of making cleaning of a treated article easier. Protection of leather and/or textile articles, such as shoes; accessories such as purses and briefcases; and baggage such as totes or luggage, are examples of articles made of finished leather and/or textile material(s) which consumers like to continually look good and to give good product performance by extending the life of the product through simple maintenance of the external surface of the product material.

SUMMARY OF THE INVENTION

[0006] The invention involves a composition for protecting external surfaces of leather and/or textile articles from multiple environmental factors, such as water and dirt. Articles to be protected are described herein as "leather and/or textile" articles since protection may be provided to articles made from all leather, all textile, or a combination of leather and textile. "Leather" is understood to encompass natural or genuine leather or synthetic leather. "Articles" are finished products made of leather and/or textile materials which have been manufactured and made into a desired consumer item, for example, shoes; accessories such as purses, briefcases or other personal articles; baggage such as totes and luggage; and the like.

[0007] The composition is preferably applied to an external surface of a leather and/or textile article by a spray delivery system. After application and drying, protection of the leather and/or textile article is

provided in the form of both water repellency and dirt repellency. A non-aerosol spray delivery system is preferred, for example, a pump spray container system.

[0008] The composition for providing both water repellency and dirt repellency to an external surface of a leather and/or textile article includes (a) a solvent system comprising at least one linear C2-C6 alcohol solvent, optionally at least one aliphatic C6-C16 alkane, and optionally at least one ester solvent; (b) at least one oxide of metal or metalloid nanoparticles, the nanoparticles having a size in a range of about 10 to about 1000 nanometers (nm); and (c) an organosilicon component comprising one or more of a silicone oil, silicone wax, or silicone resin. The composition is substantially free of water. Additionally, the composition is substantially free or free of fluorine-containing compounds. "Substantially free" is understood to mean that the named compound is not itself present as an independent component in the composition and may only be present in a minor or trace amount of the named compound in relation to another compound present in the composition so that the named compound is not an active and does not interfere with the active compounds/components of the composition.

[0009] A key to the composition achieving the desired results of both water repellency and dirt repellency is the synergism present between the nanoparticles and the organosilicon component.

[0010] The nanoparticles of the composition are composed of at least one oxide of metal or metalloid nanoparticles, wherein the nanoparticles have a size in a range of about

10 to about 1000 nm. The oxide of metal or metalloid provide the core of the nanoparticles. Preferably, the core has a coating on the exterior surface thereof. The coating is preferably a polymeric coating.

[0011] The polymer coating provides a thin layer of polymer chains bonded chemically to the core or particle surface. One mechanism responsible for the desired repellency results from the chemical nature of the coating, i.e., the polymer utilized will include end groups that are present on the surface of the core. These end groups provide low energy at the surface while the backbone of the coating polymer enables intra-molecular rotation to make the exposure of the end groups to the surface. Water and dirt coming to the surface are unfavorable from an energetic point of view and, thus, the likelihood of the water and dirt sticking to the surface of the treated material or article is minimal resulting in repellency of the water and the dirt. Further, due to the size of the nanoparticles, the nanoparticles deposited on a surface of the material or article following application of the composition will make the surface “nano-rough” which physically limits the surface area available for contact between the protected surface and the water and/or dirt. Due to this limited contact surface, any interaction leading to adhesion of water and/or dirt to the surface of the article is further limited.

[0012] The organosilicon component, which can be one or more silicones having a linear, branched or cage-like structure, has a structure characterized by including a different ability to penetrate within the matrix of the

protected material (i.e., the fibrils of the leather or textile), different molecular mobility, film-forming properties, and abrasion resistance. In general, silicones suitable for use in the inventive composition have high molecular mobility which, in combination with non-polar functional groups result in their ability for taking a low-surface energy configuration and hydrophobic nature at the surface. Additionally, the silicones embed nanoparticles and hold the nanoparticles at the surface to be protected. This prevents the nanoparticles from being susceptible to rubbing off.

[0013] The solvent system includes non-polar hydrocarbon molecules which favorably interact with the silicone chains of the silicon component in terms of energetic efficiency which causes the silicones to dissolve, i.e., disperse on a molecular level. The silicones, therefore, do not sediment or aggregate in the composition. This avoids the need to shake the composition prior to use. The alcohol of the solvent system increases the evaporation rate of the solvent system from the treated surface thereby reducing the chance of damage to the surface by the solvent. This feature also allows the solvent system to act as a carrier for the silicon component and nanoparticles which improves their spreadability upon application to an article. Further, the favorable energetic interaction between the solvent system and the nanoparticles allow the nanoparticles to stay in a dispersed state and limits the formation of macroscopic aggregates which insures surface roughness on a microscopic scale.

[0014] A single composition is provided for a simple treatment of finished leather and/or textile article of both dirt (including wet and dry dirt) repellency and water repellency. Compositions containing silicone(s) alone do not provide dirt repellency, especially not dry dirt repellency. Compositions currently on the commercial market which provide both water repellency and dirt repellency contain PFCs, which are not desirable in relation to the environment or living organisms, including the human body. The composition of the invention, to the contrary, provides an all-in-one composition for repellency of both water and dirt which can be readily applied in spray form. Further, due to the very weak interactions between the treated article surface and environmental factors (e.g., both wet and dry dirt) as described above, the composition makes it easier to remove any minute amount of dirt that was deposited on the surface, e.g., due to the force of gravity or friction. Cleaning can be achieved by a gentle wiping off with a soft cloth and/or by pouring clean water over the contaminated surface.

DETAILED DESCRIPTION OF THE INVENTION

[0015] A composition, and product including the composition, for treating a leather and/or textile article to provide both water repellency and dirt repellency to an external surface thereof is described. The dirt repellency provided is of both wet dirt and dry dirt. The composition is suitable for spray dispensing, preferably by a non-aerosol dispensing system. The composition and manner of dispensing are both safer for the environment and living

organisms, including the human body, over prior available commercial products.

[0016] The composition includes (a) a solvent system comprising at least one linear C2-C6 alcohol solvent, optionally at least one aliphatic C6-C16 alkane, and optionally at least one ester solvent; (b) at least one oxide of metal or metalloid nanoparticles, said nanoparticles having a size in a range of about 10 to about 1000 nanometers (nm); (c) an organosilicon component comprising one or more of a silicone oil, silicone wax, or silicone resin. Preferably, the composition is substantially free of water. Further, the composition is substantially free or free of fluorine-containing compounds.

[0017] Synergism occurs due to the inclusion of both the nanoparticles and the organosilicon component. This combination provides for both water repellency and dirt repellency (both wet dirt and dry dirt) without the need for inclusion of PFCs which are undesirable for the environment and are bio-accumulative in living organisms, including the human body. The components of the composition are described in more detail below. It is noted that weight percent (wt.%) as set forth in the description and claims is in relation to the total composition being based on 100 wt.%. The ingredient wt.% given, unless otherwise noted, is based on the wt.% of the overall ingredient (i.e., active(s), carrier and/or impurities).

[0018] The nanoparticles include a core which is composed of at least one oxide of metal or metalloid of the

d-block and the p-block, respectively, of the Periodic Table of Elements. The metalloids of the p-block are boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), tellurium (Te), and astatine (At). The metals of the d-block are the transition metals of scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), colbalt (Co), nickel (Ni), copper (Cu), zinc (Zn), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), technetium (Tc), ruthenium (Ru), rhodium (Rh), palladium (Pd), silver (Ag), cadium (Cd), hafnium (Hf), tantalum (Ta), tungsten (W), rhenium (Re), osmium (Os), iridium (Ir), platinum (Pt), gold (Au), mercury (Hg), rutherfordium (Rf), dubnium (Db), seaborgium (Sg), bohrium (Bh), and hassium (Hs). The preferred metals and metalloids are those having an atomic number not greater than 30, i.e., B, Si, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn. The most preferred core is composed of at least one oxide of Si, Ti or Zn.

[0019] The preferred shape of the nanoparticles is spheroidal or spherical. A spherical or spheroidal shape promotes an even distribution of particle surface energy, which helps avoid aggregates in the finished composition. When deposited on a surface during treatment of an article, a nanoparticle having a spherical or spheroidal shape will allow for less possible contact surface area between the treated article and environmental factors, as compared to, for instance, rod-shaped nanoparticles. The diameter of the nanoparticles is in the range of from about 10 to about 1000 nanometers (nm), preferably about 20 nm to about 500 nm.

[0020] To obtain optimum performance, the core of the nanoparticles preferably has a coating on the exterior surface thereof. The thickness of the coating is generally a property of the coating process used to make the nanoparticles and can vary without being detrimental to the object of the invention. The thickness of the coating is not critical to the functionality of the coating. The thickness, however, should not be so great as to interfere with the overall size of the nanoparticles. The nanoparticles, with or without a coating, have a diameter of up to about 1000 nm. The coating is composed of at least one organic compound that is covalently grafted onto the exterior surface of the core. These coating compounds serve to lower the surface energy of the nanoparticle.

[0021] A preferred coating for the core useful is polymeric and is based on silicon chemistry, for example, polyhedral oligomeric silsesquioxanes (POSS) or polysiloxanes, and derivatives thereof. More preferably, the coating is composed of linear or cross-linked polysiloxanes bearing end-groups that are presented on the surface. Examples of polymers suitable for providing the polymeric coating include the polymers of (3-glycidyloxypropyl)trimethoxysilane, the polymers of 3-(trimethoxysilyl)propyl methacrylate, the polymers of 3-aminopropyl triethoxysilane, and the derivatives thereof which bear pendant alkane groups.

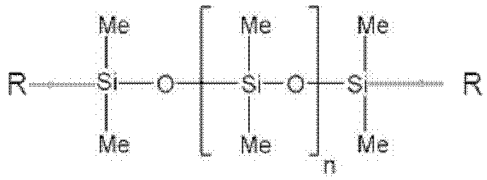
[0022] While a polymer coating could be provided having a backbone of polysiloxane or paraffin with perfluorinated end-groups, the perfluorinated compounds are undesirable from an environmental perspective.

[0023] The nanoparticles are present in an amount in a range of about 0.1 to about 4 wt.%, preferably in an amount of about 0.1 to about 3 wt.%, more preferably in an amount of about 0.2 to about 3 wt.%, and yet more preferably about 0.45 to about 2.5 wt.%.

[0024] The organosilicon component is composed of one or more of a silicone oil, silicone wax or silicone resin. Mixtures including silicone wax are preferred.

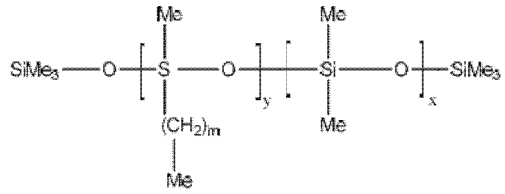
[0025] The organosilicon component is present in an amount greater than 0 to about 8 wt.%, more preferably in an amount of about 1 to about 6 wt.%, more preferably about 1 to about 5 wt.%, more preferably about 1.8 to about 5 wt.%, and yet more preferably about 1.8 to about 4.4 wt.%. Examples of silicones suitable for use in the organosilicon component are set forth below.

[0026] Silicone oils suitable for use preferably are selected from dimethicone having the structure -



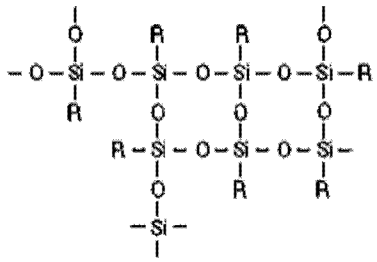
wherein 0<n<300 (preferably 5<n<150), R is methyl. The viscosity of the silicone oil is in a range of about 10 to about 500 centistokes (Cst) and mixtures thereof and preferably about 100 to about 350 Cst.

Silicone waxes suitable for use are selected from alkyl methicone (x=0) or alkyl dimethicone, and mixtures thereof, of the following structure -



wherein $1<m\leq 29$, $x+y<100$, $0\leq x<100$, $0<y<100$; preferably $17<m\leq 29$.

[0027] Silicone resins suitable for use have a structure as follows –



wherein R=C1 to C6 alkyl, phenyl and mixtures thereof; preferably methyl, i.e., trimethylsiloxysilicate.

[0028] The nanoparticles and organosilicon component in combination provide for the ultimate performance of both water repellency and dirt repellency as to external surfaces of leather and/or textile articles following treatment of the article with the composition. Treatment includes simple application of the composition to a desired surface and allowing the composition to dry.

[0029] The organosilicon component, depending on the compound(s) selected to compose the component, can be linear, branched or cage-like in molecular structure. Any of these structures is characterized by the different ability to penetrate within the matrix of protected material (i.e., fibrils of leather or textile), different

molecular mobility, film-forming properties, abrasion resistance, and the like. In general, the silicones suitable for use in providing the organosilicon component have high molecular mobility which in combination with non-polar functional groups result in their ability to take low surface energy configurations and provide a hydrophobic nature to the treated surface. Further, the silicones embed the nanoparticles and hold the nanoparticles at the protected surface so that the nanoparticles are not susceptible to rubbing off.

[0030] The nanoparticles improve the water repellency of the silicones and provide for dirt repellency. This is achieved by two mechanisms based on the nanoparticles core being coated with a thin layer of polymer chains bound chemically to the particle surface.

[0031] One mechanism for providing repellency is from the chemical nature of the coating. The end-groups of the compound making up the coating, as referred to above, provide low energy to the surface while the backbone of the coating polymer enables intra-molecular rotation to make the exposure of these groups to the surface possible. The inter-molecular interaction between the surface groups of the coating and the incoming water and dirt are unfavorable from an energetic point of view and, thus, the likelihood of water and dirt sticking to the treated surface is minimal.

[0032] Another mechanism relies on the size of the nanoparticles. The deposited nanoparticles are capable of making the surface “nano-rough” which in turn physically limits the surface area available for contact between the

protected material and the water and/or dirt. With limited contact surface being available, any interaction leading to adhesion is further limited.

[0033] The solvent system includes about 1 to about 97.5 wt.%, preferably about 1 to about 92 wt.% of an alcohol solvent, preferably about 20 to about 90 wt.%, more preferably about 20 to about 60 wt.%, and yet more preferably about 22.5 to about 50 wt.%. The alcohol solvent is a linear C2-C6 alcohol or mixtures thereof.

[0034] The solvent system can optionally include a hydrocarbon solvent. The hydrocarbon solvent is an aliphatic C6-C16 alkane or mixtures thereof, and preferably an aliphatic C6-C12 alkane or mixtures thereof. Impurities, such as aromatics, cyclics and other alkanes can be present in a total amount of less than about 5 wt.% of the hydrocarbon solvent. The hydrocarbon solvent is present in a range of 0 to about 98.5 wt.%, preferably 0 to about 70 wt.%, more preferably 0 to about 65 wt.%, and yet more preferably about 40 to about 70 wt.%.

[0035] The solvent system may further optionally include an ester solvent. The ester solvent is preferably of the formula R_1COOR_2 wherein R_1 is C1-C4 alkyl, preferably a methyl group, and R_2 is a C2-C4 alkyl, preferably n-butyl. The main function of the ester solvent is to moderate or decrease the solvent smell. The ester solvent does not impact the performance of the overall composition as to water repellency and dirt repellency. The ester solvent is present in a range of 0 to about 10 wt.%, preferably 0 to about 8 wt.%, more preferably about 0 to about 6.5 wt.%, and yet more preferably about 4 to about 6.5 wt.%.

[0036] The solvent system preferably includes the alcohol solvent and a hydrocarbon solvent, more preferably where the hydrocarbon solvent is composed of two grades of hydrocarbons. The non-polar hydrocarbon molecules have favorable interactions with silicone chains in terms of energetic efficiency which causes the silicones to dissolve, i.e., to disperse on a molecular level. The silicones will, therefore, not sediment or aggregate in the composition which in turn allows the composition to be dispensed without shaking the dispensing container holding the composition prior to use. The alcohol solvent serves to increase the evaporation rate of the solvent system and makes the solvents evaporate faster from a treated leather and/or textile surface, thereby reducing possible damage to the treated surface.

[0037] The solvent system, while the composition is freshly applied to a surface and still in a liquid state, allows the silicone molecules to move freely and adhere to the surface by the mechanism described above as to the silicone component. Thus, the solvent system acts also as a carrier for the silicones and nanoparticles and improves their spreadability.

[0038] An optional additive to the composition is one or more fragrance. The fragrance(s) can be present in an amount of about 0.5 to about 2 wt.%.

[0039] The leather and/or textile treatment composition as described is preferably applied in use to a desired surface by a storage and dispensing container including a body for holding or storing the composition, and a spray delivery mechanism for dispensing the composition from the

body onto an exterior surface of a leather and/or textile article. The spray mechanism can be as conventionally known in the art of non-aerosol and aerosol dispensers. Preferred dispensers include a spray mechanism which is a non-aerosol spray mechanism, more preferably a pump mechanism. Alternatively, an aerosol dispenser may be used which requires a propellant, which can be, for example, a compressed gas, or hydrocarbon and mixtures thereof. While the composition may be applied to a suitable applicator material, such as a sponge or cloth for example, a non-aerosol or aerosol spray is simpler and allows for application in a one step process with the user not having to physically contact the composition. With a spray container, the composition is easy and quick to use, i.e., spray, allow the composition to dry and the composition is ready to act as a repellent to both water and dirt (both wet and dry dirt) and thereby protect the treated surface.

[0040] Examples of composition formulas of the invention are set forth below. Certain of these compositions were used in the testing described below to show the efficacy of the compositions.

[0041] EXAMPLES

INGREDIENTS	WEIGHT %						
Example Number	1	2	3	4	5	6	7
WACKER Release Agent TPR (Reaction product of Silicone Resin with Silicone Fluids)	3.8	0	2.55	0	0	1.8	0
WACKER 23 Silicone Wax (Polymethylsiloxane)	0.6	3.5	0	1.8	3	0	2.55
Nanoparticles	2.5	2.5	0.45	1.2	2	1.2	0.45
Ethanol	22.5	22.5	0	0	0	0	0
Isopropanol	0	0	26.57	26.57	26.57	26.57	26.57
EXXSOL D 80/110 (Dearomatized hydrocarbons)	29.1	30	0	0	0	0	0
EXXSOL D145/160 (Dearomatized hydrocarbons)	35	35	0	0	0	0	0
Heptane	0	0	70.43	70.43	68.43	70.43	70.43
Butyl Acetate	6.5	6.5	0	0	0	0	0
Total	100	100	100	100	100	100	100

INGREDIENTS	WEIGHT %						
Example Number	8	9	10	11	12	13	14
WACKER Release Agent TPR (Reaction product of Silicone Resin with Silicone Fluids)	4.25	3	0	4	0	3.8	1
WACKER 23 Silicone Wax (Polymethylsiloxane)	0	0	4.25	3	2	0.6	2
Nanoparticles	0.75	2	0.75	0.5	2	1	3
Ethanol	0	0	0	10	20	25	0
Isopropanol	26.57	26.57	26.57	20	30	0	30
EXXSOL D 80/110 (Dearomatized hydrocarbons)	0	0	0	0	0	0	25
EXXSOL D145/160 (Dearomatized hydrocarbons)	0	0	0	57.5	0	0	30
Heptane	68.43	68.43	68.43	0	46	64	0
Butyl Acetate	0	0	0	5	0	5.6	9
Total	100	100	100	100	100	100	100

INGREDIENTS	WEIGHT %				
Example Number	15	16	17	18	19
WACKER Release Agent TPR (Reaction product of Silicone Resin with Silicone Fluids)	2.5	5	0.8	1	5.5
WACKER 23 Silicone Wax (Polymethylsiloxane)	0.4	0	0.2	1	0.5
Nanoparticles	0.5	4	4	0.2	0.1
Ethanol	20	0	0	20	0
Isopropanol	20	30	80	40	30
EXXSOL D 80/110 (Dearomatized hydrocarbons)	24.3	0	0	0	0
EXXSOL D145/160 (Dearomatized hydrocarbons)	24.3	0	12	0	30
Heptane	0	56	0	37.8	30
Butyl Acetate	8	5	3	0	3.9
Total	100	100	100	100	100

[0042] Examples 1-16 are each non-aerosol spray compositions. The core of the nanoparticles is silicon oxide. The nanoparticles are coated with a polymeric

coating of an aminosilicone polymer. The nanoparticles had a diameter in the range of about 20 to about 800 nm.

[0043] In determining water repellency and dirt repellency as provided by the composition of the invention, the following standards were used.

[0044] Water repellency is based on the AATCC (American Association of Textile Chemists and Colorists) Test Method 22-2005 entitled "Water Repellency: Spray Test" at pages 67-69 of the AATCC Technical Manual, vol. 85, 2010 (which is incorporated herein by reference). Water repellency herein, based on AATCC Test Method 22-2005, provides for a spray test rating of ≥ 50 after 10 rain cycles. The same test method is used herein for both leather and textiles. The test method is applicable to any composition or product claiming to provide water repellency or water proofing. The method measures the resistance of the treated material to wetting by water.

[0045] Wet dirt repellency is determined by (1) preparing a coffee stain by combining coffee and water in a ratio of 1:8 of coffee:water, (2) rinsing a surface treated with a composition to be water repellent with 250 ml of the coffee stain for a period of 5 minutes using a spray tester as described in AATCC Test Method 22-2005, (3) rinsing the treated surface with 250 ml water using the spray tester, and (4) providing a visual score after drying using the standard spray test ratings of AATCC Test Method 22-2005.

[0046] Dry dirt repellency was determined by (1) preparing dry dirt soil by combining Kaolin:Carbon Black in a ratio of 95:5, respectively, and mixing until uniform, (2) weighing the substrate treated to be dirt repellent,

(3) putting 100 ml of the soil in a 500 ml beaker followed by pouring and strewing the soil on the treated substrate to make the soil cover the whole surface, (4) slightly knock off the soil, (5) re-weigh the treated substrate to get the dry dirt gain weight, and (6) make visual assessment of the presence of dry dirt. The treated substrate is considered dirt repellent when the amount of dry dirt adhered to the surface is less than to a non-treated substrate, as evaluated visually and by the weight of the adhered dirt.

[0047] Results for the Water Repellency Test, Wet Dirt (coffee stain) Test and Dry Dirt (soil based on Kaolin and carbon black) Repellency Test for Example Nos. 1-10 above are set forth below.

[0048] Water Repellency Test – Rain Water – AATCC 22-205
Visual Test Score: 0 = worst and 100 = best
Water gain in grams (g) = the lower the number of grams, the better the repellency results.

Example No.	1	2	3	4	5	6	7	8	9	10
Visual Score Leather	70	80	0	70	60	60	70	50	70	80
Water Gain(g) Leather	0.63	0.77	7.00	0.95	1.83	1.68	0.99	2.68	2.37	0.53
Water Gain(g) Canvas	1.97	1.69	4.21	1.52	1.20	1.28	2.08	1.91	1.12	1.26

[0049] Wet Dirt (coffee stain) Repellency Test
Visual Test Score: 1 = worst, 5 = best.

Example No.	1	2
Visual Score Leather	3	5
Visual Score Canvas	4	5

[0050] Dry Dirt (soil prepared with Kaolin and Carbon Black) Repellency Test – Visual Test Score: 1 = worst, 5 = best; soil gain in grams (g) = the lower the number of grams, the better the repellency results.

Example No.	1	2	3	4	5	6	7	8	9	10
Visual Score Leather	5	5	4	4	1	3	2	4	3	2
Soil Gain (g) Leather	0.00	0.00	0.03	0.01	0.09	0.04	0.06	0.03	0.04	0.03
Visual Score Canvas	2	4	2	4	3.5	2	3	2	3	3
Soil Gain (g) Canvas	0.09	0.03	0.23	0.06	0.12	0.26	0.09	0.13	0.11	0.09

[0051] The exemplary embodiments herein disclosed are not intended to be exhaustive or to unnecessarily limit the scope of the invention. The exemplary embodiments were chosen and described in order to explain the principles of the present invention so that others skilled in the art may practice the invention. As will be apparent to one skilled in the art, various modifications can be made within the scope of the aforesaid description. Such modifications

being within the ability of one skilled in the art form a part of the present invention.

[0052] It is noted that terms like "specifically", "preferably", "typically", "generally", and "often" are not utilized herein to limit the scope of the claimed invention or to imply that certain features are critical, essential, or even important to the structure or function of the claimed invention. Rather, these terms are merely intended to highlight alternative or additional features that may or may not be utilized in a particular embodiment of the present invention. It is also noted that terms like "substantially" and "about" are utilized herein to represent the inherent degree of uncertainty that may be attributed to any quantitative comparison, value, measurement, or other representation.

[0053] The dimensions, values and ranges disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "50 mm" is intended to mean "about 50 mm." Any range described herein includes any and all sub-ranges within the ranges recited even if not specifically named.

IT IS CLAIMED:

1. A leather and/or textile spray treatment composition comprising

(a) solvent system comprising at least one linear C2-C6 alcohol solvent, optionally at least one aliphatic C6-C16 alkane, and optionally at least one ester solvent;

(b) at least one oxide of metal or metalloid nanoparticles, said nanoparticles having a size in a range of about 10 to about 1000 nanometers (nm);

(c) an organosilicon component comprising one or more of a silicone oil, silicone wax, or silicone resin;

wherein said composition is substantially free of water; and

wherein (a), (b) and (c) are present in amounts sufficient for said composition to render water repellent and dirt repellent an external surface of a leather and/or textile article having said composition present thereon.

2. The composition of claim 1, wherein said composition is substantially free or free of fluorine-containing compounds.

3. The composition of claim 1, wherein said solvent system comprises said at least one linear C2-C6 alcohol solvent and said at least one aliphatic C6-C16 alkane.

4. The composition of claim 1, wherein said solvent system comprises said at least one linear C2-C6 alcohol

solvent, said at least one aliphatic C6-C16 alkane and said at least one ester solvent.

5. The composition of claim 4, wherein said at least one ester solvent has a formula of R_1COOR_2, wherein R_1=C1-C4 alkyl and R_2=C2-C4 alkyl.

6. The composition of claim 1, wherein said at least one alcohol solvent is present in an amount of about 1 to about 97.5 wt.%; said at least one alkane solvent is present in an amount of 0 to about 98.5 wt. %; said at least one ester solvent is present in an amount of 0 to about 10 wt.%; said at least one nanoparticles is present in an amount of about 0.1 to about 4 wt.%; and said organosilicon component is present in an amount of greater than 0 to about 8 wt.%.

7. The composition of claim 1, wherein said composition is a non-aerosol spray composition.

8. The composition of claim 1, wherein the metal of said at least one oxide of metal or metalloid nanoparticles is selected from the "d" block of the Periodic Table of Elements and the metalloid of the at least one oxide of metal or metalloid nanoparticles is selected from the "p" block of the Periodic Table of Elements.

9. The composition of claim 8, wherein the metal and the metalloid have an atomic number $\leq$ 30.

10. The composition of claim 1, wherein said nanoparticles are spheroid or spherical in shape.

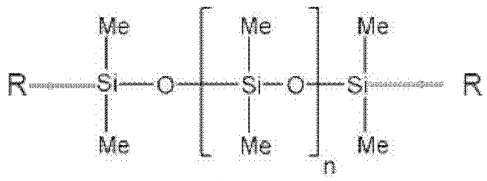
11. The composition of claim 1, wherein said nanoparticles have a size in the range of about 20 to about 500 nm.

12. The composition of claim 1, wherein said nanoparticles include a core and a coating on the external surface of said core.

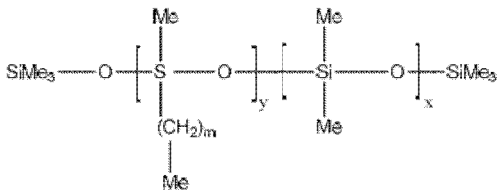
13. The composition of claim 12, wherein said coating is polymeric and is grafted to the external surface of the core.

14. The composition of claim 12, wherein said coating is composed of polysiloxane or a derivative thereof.

15. The composition of claim 1, wherein said silicone oil has a viscosity of about 10 to about 500 centistokes and is a dimethicone of the formula:

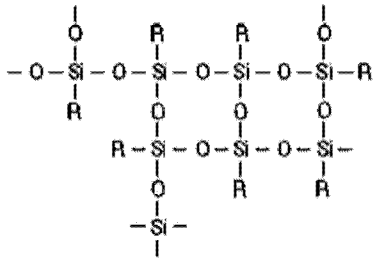


wherein $0<n<300$, $R=CH_3$; said silicone wax is alkyl methicone or alkyl dimethicone of the formula:



wherein $1<m\leq29$, $x+y<100$, $0\leq x<100$, and $0<y<100$; and

said silicone resin is of the formula



wherein R is C1-C6 alkyl, phenyl or mixtures thereof.

16. A leather and/or textile spray treatment system comprising

(a) a composition comprising

(i) solvent system comprising at least one linear C2-C6 alcohol solvent, optionally at least one aliphatic C6-C16 alkane, and optionally at least one ester solvent;

(ii) at least one oxide of metal or metalloid nanoparticles, said nanoparticles having a size in a range of about 10 to about 1000 nanometers (nm);

(iii) an organosilicon component comprising one or more of a silicone oil, silicone wax, or silicone resin;

wherein said composition is substantially free of water;

(b) a storage and dispensing container comprising

(i) a body for holding said composition, and

(ii) a spray delivery mechanism for dispensing said composition from said body onto an external surface of a leather and/or textile article; and

wherein (a), (b) and (c) are present in amounts sufficient for said composition to render water repellent and dirt repellent the external surface of the leather and/or textile article having said composition present thereon.

17. The system of claim 16, wherein said composition is substantially free or free of flourine-containing compounds.

18. The system of claim 16, wherein, in said composition, said solvent system comprises said at least one linear C2-C6 alcohol solvent and said at least one aliphatic C6-C16 alkane.

19. The system of claim 16, wherein, in said composition, said solvent system comprises said at least one linear C2-C6 alcohol solvent, said at least one aliphatic C6-C16 alkane and said at least one ester solvent.

20. The system of claim 19, wherein, in the composition, said at least one ester solvent has a formula of R_1COOR_2, wherein R_1=C1-C4 alkyl and R_2=C2-C4 alkyl.

21. The system of claim 16, wherein, in said composition, said at least one alcohol solvent is present in an amount of about 1 to about 92 wt.%; said at least one alkane solvent is present in an amount of 0 to about 98.5

wt. %; said at least one ester solvent is present in an amount of 0 to about 10 wt.%; said at least one nanoparticles is present in an amount of about 0.1 to about 4 wt.%; and said organosilicon component is present in an amount of greater than 0 to about 8 wt.%.

22. The system of claim 16, wherein said spray delivery mechanism is a non-aerosol pump spray mechanism.

23. The system of claim 16, wherein, in said composition, the metal of said at least one oxide of metal or metalloid nanoparticles is selected from the "d" block of the Periodic Table of Elements and the metalloid of the at least one oxide of metal or metalloid nanoparticles is selected from the "p" block of the Periodic Table of Elements.

24. The system of claim 23, wherein the metal and the metalloid have an atomic number ≤ 30.

25. The system of claim 16, wherein, in the composition, said nanoparticles are spheroid or spherical in shape.

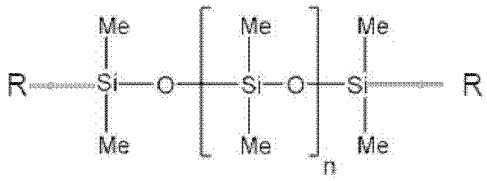
26. The system of claim 16, wherein, in the composition, said nanoparticles have a size in the range of about 20 to about 500 nm.

27. The system of claim 16, wherein, in the composition, said nanoparticles include a core and a coating on the external surface of said core.

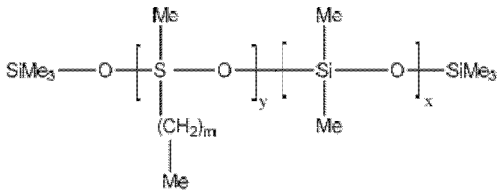
28. The system of claim 27, wherein said coating is polymeric and is grafted to the external surface of the core.

29. The system of claim 28, wherein said coating is composed of polysiloxane or a derivative thereof.

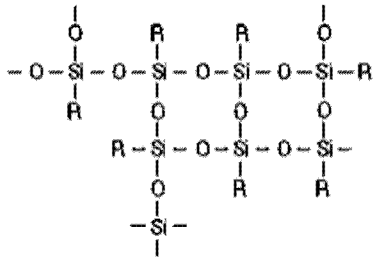
30. The system of claim 16, wherein, in the composition, said silicone oil has a viscosity of about 10 to about 500 centistokes and is a dimethicone of the formula:



wherein $0<n<300$, $R=CH_3$; said silicone wax is alkyl methicone or alkyl dimethicone of the formula:



wherein $1<m\leq29$, $x+y<100$, $0\leq x<100$, and $0<y<100$; and said silicone resin is of the formula



wherein R is C1-C6 alkyl, phenyl or mixtures thereof.

31. A leather and/or textile spray treatment composition comprising

(a) solvent system comprising about 20 to about 90 wt.% of at least one linear C2-C6 alcohol solvent, optionally up to about 70 wt.% at least one aliphatic C6-C16 alkane, and optionally greater than 0 to about 8 wt.% of at least one ester solvent;

(b) about 0.1 to about 3 wt.% of at least one oxide of metal or metalloid nanoparticles, said nanoparticles having a size in a range of about 10 to about 1000 nanometers (nm); and

(c) about 1 to about 6 wt.% of an organosilicon component comprising one or more of a silicone oil, silicone wax, or silicone resin;

wherein said composition is substantially free of water; and

wherein (a), (b) and (c) are present in amounts sufficient for said composition to render water repellent and dirt repellent an external surface of a leather and/or textile article.

32. The composition of claim 31, wherein said composition is substantially free or free of fluorine-containing compounds.

33. The composition of claim 31, wherein the metal and metalloid have an atomic number of ≤ 30.

34. The composition of claim 31, wherein said nanoparticles are an oxide of at least one of titanium, silicon or zinc.

35. The composition of claim 31, wherein said nanoparticles include a core and a coating on the external surface of said core.

36. The composition of claim 35, wherein said coating is polymeric and is grafted to the external surface of the core.

37. The composition of claim 31, wherein said composition includes one or more of said at least one aliphatic C6-C16 alkane.

38. The composition of claim 37, wherein said at least one aliphatic C-6-C16 alkane is present in an amount of about 40 to about 70 wt.%.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2020/128550

A. CLASSIFICATION OF SUBJECT MATTER

D06M 15/643(2006.01)i; D06M 11/46(2006.01)i

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)

D06M15; D06M11

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)

CNPAT, EPODOC, WPI, CNKI, ISI, STN, nanoparticle+, spray, +silicone, alcohol, leather, textile, metal, alkane, ester

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 109518462 A (UNIV. SOUTHEAST) 26 March 2019 (2019-03-26) description, paragraphs 5-25, example 1	1-38
A	WO 2012018403 A1 (BIOFILM IP LLC et al.) 09 February 2012 (2012-02-09) claims 1-199	1-38
A	US 2010317780 A1 (IND. TECH. RES. INST.) 16 December 2010 (2010-12-16) claims 1-11	1-38
A	WO 2011151025 A1 (MAX PLANCK GES FOERDERUNG WISSENSCHAFTEN) 08 December 2011 (2011-12-08) claims 1-15	1-38
A	WO 2019241138 A1 (SABIC GLOBAL TECHNOLOGIES B.V. et al.) 19 December 2019 (2019-12-19) claims 1-20	1-38
A	CN 104987520 A (UNIV. BEIHANG) 21 October 2015 (2015-10-21) claims 1-10	1-38

☐ 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	Date of mailing of the international search report
13 July 2021	**29 July 2021**
Name and mailing address of the ISA/CN **National Intellectual Property Administration, PRC** **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing** **100088** **China**	Authorized officer **ZHANG,Aixin**
Facsimile No. **(86-10)62019451**	Telephone No. **86-(010)-53962204**

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2020/128550

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)			Publication date (day/month/year)
CN	109518462	A	26 March 2019	None			
WO	2012018403	A1	09 February 2012	CA	2807336	A1	09 February 2012
				EP	2601245	A1	12 June 2013
				CN	103154095	A	12 June 2013
				US	9175141	B2	03 November 2015
				JP	2013539484	A	24 October 2013
				US	2012064022	A1	15 March 2012
US	2010317780	A1	16 December 2010	US	8575235	B2	05 November 2013
WO	2011151025	A1	08 December 2011	US	2013210969	A1	15 August 2013
				EP	2392543	A1	07 December 2011
WO	2019241138	A1	19 December 2019	None			
CN	104987520	A	21 October 2015	CN	104987520	B	17 April 2018