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(54) Title: POLYSILOXANE-BASED WATER REPELLANTS FOR TEXTILES

(57) Abstract: An aqueous emulsion including a discontinuous oil phase comprising: a) a polyorganohydrogensiloxane, b) an amino-modified polyorganosiloxane comprising at least one amino group located at a terminal position and c) a blocked isocyanate.

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POLYSILOXANE-BASED WATER REPELLANTS FOR TEXTILES

CROSS REFERENCE TO RELATED APPLICATIONS: This application claims the benefit of U.S. Provisional Patent Application Serial No. 63/210517 filed on 15 June 2021 under 35 U.S.C. §119 (e).

5 U.S. Provisional Patent Application Serial No. 63/210517 is hereby incorporated by reference.

FIELD:

The present invention is directed toward polysiloxane-based compositions useful for treating textiles. The subject compositions and related treatment methods find utility in treating fabrics used in clothing to improve their water repellency.

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INTRODUCTION:

Textiles such as fabrics used in clothing are commonly treated to improve water repellency. While fluoropolymers have been historically used in such treatments, environmental and health concerns have curtailed their use. A known alternative approach utilizes polysiloxane-based coating compositions. Applicable compositions include one or more types of polysiloxanes including resins (e.g. MQ resins), polydiorganosiloxanes (e.g. polydimethylsiloxanes), polyorganoalkenylsiloxanes (e.g. polyorgano-
15 siloxanes including one or more alkenyl groups) and amino-modified polyorganosiloxanes. By way of example, US8329255 describes a composition including an alkoxy-substituted polyorganosiloxane (which may also include amino-functionality) along with a blocked isocyanate crosslinker. US2019/0375897 describes a composition including a silicone resin, an amino-modified polysiloxane and a blocked isocyanate. US9777105 and US10040891 describe the use of amino-modified or alkoxy polyorganosiloxanes along with blocked isocyanates and catalysts.

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Another known class of compositions include polyorganohydrogensiloxanes, i.e. polyorganosiloxanes including one or more -SiH groups. For example, US3247281 describes a composition including polyorganohydrogensiloxanes having at least 5 wt% SiH groups along with a catalytic amount of a water soluble aminosilane. US5409620 describes a hydrosilylation-based system including a polyorganohydrogensiloxane, an unsaturated acetate, an organosilicon such as a polyorganoalkenylsiloxane and a metal catalyst. As is known in the art, amino-containing constituents poison platinum catalysts and as such, amino-modified polysiloxanes are excluded from such
25 hydrosilylation-based systems.

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While not directed toward water repellency, polyorganosiloxanes are also known for use in the treatment of textiles to improve other properties such as softness, lubricity, durability, fiber shrinkage. For example, US4177176 describes a composition for preventing fiber shrinkage including an amino-modified, hydroxyl or alkoxy terminated polyorganosiloxane and polyorganohydrogensiloxane. JP2002/146680 describes a composition for improving washing resistance and softness of cellulosic fiber
35 cloth while eliminating the “sliminess” associated with the use of silicon resins. The described

compositions include an amino-modified polyorganosiloxane and a polyorganohydrogensiloxane along with a urethane prepolymer and blocked isocyanate. The described amino-modified polyorganosiloxanes include amino groups located in a pendant position with respect to the polysiloxane.

Another class of compositions include polyorganoalkenylsiloxanes and polyorganohydrogen-
siloxanes along with a platinum catalyst which when applied to a substrate, undergo a hydrosilylation
reaction to form a crosslinked reaction product. These hydrosilylation-based systems have been
described for preparing release and water repellant coatings for paper and PET films (e.g. see
US2005/0053793) and for improving adhesion between fabrics and airbags, (e.g. see US7534499 and
WO2019/001901).

The industry continues to seek improved water repellant compositions and related textile
treatments.

SUMMARY:

The inventors of the present invention discovered an unexpected improvement in water
repellency associated with the use of treatment compositions based upon polyorganohydrogensiloxanes,
amino silicones and blocked isocyanates. More specifically, the inventors discovered that the use of
terminal amino silicones in such compositions provides far superior water repellency as compared with
the use of corresponding pendant varieties. The present invention includes such compositions along with
their preparation and use in treating textiles as well as the resulting textiles. Many embodiments are
described.

In one aspect, the present invention includes an aqueous emulsion including an aqueous
continuous phase and a discontinuous oil phase, wherein the discontinuous oil phase includes the
following constituents: a) 50 to 95 wt% of a polyorganohydrogensiloxane; b) 0.1 to 45 wt% of an amino-
modified polyorganosiloxane comprising at least one amino group located at a terminal position; and c)
5 to 30 wt% of a blocked isocyanate. In another aspect, the invention includes the aforementioned
emulsion where the discontinuous oil phase includes at least one of the following: i) 0.5 to 1.5 H wt%
and ii) 0.004 to 0.2 N wt%. In yet another aspect of the invention, the aforementioned emulsion further
includes constituent d): 0.1 to 10 wt% of a polyorganosiloxane including at least one silanol group.

BRIEF DESCRIPTION OF THE DRAWINGS:

Figure 1 is a plot of Bundesmann water pickup after one wash cycle as a function of the amine
concentration (N wt%) of the terminal amino silicone used in Example coating emulsions 1-6 provided in
Table 2a.

DETAILED DESCRIPTION:

As used herein, the term “textile” refers to a flexible material consisting of a network of natural or
synthetic fibers. Representative fibers include cotton, flax, hemp, silk, wool, rayon, cellulose, linen, nylon,
polypropylene, polyether-polyurea copolymer (e.g. “spandex”) and polyester. “Textiles” specifically

include non-woven and woven fabrics produced by weaving, knitting, spreading, felting, stitching, crocheting or bonding such fibers. In selected embodiments of the invention, the fabric of interest is that used in the manufacture of clothing (e.g. garments) where softness, water resistance and durability after repeated cleaning (washing, dry cleaning, etc.) are desired.

5 The subject compositions are preferably provided as an emulsion including a continuous aqueous phase. The water used to prepare the emulsion may be from any source and may optionally be purified, e.g. through filtration, distillation, reverse osmosis techniques, etc. As will be more fully described, the emulsion further comprises a surfactant. The surfactant (alternatively referred to as an “emulsifier”) serves to emulsify a discontinuous polysiloxane (oil) phase within the aqueous continuous phase. The
10 discontinuous oil phase of the emulsions preferably comprises from 1 to 10 wt% and more preferably from 2 to 5 wt% of the total weight of the emulsion (i.e. including water, surfactant along with any other additives, solvents, etc.). As will be described below, the subject emulsion may be prepared prior to use by combining previously prepared emulsions of different polysiloxane compositions.

The discontinuous oil phase of the emulsion comprises: a) a polyorganohydrogensiloxane (“SiH
15 polymer”), b) an amino-modified polyorganosiloxane comprising at least one “amino” group located in a terminal position of polyorganosiloxane (“terminal amino silicone”) and c) a blocked isocyanate. The discontinuous oil phase may optionally include: d) a polyorganosiloxane including at least one silanol group (-SiOH). In a select class of embodiments, the subject emulsion comprises the following weight percentages of each the aforementioned constituents (wherein constituents a + b + c + d = 100%):

20 a) 50 to 95 wt%, preferably 60 to 95 wt% and more preferably 60 to 90 wt% of a polyorganohydrogensiloxane;

b) 0.1 to 45 wt%, preferably 1 to 20 wt% of a terminal amino silicone;

c) 5 to 30 wt%, preferably 10 to 25 wt% of a blocked isocyanate; and optionally

d) 0.1 to 10 wt%, preferably 0.5 to 5 wt% of a polyorganosiloxane including at least one
25 silanol group. In sub-class of embodiments, the subject emulsion further comprises at least one and preferably both the following:

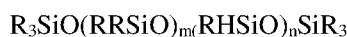
i) 0.5 to 1.5 H wt% (as -SiH) as determined by FTIR and

ii) 0.004 to 0.2 N wt% and more preferably 0.005 to 0.15 (as “amino”) as determined
by acid-base titration.

30 a) Polyorganohydrogensiloxane (“SiH polymer”)

The class of applicable polyorganohydrogensiloxanes designated as constituent a) is not particularly limited and includes a wide range of conventional and commercially available materials. Such materials include cyclic, linear and branched polyorganohydrogensiloxanes with linear polymers being
35 preferred. Applicable polymers preferably have a weight average molecular weight (Mw) of 500 to 6000 AMU (Daltons) and more preferably from 1000 to 4500 AMU (Daltons). Applicable polymers may have viscosities from 5 to 50 cSt, more preferably from 10 to 35 cSt measured at 25°C according to ASTM

D2196-05. Different polyorganohydrogensiloxanes may be used in combination, e.g. those having different chemical structures, molecule weights and/or viscosities. The subject polyorganohydrogensiloxanes include at least one, preferably at least two and more preferably at least three –SiH groups which may be located on the polysiloxane backbone at terminal (end) and/or intermediate (pendant) positions. In preferred embodiments, the –SiH groups are predominantly located at pendant positions, i.e. greater than 90 wt% and more preferably greater than 95 wt% and still more preferably greater than 99 wt% of all –SiH groups are located at pendant positions along the polysiloxane chain as determined by ²⁹Si NMR. Representative polyorganohydrogensiloxanes include those of the general formula:



where m+n = 10 to 100, preferably 10 to 60, n is preferably at least 3, m is preferably at least 7, n/(n+m) is preferably greater than 0.375, and “R” may be the same or different and is selected from substituted or unsubstituted monovalent hydrocarbon groups having from 1 to 18 carbon atoms and more preferably from 1 to 8 carbon atoms. Representative hydrocarbon groups include: a) alkyl groups such as: methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclohexyl and heptyl; b) aryl groups such as phenyl, tolyl, xylyl and naphthyl; and c) aralkyl groups such as benzyl and phenethyl; however methyl and phenyl groups are preferred with methyl being most preferred. Applicable commercially available polyorganohydrogensiloxanes include: XIAMETER™ MEM-0075, DOWSIL™ MH 1107 FLUID, XIAMETER™ OFX-5084, SYL-OFF™ 7672 and SYL-OFF™ 7678, all available from The Dow Chemical Company.

b) Amino-modified polyorganosiloxane (“terminal amino silicone”)

The class of applicable amino-modified polyorganosiloxane designated as constituent b) is not particularly limited and includes a wide range of conventional and commercially available materials so long as at least one amino group is located at a terminal (chain end) position of the polyorganosiloxane. As demonstrated in the Examples below, polyorganosiloxane species including amino groups located at terminal positions of the polyorganosiloxane chain performed far superior to those with amino groups located solely at pendant (intermediate) positions when used in combination with constituents a) and c). And while the subject amino silicones may include amino groups located at both terminal and pendant positions, in a preferred class of embodiments the amino groups are predominately located at terminal positions, i.e. greater than 90 wt % and more preferably greater than 95 wt%, and still more preferably greater than 99 wt% of the amino groups are located at terminal positions as determined by ²⁹Si NMR. Such polymers include linear and branched structures with linear polymers being preferred. Applicable polymers preferably have a weight average molecular weight (Mw) of 200 to 10,000 AMU (Daltons) and more preferably from 400 to 8000 AMU (Daltons). Applicable polymers preferably have viscosities of from 2 to 200 cSt, more preferably 5 to 150 cSt as measured at 25°C according to ASTM D2196-05. Different amino-modified polyorganosiloxanes may be used in combination, e.g. those having different chemical structures, molecular weights and/or viscosities. Representative amino-modified polyorganosiloxanes include those of the general formula:



where q is 2 to 200, preferably 25 to 100, R is as defined above, and X is an amino group include including one or more (preferably one to three) primary or secondary amine groups including 1 to 6 carbon atoms. Representative amino groups include those of the general formula:



where R' is a divalent hydrocarbon group (e.g. an alkylene group) having from 2 to 6 carbon atoms and R'' is the same or different and is selected from H (hydrogen) or a monovalent hydrocarbon group (e.g. an alkyl group) having from 1 to 6 carbon atoms which may be unsubstituted or substituted with one or more hydrocarbon groups (such that the total carbon atoms in such substituted monovalent hydrocarbon group is from 1 to 6), primary amine groups and secondary amine groups including a monovalent hydrocarbon group (e.g. an alkyl group) having from 1 to 6 carbon atoms. Representative examples include: $-(\text{CH}_2)_3\text{NH}_2$, $-(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2$, $-(\text{CH}_2)_4\text{NHCH}_2\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, $-(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$ and $-(\text{CH}_2)_3\text{NH}(\text{CH}_2)_2\text{CH}(\text{CH}_2\text{CH}_2\text{NH}_2)(\text{CH}_2)_3\text{NH}_2$. Most preferred structures include: $-(\text{CH}_2)_3\text{NH}_2$ and $-\text{CH}_2\text{CHR}'''\text{CH}_2\text{NHR}'''$ where R''' is H or an alkyl group of 1 to 6 carbon atoms. Applicable species are further described in US9777105. Applicable commercially available amino-modified polyorganosiloxanes include: DMS-A15, DMS-A21 and DMS-A31 available from Gelest.

c) Blocked Isocyanate

The class of applicable blocked isocyanates designated as constituent c) is not particularly limited and includes a wide range of conventional and commercially available materials. The term "blocked isocyanate" as used herein refers to a reaction product of an isocyanate and a blocking agent, wherein the blocking agent is removable from the isocyanate under the thermal conditions, i.e. those typically used while treating a textile. Conventional blocking agents include aryl alcohols, alkanone oximes, aryl thioles, organic active hydrogen compounds, sodium bisulfite and hydroxylamine. Preferred blocking agents include alkanone oximes (ketoximes) which can be de-blocked at a relatively low temperature such as used during a typical textile treatment process. For purposes of the present invention, "aromatic" blocked polyisocyanates are preferred. In this context the term "aromatic" means isocyanate compounds with at least one aromatic group, such as materials based on toluene diisocyanate, diphenylmethane 4,4' diisocyanate, diphenylmethane 2,4' diisocyanate, polymethylene-polyphenyl isocyanate, 4,4' methylene bisphenol isocyanate, and derivatives thereof. Suitable isocyanates $\text{A}(\text{CNO})_z$ for preparation of the blocked isocyanate are those wherein A is an aromatic compound, and z is 1, 2, 3 or 4. These include isocyanates or derivatives such as toluene diisocyanate, polymethylenepolyphenyl isocyanate, and 4,4' methylene bisphenol isocyanate, and include those aromatic isocyanates sold commercially for this purpose. Typical commercial products include products such as the adduct of toluene diisocyanate and trimethylolpropane (1,1,1 trihydroxymethyl propane) DESMODUR CB-75; (available from Covestro), aromatic isocyanates based on the polymethylenepolyphenylene ester of isocyanic acid, such as MONDUR MR-100 (available

from Covestro), and aromatic isocyanates based on polymethylenepolyphenyl isocyanate containing 4,4' methylene bisphenol isocyanate (available from The Dow Chemical Co.). Also available commercially are ready-made blocked aromatic isocyanates such as HYDROPHOBOL DL, PHOBOL XAN Extender (available from Huntsman), DM-6400, MEIKANATE FM-1, MEIKANATE ST, MEIKANATE PRO, MEIKANATE TP-10, MEIKANATE WEB, MEIKANATE ST (available from Meisei Chemical Works, Ltd.). Further background information regarding such isocyanates is provided in US2019/0375897, US839255 and US6451717.

d) Polyorganosiloxane including at least one silanol group (-SiOH).

The class of applicable polyorganosiloxanes including at least one silanol group designated as constituent d) is not particularly limited and includes a wide range of conventional and commercially available materials. Such materials include cyclic, linear and branched structures with linear polymers being preferred. Applicable polymers preferably have a weight average molecular weight (Mw) of 200 to 5500 AMU (Daltons). Applicable polymers may have viscosities of from 30 to 100 cSt measured at 25°C according to ASTM D2196-05. Different polyorganosiloxanes may be used in combination, e.g. those having different chemical structures, molecule weights and/or viscosities. The subject polyorganosiloxanes include at least one, preferably at least two and more preferably at least three silanol (-SiOH) groups which may be located on the polysiloxane backbone at terminal (end) and/or intermediate (pendant) positions. In preferred embodiments, the -SiOH groups are predominantly located at pendant positions, i.e. greater than 90 wt% and more preferably greater than 95 wt% and still more preferably greater than 99 wt% of all -SiOH groups are located at pendant positions along the polysiloxane chain as determined by ²⁹Si NMR. The subject polyorganosiloxanes preferably have a silanol content of from 1% to 10% weight percent as determined by FTIR. Representative polyorganosiloxanes include those of the general formula:



where t is a number from 2 to 50, Y may be the same or different and is selected from substituted or unsubstituted monovalent hydrocarbon groups having from 1 to 18 carbon atoms and more preferably from 1 to 8 carbon atoms and hydroxyl groups (i.e. a sufficient number of hydroxyl groups to meet the criteria described above), and R may be the same or different and is selected from substituted or unsubstituted monovalent hydrocarbon groups having from 1 to 18 carbon atoms and more preferably from 1 to 8 carbon atoms. Representative hydrocarbon groups include: a) alkyl groups such as: methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclohexyl and heptyl; b) aryl groups such as phenyl, tolyl, xylyl and naphthyl; and c) aralkyl groups such as benzyl and phenethyl; however methyl and phenyl groups are preferred with methyl being most preferred. Applicable commercially available products include: DOWSIL™ Q1-3563 Fluid, and XIAMETER™ PMX-0930 Silanol Fluid all available from The Dow Chemical Company.

Surfactant (Emulsifier)

The class of applicable surfactants for use in preparing the subject emulsions is not particularly limited and includes a wide range of conventional and commercially available materials. The surfactant may be an anionic surfactant, cationic surfactant, nonionic surfactant, amphoteric surfactant, or a mixture thereof with cationic and nonionic surfactants being preferred.

Examples of applicable anionic surfactants include, but are not limited to, alkali metal, amine, or ammonium salts of higher fatty acids, alkylaryl sulphonates such as sodium dodecyl benzene sulfonate, long chain fatty alcohol sulfates, olefin sulfates and olefin sulfonates, sulfated monoglycerides, sulfated esters, sulfonated ethoxylated alcohols, sulfosuccinates, alkane sulfonates, phosphate esters, alkyl isethionates, alkyl taurates, alkyl sarcosinates, and mixtures thereof. Further examples of applicable anionic surfactants include carboxylates (sodium 2-(2-hydroxyalkyloxy) acetate)), amino acid derivatives (N-acylglutamates, N-acylglycines or acylsarcosinates), alkyl sulfates, alkyl ether sulfates and oxyethylenated derivatives thereof, sulfonates, isethionates and N-acylisethionates, taurates and N-acyl N-methyltaurates, sulfosuccinates, alkylsulfoacetates, phosphates and alkyl phosphates, polypeptides, anionic derivatives of alkyl polyglycoside (acyl-D-galactoside uronate), and fatty acid soaps, and mixtures thereof. Commercial examples of applicable anionic surfactants include: STEPANOL® WA-100, CALIMULSE® SLS, POLYSTEP® A-16, POLYSTEP® B-11, POLYSTEP® B-19, TRITON™ QS-15, TRITON™ XN-45S and DOWFAX™ 2A1.

Examples of applicable cationic surfactants include, but are not limited to, alkylamine salts, quaternary ammonium salts, sulphonium salts, and phosphonium salts. Applicable commercial examples of cationic surfactants include: ARQUAD® 16-29, ARQUAD® 18-50, ARLASILK EFA. ATLAS G-265, SYNPROLAM 35X15, VARISOFT® PATC, and VARISOFT® BT-85.

Examples of applicable amphoteric surfactants include, but are not limited to, imidazoline compounds, alkylaminoacid salts, betaines, and mixtures thereof.

Examples of applicable nonionic surfactants include, but are not limited to, condensates of ethylene oxide with long chain fatty alcohols or fatty acids such as a C12-16 alcohol, condensates of ethylene oxide with an amine or an amide, condensation products of ethylene and propylene oxide, esters of glycerol, sucrose, sorbitol, fatty acid alkylol amides, sucrose esters, fluoro-surfactants, fatty amine oxides, and mixtures thereof. Further examples of nonionic surfactants include polyoxy-ethylene fatty alcohols such as polyoxyethylene (23) lauryl ether, polyoxyethylene (4) lauryl ether; ethoxylated alcohols such as ethoxylated trimethylnonanol, C12-C14 secondary alcohol ethoxylates, ethoxylated, C10-Guerbet alcohol, ethoxylated, iso-C13 alcohol; poly(oxyethylene)-poly(oxypropylene)-poly(oxyethylene) tri-block copolymer (also referred to as poloxamers); tetrafunctional poly(oxyethylene)-poly(oxypropylene) block copolymer derived from the sequential addition of propylene oxide and ethylene oxide to ethylene diamine (also referred to as poloxamines), silicone polyethers, polyoxyethylene alkyl ethers, polyoxyethylene alkylphenol ethers, polyoxy-ethylene lauryl ethers, polyoxyethylene sorbitan monoleates, polyoxyethylene alkyl esters, polyoxy-ethylene sorbitan alkyl esters, polyethylene glycol, polypropylene glycol, diethylene

glycol, ethoxylated trimethylnonanols, and polyoxyalkylene glycol modified polysiloxane surfactants, and combinations thereof. Further examples of applicable nonionic surfactants include polyoxyethylene alkyl ethers, polyoxyethylene alkylphenol ethers, polyoxyethylene lauryl ethers, straight-chain, primary alcohol alkoxylates, straight-chain secondary alcohol alkoxylates, alkyl phenol alkoxylates, olefinic alkoxylates, 5 branched chain alkoxylates, polyoxyethylene sorbitan monoleates, polyoxy-ethylene alkyl esters, polyoxyethylene sorbitan alkyl esters, polyethylene glycol, polypropylene glycol, diethylene glycol, ethoxylated trimethylnonanols, polyoxyalkylene-substituted silicones (rake or ABn types), silicone alkanolamides, silicone esters, silicone glycosides, and mixtures thereof. Additional examples of applicable nonionic surfactants include dimethicone copolyols, fatty acid esters of polyols, for instance 10 sorbitol or glyceryl mono-, di-, tri- or sesquioleates or stearates, glyceryl or polyethylene glycol laurates; fatty acid esters of polyethylene glycol (polyethylene glycol monostearate or monolaurate); polyoxyethylenated fatty acid esters (stearate or oleate) of sorbitol; polyoxyethylenated alkyl (lauryl, cetyl, stearyl or octyl)ethers. Examples of applicable commercial non-ionic surfactants include: TERGITOL™ 15-S-3, TERGITOL™ 15-S-5, TERGITOL™ 15-S-7, TERGITOL™ 15-S-9, TERGITOL™ 15-S-12, 15 TERGITOL™ 15-S-15, TERGITOL™ 15-S-15, TERGITOL™ 15-S-20, BRIJ™ L23, BRIJ™ L4, LUTENSOL® TO3, LUTENSOL® TO5, LUTENSOL® TO7, LUTENSOL® TO10, LUTENSOL® TO12, LUTENSOL® TO15, LUTENSOL® TO20, LUTENSOL® XP30, LUTENSOL® XP100 and LUTENSOL® XP140.

Further examples of applicable amphoteric and zwitterionic surfactants include betaines, N- 20 alkylamidobetaines and derivatives thereof, proteins and derivatives thereof, glycine derivatives, sultaines, alkyl polyaminocarboxylates and alkylamphoacetates, and mixtures thereof.

Additional water-soluble constituents may be added to the aqueous phase including thickeners and preservatives.

In selected embodiments, the subject emulsions are substantially free of one or more of the 25 following constituents including all possible combinations of such constituents:

- i) Fluoropolymers;
- ii) Organic materials including ethylenically unsaturated groups (e.g. unsaturated acetates, allyl esters, vinyl esters;
- iii) Polyorganosiloxanes including ethylenically unsaturated groups (e.g. vinyl);
- 30 iv) Platinum-containing catalyst;
- v) Resinous materials (e.g. polysiloxane resins and polyurethane resins) and
- vi) All metal catalyst.

In this context, the term “substantially free” means less than 1 wt%, preferably less 0.5 wt% and more preferably less than 0.1 wt% and still more preferably less than 0.01 wt%, based upon the total weight of 35 the discontinuous oil phase.

The subject emulsions may be prepared by combining the aforementioned constituents a), b), c) and optionally d) in water along with one or more surfactants with mixing. Mixing may occur using any

known technique. Representative mixing devices include homogenizer, sonolator, rotor-stator turbines, colloid mill, microfluidizer, sonicator, blades, helix and combination thereof. Representative methodologies are described in US6013682, US8877293 and US2015/0010711. In a preferred embodiment, constituents a) and optional constituent d) are combined in water with surfactant and mixed to form a first emulsion, constituent b) is combined in water with surfactant and mixed to form a second emulsion, constituent c) is combined in water with surfactant and mixed to form a third emulsion. A homogenizer or sonic probe may be used to achieve desired particle size. The first, second, and third emulsions may be stored and subsequently combined prior to use. Alternatively, constituent(s) c) and/or d) may be included in the first emulsion (containing constituent a)), the second emulsion (containing component b)), or a third emulsion.

The particles of the discontinuous oil phase preferably have an average volume particle size “Dv(0.5)” of from 100 to 5000 nm and more preferably from 100 to 2000 nm as determined via laser diffraction using a Malvern 3000 and in accordance with ISO 13320 (2009). As used herein, the term “particles” refers to the oil phase droplets.

Applicable methods of treating textiles with the subject emulsions are not particularly limited and include applying the emulsion to the textile by dipping, padding (e.g. via a roll padder), curtain coating, brush coating, roll coating and spraying methods such as air-atomized spray, air-assisted spray, airless spray, high volume low pressure spray and air-assisted airless spray. The resulting coating is then dried (cured) at elevated temperature from 80 to 180°C for 1 to 3 minutes. Examples of the drying steps include air drying at room temperature, hot air drying and infrared heating. Typical coating coverages are in the range of 0.5 to 15 grams dry weight per square meter (g/m²).

Many embodiments of the invention have been described and, in some instances, certain embodiments, selections, ranges, constituents, or other features have been characterized as being “preferred.” Such designations of “preferred” features should in no way be interpreted as an essential or critical aspect of the invention. Expressed ranges specifically include designated end points. As used herein, the terms “molecular weight” and “Mw” refer to the weight average molecular weight as measured by gel permeation chromatography (GPC).

EXAMPLES:

Unless otherwise indicated, all preparation and testing were conducted at room temperature (RT) at standard pressure (1 atm or 760 mm Hg). The following materials were used in the preparation and testing of aqueous emulsions:

Table 1: Description of materials used in Examples

Material Type	Product Name	Chemical Description	Molecular Weight	Source
Terminal amino silicone polymer	DMS-A15 (Ter-Amino1)	Aminopropyl terminated polydimethylsiloxanes	3000	Gelest

Terminal amino silicone polymer	DMS-A21 (Ter-Amino2)	Aminopropyl terminated polydimethylsiloxanes	5000	Gelest
Terminal amino silicone polymer	DMS-A31 (Ter-Amino4)	Aminopropyl terminated polydimethylsiloxanes	25000	Gelest
Terminal amino silicone polymer	(Ter-Amino 3)	Aminopropyl terminated polydimethylsiloxanes	6300	Ex. VII-n of WO2021/108068
Pendant amino silicone polymer	AMS-132 (Pen-Amino1)	Aminopropylmethylsiloxane-dimethylsiloxane copolymers	4500-6k	Gelest
Pendant amino silicone polymer	AMS-152 (Pen-Amino2)	Aminopropylmethylsiloxane-dimethylsiloxane copolymers	7000-9k	Gelest
Pendant amino silicone polymer	AMS-162 (Pen-Amino3)	Aminopropyl methylsiloxane-dimethylsiloxane copolymers	4000-5k	Gelest
Water soluble amino silane	DOWSIL™ Z-6137	(3-((2-Aminoethyl) amino) propyl) silanetriol homopolymer	180	Dow
SiH emulsion	XIAMETER™ MEM-0075	Polyorganohydrogensiloxane & silanol functional polyorganosiloxane emulsion	4000	Dow
Polyorgano-hydrogensiloxane	XIAMETER™ OFX-5084	SiMeH-SiMe ₂ copolymer	1300	Dow
Polyorgano-hydrogensiloxane	DOWSIL™ MH 1107 FLUID	Methylhydrogensiloxane in MEM0075 emulsion	4000	Dow
Surfactant	BRIJ L23	non-ionic surfactant		Croda
Surfactant	BRIJ L4	non-ionic surfactant		Croda
Surfactant	ARQUAD 16-29	cationic surfactant		AkzoNobel
Blocked isocyanate	PHOBOL™ XAN Extender	cationic dispersion of blocked isocyanate		Huntsman
Fabric	PES Fabric	Polyester, No. 4774 075		Burlington

Sample emulsions were prepared according to the following methodologies:

Emulsions of Ter-Amino1 and Ter-Amino 4:

- 5 Amino silicone emulsions were prepared by combining respective amino silicones (4.00 g), BRIJ L23 (0.07 g), BRIJ L4 (0.04 g), and water (35.88 g) in a dental cup and mixed on a Flak-Tek speedmixer (Model 150.1 FZV) at 3500 rpm for 1 minute. Emulsion particle size was then reduced using a sonic probe (Fisherbrand Model 705) at 50% power for 30 seconds.

Emulsion of Ter-Amino2:

- 10 An amino silicone emulsion was prepared by combining Ter-Amino 2 (20.00 g), BRIJ L23 (1.12 g), BRIJ L4 (0.7 g), acetic acid (10 wt% in water, 0.5 g) and water (27.68 g) in a dental cup and mixed on a Flak-Tek speedmixer (Model 150.1 FZV) at 3500 rpm for 30 seconds. Water (27.68 g) was added to the mixture which was twice passed through a 1-stage homogenizer (APV Systems SPX 2000) at 15000 psi. After homogenization, acetic acid (10wt%, 2.65 g) was added to 135.95 g of the emulsion.

15 Emulsions of Pen-Amino1, 2 & 3 and Ter-Amino3:

Amino silicone emulsions were prepared by combining the respective amino silicones (4.00 g), BRIJ L23 (0.07 g), BRIJ L4 (0.05 g), and water (35.88 g) in a dental cup and then homogenizing using a sonic probe (Fisherbrand Model 705) at 50% power for 1 minute.

Organohydrogen Siloxane Containing Emulsion:

XIAMETER™ OFX-5084 (60.51 g), BRIJ L23 (1.12 g), BRIJ L4 (0.61 g), and water (4.5 g) were added to the mixture and combined on a Flak-Tek speedmixer (Model 150.1 FZV) at 3500 rpm for 30 seconds. The emulsion was then diluted with water (33.26 g) and twice passed through a 1-stage homogenizer (APV
5 Systems SPX 2000) at 15000 psi. An emulsion containing DOWSIL™ MH 1107 FLUID (60.51 g) was prepared using the same procedure.

1107/PDMS Blend Emulsion:

A solution of 50 cSt 200 Fluid and DOWSIL™ MH 1107 FLUID was prepared by mixing the components in a 1:1 ratio until homogeneous and clear. To this solution (27.99 g) was added ARQUAD 16-29 (2.16 g)
10 and water (4.04 g) in a plastic cup and mixed on a Flak-Tek speedmixer (Model 150.1 FZV) at 3500 rpm for 30 seconds. The emulsion was diluted with water (10.93 g) and mixed via speedmixer at 3500 rpm for 30 seconds.

Coating emulsions were prepared by mixing the aforementioned emulsions along with any additional constituents as indicated in Tables 2a, 2b, 2c and 2d (where all quantities are in grams). The
15 resulting coating emulsions were then applied to standard polyester (PES Style Number 4774 075) fabrics from Burlington by padding followed by curing in a Mathis oven (LTF 81782) at 160°C for 3 minutes. All coated fabric samples were conditioned at room temperature for at least 24 hours before testing. The coated fabric samples were then allowed to equilibrate at room temperature/humidity for approximately 12 hours. After which, the water repellency was evaluated using ISO 9865 “Textiles—Determination of water
20 repellency of fabrics by the Bundesmann rain-shower test,” where samples are fixed into the sample holder and showered with water for 10 minutes. Three parameters can be determined from the test: the penetration of water through the fabric, water absorption by the fabric, and visual appearance (5 = best, 1 = worst/complete saturation of fabric surface by water). Water absorption is calculated by: (Final Fabric Weight – Initial Fabric Weight)/Initial Fabric Weight. Durability was measured by conducting
25 Bundesmann testing after multiple wash/dry cycles using a standard residential washer and dryer using TIDE® Free detergent. The wash cycle was set at 90°C followed by a cold-water rinse. The drying cycle was set at high temperature with auto-sense shut-off.

Table 2a. Summary of coating emulsion formulations and test results:

		Solids conc. (%)	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6
Amino silicone emulsions	Ter- Amino1	10					1	
	Ter- Amino2	10	0.5	1	2.5	5.01		
	Ter- Amino3	20						0.5
	Ter- Amino4	10						
	Pen- Amino1	10						
	Pen- Amino2	10						
	Pen- Amino3	10						
	Water Sol. Amino silane	23.0						
Crosslinker	PhobolXan crosslinker	30	2.09	2.09	2.09	2.09	2.09	2.09
SiH emulsion	MEM0075	58.50	4.19	4.11	3.85	3.42	4.11	4.11
Water	DI water	100.00	93.22	92.8	91.56	89.48	92.8	93.3
Bundesmann Water Pickup	0 Wash		10%	16%	5%	12%	6%	20%
	1 Wash		37%	25%	14%	28%	23%	30%
	10 Wash		37%	16%	16%	17%		
N wt% (N as amino)			0.0090	0.0179	0.0448	0.0896	0.0280	0.0123
H wt% (as -SiH)			1.18	1.16	1.08	0.96	1.16	1.16

Table 2b. Summary of coating emulsion formulations and test results:

		Solid conc. (%)	Comp Ex 4	Comp Ex 5	Comp Ex 6	Comp Ex 7	Comp Ex 8
Amino silicone emulsions	Ter-Amino 1	10					
	Ter-Amino 2	10					
	Ter-Amino 3	20					
	Ter-Amino 4	10				1	
	Pen-Amino 1	10	1				
	Pen-Amino 2	10		1			
	Pen-Amino 3	10			1		
	Water Soluble Amino silane	23.0					0.44
Crosslinker	PhobolXAN crosslinker	30	2.09	2.09	2.09	2.09	2.09
SiH emulsion	MEM0075	58.50	4.11	4.11	4.11	4.11	4.11
Water	DI water	100.00	92.8	92.8	92.8	92.8	93.36
Bundesmann Water Pickup	0 Wash		27%	10%	8%	59%	45%
	1 Wash		58%	40%	46%	63%	57%
	10 Wash						
N wt% (N as amino)			0.0210	0.0280	0.0700	0.0036	0.2800
H wt% (as SiH)			1.16	1.16	1.16	1.16	1.16

Table 2c. Summary of coating emulsion formulations and test results:

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		Solids Conc (%)	Ex2	Ex7	Comp Ex1	Comp Ex2	Comp Ex3	Comp Ex9
Amino Silicone emulsion	Ter-Amino2-(2500)	10	1	2.5	1	0	25.03	0
Crosslinker	PhobolXAN	30	2.09	2.09	0	2.09	2.09	2.09
SiH emulsion	MH1107 /PDMS (50:50) blend	58.50						
	OFX-5084	60.50		3.72				4.14
	MEM-0075	58.50	4.11		4.11	4.28		
Water	DI water	100	92.8	91.69	94.89	93.63	72.88	93.77
Bundesmann Water Pickup	0 Wash		16%	36%	31%	59%	56%	86%
	1 Wash		25%	22%	70%	64%	75%	125%
	10 Wash		16%		60%	67%		
N wt% (N as amino)			0.0179	0.0448	0.0224	-	0.4480	-
H wt% (SiH)			1.16	0.58	1.44	1.19	0.00	0.64

Table 2d. Summary of coating emulsion formulations and test results:

		Solids conc. (%)	Ex8	Comp Ex10	Ex9
Amino Silicone Emulsion	Ter-Amino2-(2500)	10	1	0	1
Crosslinker	Phobol XAN	30	2.09	2.09	2.09
SiH Emulsion	MH 1107	60.50			3.85
	MEM-0075	58.50	4.11	4.28	
Additive	Di-propylene glycol		1.25	1.25	0
Water	DI Water	100	91.55	92.38	93.06
Bundesmann Water Pickup	0 Wash		5%	38%	14%
	1 Wash		4%	48%	21%
	10 Wash		6%	65%	23%
Calculated N wt% (N as amino)			0.02	0.00	0.04
Calculated H wt% (as SiH)			1.16	1.20	1.15

CLAIMS:

1. An aqueous emulsion comprising an aqueous continuous phase and a discontinuous oil phase, wherein the discontinuous oil phase comprises the following constituents:

a) 50 to 95 wt% of a polyorganohydrogensiloxane;

b) 0.1 to 45 wt% of an amino-modified polyorganosiloxane comprising at least one amino group located at a terminal position; and

c) 5 to 30 wt% of a blocked isocyanate.

2. The emulsion of claim 1 wherein the discontinuous oil phase comprises:

i) 0.5 to 1.5 H wt% and

ii) 0.004 to 0.2 N wt%.

3. The emulsion of any preceding claim wherein the discontinuous oil phase further comprises constituent d): 0.1 to 10 wt% of a polyorganosiloxane including at least one silanol group.

4. The emulsion of any preceding claim wherein constituent a) has a weight average molecular weight (Mw) of 500 to 6000 AMU and constituent b) has a weight average molecular weight (Mw) of 200 to 10,000 AMU.

5. The emulsion of any preceding claim wherein constituent b) is represented by at least one of the following formulae: i) $(CH_2)_3NH_2$ and ii) $CH_2CHR'''CH_2NHR'''$ where R''' is either H or an alkyl group of 1 to 6 carbon atoms.

6. The emulsion of any preceding claim wherein the discontinuous oil phase comprises the following constituents:

a) 60 to 90 wt% of a polyorganohydrogensiloxane;

b) 1 to 20 wt% of an amino-modified polyorganosiloxane comprising at least one amino group located at a terminal position; and

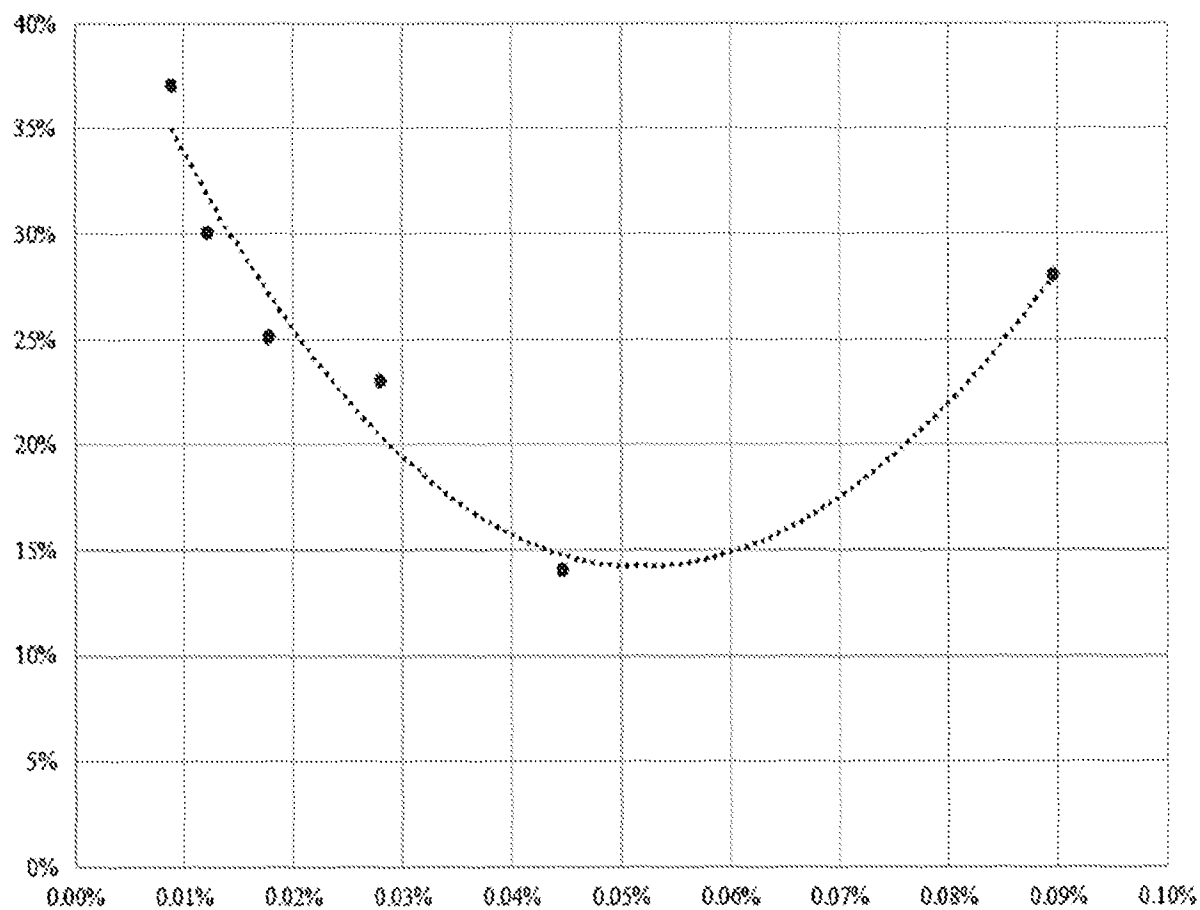
c) 10 to 25 wt% of a blocked isocyanate.

7. The emulsion of any preceding claim further characterized by being substantially free of organic materials comprising ethylenically unsaturated groups.

8. The emulsion of any preceding claim further characterized by being substantially free of platinum-containing catalyst.

9. The emulsion of any preceding claim further characterized by being substantially free of resinous materials.

Figure 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/US2022/072147

A. CLASSIFICATION OF SUBJECT MATTER INV. D06M13/395 D06M15/643 D06M15/653 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) D06M		
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, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 282 656 B1 (CIBA SPEZIALITAETENCHEMIEPFERS [DE]) 11 February 2004 (2004-02-11) paragraph [0007] paragraph [0012] paragraph [0013] claims 1,9	1-9
A	JP 5 947628 B2 (OHARA PALLADIUM KAGAKU KK) 6 July 2016 (2016-07-06) claims 1-17	1-9
☐ 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 22 September 2022		Date of mailing of the international search report 04/10/2022
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 Rella, Giulia

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2022/072147

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