



## (51) International Patent Classification:

**D06M 13/513** (2006.01) **C03C 25/40** (2006.01)  
**D06M 15/647** (2006.01)

## (21) International Application Number:

PCT/US20 14/037 188

## (22) International Filing Date:

7 May 2014 (07.05.2014)

## (25) Filing Language:

English

## (26) Publication Language:

English

## (30) Priority Data:

1372/DEL/2013 8 May 2013 (08.05.2013) IN

(71) Applicants: **DOW CORNING CORPORATION**

[US/US]; 2200 West Salzburg Road, P. O. Box 994, Midland, Michigan 48686 (US). **DOW CORNING INDIA PRIVATE LIMITED** [IN/IN]; Wockhardt Towers, East Wing Level 2, Bandra Kurla Complex Bandra East, Mumbai, Maharashtra (IN).

(72) Inventors: **KAPOOR, Sandeep Virat**; B13, Flat 63, Vijay

Nagari Annex, Ghodbunder Road, Thane 400607 (IN). **MILLER, Scott**; 11078 Thornberry Drive, Freeland, Michigan 48623 (US).

(74) Agents: **PERDOK, Monique M.**, et al; Schwegman, Lundberg & Woessner, P.A., P. O. Box 2938, Minneapolis,

Minnesota 55402 (US).

## (81) Designated States (unless otherwise indicated, for every

kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

## (84) Designated States (unless otherwise indicated, for every

kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

**Published:**

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

## (54) Title: HYDROPHILIC ORGANOSILANES FOR TREATING SURFACES SUCH AS FIBRES

(57) **Abstract:** The present disclosure relates to a fiber comprising: an organosilane having the formula:  $(R^1)_{3-n}SiR^2O(CH_2CH_2O)_a(C_3H_6O)_bR^4$  wherein: n is 1 or 2;  $a \geq 1$ , b may vary from 0 to 30, with the proviso  $a \geq b$ ;  $R^1$  is a hydrocarbon group containing 1 to 12 carbon atoms;  $R^2$  is hydrogen or an alkyl group containing 1 to 6 carbon atoms;  $R^3$  is a divalent hydrocarbon group containing 2 to 12 carbon atoms; and  $R^4$  is hydrogen,  $R^1$ , or an acetyl group. The disclosure also relates to methods of improving at least one of the absorption of moisture, wet strength via anti-fibrillation, and pilling resistance of a surface comprising treating the surface with a composition comprising the aforementioned organosilane. The present organosilane compositions may be useful for treating various surfaces to render them, among other things, more hydrophilic.



## HYDROPHILIC ORGANOSILANES FOR TREATING SURFACES SUCH AS FIBRES

## CLAIM OF PRIORITY

This application claims the benefit of priority to India Application No. 1372/DEL/2013, filed May 8, 2013, the disclosure of which is incorporated herein in its entirety by reference.

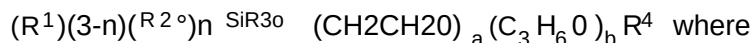
## BACKGROUND

**[0001]** There is an on-going need to develop improved composition treatments to render various surfaces more hydrophilic. Many such surfaces are naturally hydrophobic or have limited ability to absorb water or polar liquids or have these liquids wet the surface. These surfaces may include substrates such as fibers, textiles, plastics, glass, or metals. Treating the surface to render them more hydrophilic may improve properties such as moisture pick up, absorbency, surface wetting, breathability and the like. Many of the hydrophilic surface treatments are based on the physical absorption of the treatment molecules with a surface. As such, the treatments are not robust and are easily washed off or removed.

**[0002]** Thus, there is a need to identify materials that can be used to treat various surfaces to render them hydrophilic. Furthermore, there is a need to identify such hydrophilic materials that permanently (or substantially permanently or semipermanently) modify a surface and more permanently (or substantially permanently or semipermanently) bond to the surface.

## SUMMARY

**[0003]** The present inventors have discovered certain organosilanes that improve the hydrophilicity of treated surfaces. In particular, the present disclosure relates to compositions comprising an organosilane having the formula;



n is 1 or 2,

a ≥ 1, b may vary from 0 to 30, with the proviso a ≥ b,

R<sup>1</sup> is a hydrocarbon group containing 1 to 12 carbon atoms,

R<sup>2</sup> is hydrogen or an alkyl group containing 1 to 6 carbon atoms,

R<sup>3</sup> is a divalent hydrocarbon group containing 2 to 12 carbon atoms,

R<sup>4</sup> is hydrogen, R<sup>1</sup>, or an acetyl group.

**[0004]** The present organosilanes, or compositions containing reaction products derived from the present organosilanes, are particularly useful to treat various surfaces to render them, among other things, more hydrophilic. In particular, the present organosilanes and related compositions are useful to treat textiles, fibers, or hard surfaces to improve, among

other properties, the hydrophilicity of the surface. The treated surface may have improved absorbency, moisture pick up, or surface wettability properties. Furthermore, subsequent surface treatments with the present compositions are more permanent (or substantially more permanent or semipermanent) than many treatments.

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## DESCRIPTION

**[0005]** The present disclosure relates to compositions comprising an organosilane, or reaction products therefrom, having the formula;

$(R^1)(3-n)(R^2O)_nSiR^3O(CH_2CH_2O)_a(C_3H_6O)_bR^4$  where

the subscript "n" is 1 or 2, alternatively n is 2,

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the subscript "a" is equal to or greater than 1,

the subscript "b" varies from 0 to 30,

with the proviso that  $a \geq b$ ,

$R^1$  is a hydrocarbon group containing 1 to 12 carbon atoms,

alternatively  $R^1$  is an alkyl group or a phenyl group,

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alternatively  $R^1$  is methyl,

$R^2$  is hydrogen or an alkyl group contain 1 to 6 carbon atoms,

alternatively  $R^2$  is methyl or ethyl,

alternatively  $R^2$  is ethyl,

$R^3$  is a divalent hydrocarbon group containing 2 to 12 carbon atoms,

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alternatively  $R^3$  contains 2 to 6 carbon atoms,

alternatively  $R^3$  is propylene, or isobutylene,

alternatively  $R^3$  is  $-CH_2CH_2C(CH_3)_2-$

alternatively  $R^3$  is propylene,

$R^4$  is hydrogen,  $R^1$ , or an acetyl group,

25

alternatively  $R^4$  is methyl.

**[0006]** The present organosilanes contain a polyoxyalkylene moiety which is predominately a polyoxyethylene chain as designated by  $(CH_2CH_2O)_a$  in the above formula. The polyoxyalkylene group comprises predominately oxyethylene units ( $C_2H_4O$ ), but may also contain oxypropylene units ( $C_3H_6O$ ), oxybutylene units ( $C_4H_8O$ ), or mixtures thereof. When the polyoxyalkylene group comprises a mixture of ( $C_2H_4O$ ), ( $C_3H_6O$ ), and/or ( $C_4H_8O$ ) units, the oxyalkylene groups are typically randomized with the group but can also be blocked. Typically, the polyoxyalkylene group comprises a majority

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of polyoxyethylene units, as defined on a molar basis and indicated in the above formula by the "a" subscript. The subscript "a" is equal to or greater than 1,

alternatively a may vary from 4 to 30,

alternatively a may vary from 4 to 20,

5 alternatively a may vary from 4 to 10,

alternatively a may vary from 5 to 8,

alternatively a is 7.

**[0007]** The subscript "b" varies from 0 to 30,

alternatively b may vary from 1 to 30,

10 alternatively a may vary from 1 to 20,

alternatively a may vary from 10 to 20,

alternatively a may vary from 15 to 20,

with the proviso that  $a \geq b$ .

**[0008]** In one embodiment, the organosilane has the following average formula;

15  $(\text{CH}_3)(\text{CH}_3\text{CH}_2\text{O})_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_7\text{CH}_3$ .

**[0009]** In one embodiment, the organosilane has the following average formula;

$(\text{CH}_3)(\text{CH}_3\text{O})_2\text{SiCH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_{18}(\text{C}_3\text{H}_6\text{O})_{18}\text{H}$ .

**[0010]** The present organosilanes may be prepared by any method known in the art for preparing organosilanes, or alternatively the organosilanes may be prepared by the process as discussed below.

**[0011]** The organosilane may be prepared by a process comprising reacting:

a) an organosilane of the formula  $(\text{R}^1)_{(3-n)}(\text{R}^2\text{O})_n\text{SiH}$ ,

where  $\text{R}^1$  is a hydrocarbon group containing 1 to 12 carbon atoms,

$\text{R}^2$  is hydrogen or an alkyl group contain 1 to 6 carbon atoms,

25 the subscript n is 1 or 2, alternatively n is 2,

b) a polyoxyalkylene of the formula  $\text{R}^5\text{O}(\text{CH}_2\text{CH}_2\text{O})_a(\text{C}_3\text{H}_6\text{O})_b\text{R}^4$

where the subscript "a" is equal to or greater than 1,

the subscript "b" varies from 0 to 30,

with the proviso that  $a \geq b$ ,

30  $\text{R}^4$  is hydrogen,  $\text{R}^1$ , or an acetyl group,

$\text{R}^5$  is an unsaturated aliphatic hydrocarbon group

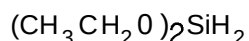
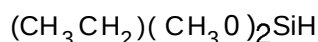
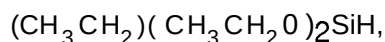
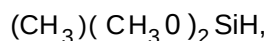
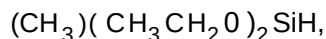
containing 2 to 12 carbon atoms, and

c) a hydrosilylation catalyst.

**[0012]** Component a) is an organosilane of the formula  $(R^1)_{(3-n)}(R^2O)_nSiH$ .

Alternately, it is possible for two or more H groups to be present on the Si atom, in which case  $R^1$  would be zero. In cases such as this, two polyether groups would subsequently be grafted onto the Si atom. Representative examples of organosilanes suitable as

5 component a) in the present process include;



**[0013]** The polyoxyalkylene useful as component b) can be any polyoxyalkylene that is terminated at one molecular chain end with an unsaturated aliphatic hydrocarbon group containing 2 to 12 carbon atoms. The polyoxyalkylene may result from the polymerization

15 of ethylene oxide, propylene oxide, butylene oxide, 1,2-epoxyhexane, 1,2-epoxyoctane, cyclic epoxides such as cyclohexene oxide or exo-2,3-epoxynorborane. The polyoxyalkylene group comprises predominately oxyethylene units ( $C_2H_4O$ ), but may also contain minor amounts of oxypropylene units ( $C_3H_6O$ ), oxybutylene units ( $C_4H_8O$ ), or

mixtures thereof. Typically, the polyoxyalkylene group comprises a majority of oxyethylene units, as defined on a molar basis and indicated in the above formula by the "a" subscript. When present, the oxypropylene units are indicated in the above formula by the "b" subscript. The unsaturated aliphatic hydrocarbon group can be an alkenyl or alkynyl group. Representative, non-limiting examples of the alkenyl groups are shown by the following structures;  $H_2C=CH-$ ,  $H_2C=CHCH_2-$ ,  $H_2C=CHC(CH_3)_2-$

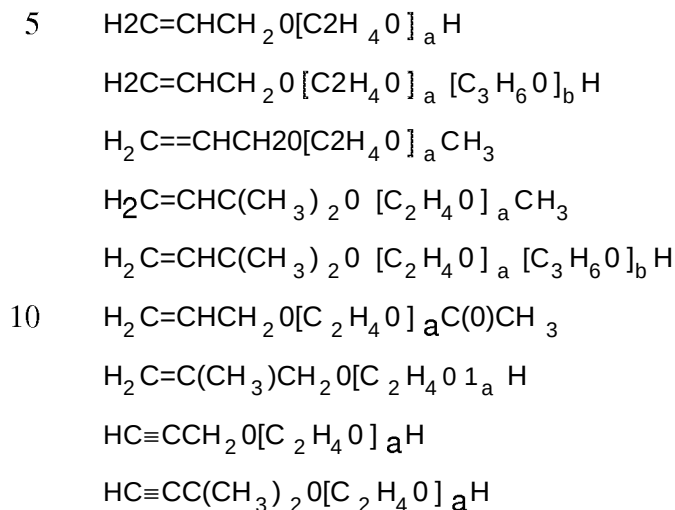
25  $H_2C=C(CH_3)CH_2-$ ,  $H_2C=CHCH_2CH_2-$ ,  $H_2C=CHCH_2CH_2CH_2-$ , and  $H_2C=CHCH_2CH_2CH_2CH_2-$ . Representative, non-limiting examples of alkynyl groups are shown by the following structures;  $HC\equiv C-$ ,  $HC\equiv CCH_2-$ ,  $HC\equiv CCH(CH_3)-$ ,  $HC\equiv CC(CH_3)_2-$ , and  $HC\equiv CC(CH_3)_2CH_2-$ .

**[0014]** In one embodiment,  $R^5$  in the polyoxyalkylene of the formula is  $H_2C=CHCH_2-$ , or

30  $H_2C=CHC(CH_3)_2-$ . The  $H_2C=CHC(CH_3)_2-$  group is a preferred embodiment for preparing the present organosilanes having a greater purity since this hydrocarbon group is not susceptible to rearrangements during the hydrosilylation reaction.

**[0015]** Polyoxyalkylenes having an unsaturated aliphatic hydrocarbon group at one molecular terminal are known in the art, and many are commercially available.

Representative, non-limiting examples of polyoxyalkylenes having an unsaturated aliphatic hydrocarbonyl at one molecular terminal include;



where a and b are as defined above.

**[0016]** Polyoxyalkylenes having an unsaturated aliphatic hydrocarbon group at one molecular terminal are commercially available from numerous suppliers including; NOF (Nippon Oil and Fat, Tokyo, Japan), Clariant Corp. (Switzerland), and Dow Chemical Corp. (Midland, MI). Commercial examples of these materials include Uniox MUS-4 from NOF, Polyglykol AM 450 from Clariant, and SF 400 and SF 443 from Dow Chemical Corp.

**[0017]** The amounts of components a) and b) used in the hydrosilylation reaction may vary. The molar ratio of the SiH units of component a) to the aliphatic unsaturated groups of component b) may range from 10/1 to 1/10, alternatively from 5/1 to 1/5, or alternatively from 1/1 to 1/2. Typically, the amounts of components a) and b) are selected to provide molar excess of the unsaturated groups of component b) to the SiH groups in component a).

**[0018]** Component c) is a hydrosilylation catalyst. The hydrosilylation catalyst may be any suitable Group VIII metal based catalyst selected from a platinum, rhodium, iridium, palladium or ruthenium. Group VIII group metal containing catalysts useful to catalyze curing of the present compositions can be any of those known to catalyze reactions of silicon bonded hydrogen atoms with silicon bonded unsaturated hydrocarbon groups. The preferred Group VIII metal for use as a catalyst to effect cure of the present compositions by hydrosilylation is a platinum based catalyst. Some preferred platinum based hydrosilylation catalysts for curing the present composition are platinum metal, platinum compounds and platinum complexes.

[0019] Suitable platinum catalysts are described in US 2,823,218 (commonly referred to as "Speier's catalyst") and U.S. Patent No. 3,923,705. The platinum catalyst may be "Karstedt's catalyst", which is described in Karstedt's U.S. Patent Nos. 3,715,334 and 3,814,730. Karstedt's catalyst is a platinum divinyl tetramethyl disiloxane complex typically containing about one-weight percent of platinum in a solvent such as toluene. Alternatively the platinum catalyst may be a reaction product of chloroplatinic acid and an organosilicon compound containing terminal aliphatic unsaturation, as described in U.S. Patent No. 3,419,593. Alternatively, the hydrosilylation catalyst is a neutralized complex of platinum chloride and divinyl tetramethyl disiloxane, as described in US 5,175,325.

[0020] Further suitable hydrosilylation catalysts are described in, for example, U.S. Patents 3,159,601; 3,220,972; 3,296,291; 3,516,946; 3,989,668; 4,784,879; 5,036,117; and 5,175,325 and EP 0 347 895 B1.

[0021] The hydrosilylation catalyst may be added in an amount equivalent to as little as 0.001 part by weight of elemental platinum group metal, per one million parts (ppm) of the total reaction composition. Typically, the concentration of the hydrosilylation catalyst in the reaction composition is that capable of providing the equivalent of at least 1 part per million of elemental platinum group metal. A catalyst concentration providing the equivalent of 1 to 500, alternatively 50 to 500, alternatively 50 to 200 parts per million of elemental platinum group metal may be used.

[0022] The reaction effected in the present process is a hydrosilylation reaction, wherein the SiH units of component a) react with the unsaturated aliphatic hydrocarbon group of component b) form an Si-C bond. The reaction may be conducted under those conditions known in the art for effecting hydrosilylations reactions.

[0023] The hydrosilylation reaction can be conducted neat or in the presence of a solvent. The solvent can be an alcohol such as methanol, ethanol, isopropanol, butanol, or n-propanol, a ketone such as acetone, methylethyl ketone, or methyl isobutyl ketone; an aromatic hydrocarbon such as benzene, toluene, or xylene; an aliphatic hydrocarbon such as heptane, hexane, or octane; a glycol ether such as propylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, or ethylene glycol n-butyl ether, a halogenated hydrocarbon such as dichloromethane, 1,1,1-trichloroethane or methylene chloride, chloroform, dimethyl sulfoxide, dimethyl formamide, acetonitrile, tetrahydrofuran, white spirits, mineral spirits, or naphtha.

[0024] The amount of solvent can be up to 70 weight percent, but is typically from 20 to 50 weight percent, said weight percent being based on the total weight of components in

the hydrosilylation reaction. The solvent used during the hydrosilylation reaction can be subsequently removed from the resulting organosilane by various known methods.

[0025] Additional components can be added to the hydrosilylation reaction which are known to enhance such reactions. These components include salts such as sodium acetate which have a buffering effect in combination with platinum catalysts.

[0026] The present disclosure also relates to the organosilane compositions produced by the aforementioned process.

[0027] The present organosilanes contain at least one alkoxy group, as represented by ( $R^2O$ ) in the formula above. As such, the present organosilanes will hydrolyze in aqueous medium, and may further condense to form oligomeric or higher molecular weight polymeric siloxanes. Thus, the present disclosure relates to the reaction products resulting from the hydrolysis and/or condensation of the aforementioned organosilanes.

The present organosilanes, or subsequently produced oligomeric or polymeric siloxanes derived from the organosilanes, may react with hydroxyl functional compounds or surfaces. Since the present organosilanes contain a polyalkylene oxide chain that is predominately ethylene oxide, the present organosilanes may be considered as "hydrophilic". Thus, the present organosilanes may be used to treat various surfaces to impart greater "hydrophilicity" to the surface. Furthermore, the reactivity of the silane moiety may allow the present compositions to bond to various surfaces to provide a longer lasting, more durable hydrophilic treatment.

[0028] When used to treat various surfaces the organosilanes, or reaction products derived therefrom, may be applied neat, as an aqueous solution, as a solution in an organic solvent, or as a component in a multi-component formulation. When applied as a solution, additional components such as acids or bases to buffer the pH may be added to the solution that are known to enhance the hydrolysis and condensation of alkoxysilanes.

[0029] The present organosilanes, or reaction products derived therefrom, may be used to improve the hydrophilicity of various surfaces. The treatments may be longer lasting or more durable than conventional treatments.

[0030] Surfaces suitable for treatment include various hard surfaces such as glass, metals, plastics, minerals, and woods. The surfaces further include fibers, fabrics or textile surfaces. Fibers or textiles that can be treated with the treatment composition include natural fibers such as cotton, silk, linen, wool, flax, kapok, hemp, flax, ramie, alpaca, cashmere, mohair, sisal, abaca, jute, kenaf, camel hair, etc.; regenerated fibers such as lycocell, rayon, acetate, viscose, cupra, polynosic, high wet modulus rayon, solvent-spun cellulose, etc.; synthetic fibers such as polyesters, polyamides, polyacrylonitriles, polyolefins (*e.g.*, polyethylenes and polypropylenes), vinylon, polyvinyl

chloride, promix, fiberglass, aramids, azlons, modacrylics, novoloids, nitrils, spandex, vinal, vinyon etc.; and combinations, and blends thereof. The form of the fibers can include threads, filaments, tows, yarns, woven fabrics, knitted materials, non-woven materials, paper, carpet, and leather. In a further embodiment, the fiber is a cellulosic fiber such as cotton.

**[0031]** The term "polyamide" or "polyamides" refers broadly to any long-chain polymer having recurring amide groups as an integral part of the polymer chain. Examples of polyamides include nylon 6; nylon 6,6; nylon 1,1; and nylon 6,10.

**[0032]** The term "polyester" refers broadly to any long-chain polymer having recurring ester groups. Examples of polyesters include aromatic polyesters, such as polyethylene terephthalate (PET), polypropylene terephthalate, polybutylene terephthalate (PBT), polytrimethylene terephthalate (PTT), and polytriphenylene terephthalate, and aliphatic polyesters, such as polylactic acid (PLA) and polyglycolide and the like.

**[0033]** The term "polyolefin" includes, for example, polypropylene, polyethylene, and combinations thereof.

**[0034]** "Polyaramid" includes, for example, poly-p-phenyleneterephthalamid (*i.e.*, Kevlar™), poly-m-phenyleneterephthalamid (*i.e.*, Nomex™), and combinations thereof.

**[0035]** Other suitable fibers include, but are not limited to, the fibers disclosed in Published U.S. Patent Appl. Nos. 2012/0277356; 2011/0015310; 2008/0153735; and 2002/0160675, the entireties of all of which are incorporated by reference as if fully set forth herein.

**[0032]** The fiber treatment composition comprising the present organosilanes, oligomeric or polymers derived therefrom, can be applied to the fiber and/or textile during making the fibers or textiles, or later via a post application process. After application, carriers (if any) can be removed from the treatment composition for example by drying the composition at ambient or elevated temperature. The amount of treatment composition applied to the fibers and textiles is typically sufficient to provide 0.1 to 15 weight percent of the composition on the fibers and textiles, based on their dry weight, preferably in an amount of 0.2 to 5 weight percent based on the dry weight of the fiber or textile.

**[0036]** In some embodiments, when fibers, textiles or surfaces are treated with or comprise the present organosilanes, or reaction products derived therefrom, the present organosilanes, or reaction products derived therefrom, improve the absorption of moisture, improve wet strength via anti-fibrillation, and/or effect pilling minimization (*i.e.*, the fiber or textiles resist pilling) of the fibers, textiles or surfaces. Pilling of textiles or fibers is undesirable because it can result in uneven dyeing, unsightly appearance and texture, reduced strength, etc. In some embodiments, the moisture absorption of fibers, textiles or

surfaces is improved by at least 20%, e.g., at least 30%, at least 40%, at least 50%, from about 20% to about 50%, from about 30% to about 45%, from about 35% to about 45% or from about 35% to about 42%, relative to fibers, textiles or surfaces that are not treated with the present organosilanes, or reaction products derived therefrom.

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## EXAMPLES

[0037] The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention. All percentages are in wt. %. All measurements were conducted at 23°C unless indicated otherwise.

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### Example 1

#### Preparation of Poly (EO) Methyl 3-(Methyldiethoxysilyl) Propyl Ether

[0038] PG SF-Allyl E07-Me (463.73 g; UNIOX MUS-4 from NOF Corporation) and sodium acetate (0.05 g; from Fisher Biotech) were loaded in a 2 L 3-necked round-bottomed flask (RBF) fitted with a crescent-shaped paddle stirring rod, a Claisen adaptor itself fitted with a water cooled condenser and a 250 mL additional funnel loaded with methyldiethoxysilane (136.52 g; from Gelest, Inc), and a thermometer adaptor itself fitted with a thermal couple, all under nitrogen purge. The reaction mixture was heated to 60 °C when 20 wt.% or 28 g of methyldiethoxysilane was fed in the RBF immediately followed by the addition of 1% Dow Corning® 2-0707 INT catalyst in IPA (-400 µL or 6 ppm). The exotherm observed instantaneously was 18 °C. The remaining methyldiethoxysilane in the additional funnel was being dispensed into the RBF at ~1.21 g/min rate while temperature was set at 80 °C and being maintained below 85 °C throughout the addition. The second charge of 1% Dow Corning® 2-0707 INT catalyst in IPA (-500 µL or 7 ppm) was done after the first hour of silane addition and - 5 °C exotherm was seen. When all methyldiethoxysilane was in the RBF, the temperature was set at 85 °C set point and the third addition of 1% Dow Corning® 2-0707 INT catalyst in IPA (-500 µL or 7 ppm) was added while no exotherm was observed. The product mixture was then allowed to reflux for another hour for hydrosilylation completion. Once the reaction was determined to be done, residual SiH was measured by IR which was 34 ppm at peak  $2150\text{ cm}^{-1}$ . On the following day, the Claisen adapter was replaced by a water cooled condenser fitted with a

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250 mL round-bottomed flask. The set-up was connected to vacuum for stripping. The product mixture was stripped for 1 h under 10-40 mmHg vacuum pressure at 90 °C. The final residual SiH content measured by IR was 4 ppm at 2150 cm<sup>-1</sup>. The final finished product was pressure-filtered on 20 µm sized filter paper to remove sodium acetate.

5 **Example 2**

Preparation of Poly (EO) Methyl 3-(Methyldimethoxysilyl) Propyl Ether

[0039] PG SF-Allyl E07-Me (489.378 g; UNIOX MUS-4 from NOF Corporation) and sodium acetate (0.1 g; from Fisher Biotech) were loaded in a 2 L 3-necked round-bottomed flask (RBF) fitted with a crescent-shaped paddle stirring rod, a Claisen adaptor itself fitted with a water cooled condenser and a 250 mL additional funnel loaded with Dow Corning® Z-6701 Silane (110.622 g), and a thermometer adaptor itself fitted with a thermal couple, all under nitrogen purge. The reaction mixture was heated to 45 °C when 10 wt.% or 11 g of Z-6701 silane was fed in the RBF immediately followed by the addition of 1% Dow Corning® 2-0707 INT catalyst in IPA (-400 µL or 6 ppm). The exotherm observed instantaneously was 2-3 °C. The remaining Z-6701 in the additional funnel was being dispensed into the RBF at ~1.67 g/min rate while temperature set at 53 °C plus 2 °C exotherm was maintained throughout the addition. When all Z-6701 was in the RBF, the temperature of mixture dropped back to the 53 °C set point and hence, there was a second addition of 1% Dow Corning® 2-0707 INT catalyst in IPA (-500 µL or 7 ppm). The mixture was then held for another 2h to allow reaction gone for completion in which the third addition of 1% Dow Corning® 2-0707 INT catalyst in IPA (-500 µL or 7 ppm) were made after the first hour of reflux. A constant 2 °C exotherm was observed after each time the catalyst was added and had lasted for 1h except for the last addition which lasted only 30 minutes. Once the reaction was determined to be done, residual SiH was measured by IR which was 35 ppm at peak 2150 cm<sup>-1</sup>. On the following day, the Claisen adapter was replaced by a water cooled condenser fitted with a 250 mL round-bottomed flask. The set-up was connected to vacuum for stripping. The product mixture was stripped for 1h under 10-20 mmHg vacuum pressure at 60 °C. The final residual SiH content measured by IR was 4 ppm at 2150 cm<sup>-1</sup>. The final finished product was pressure-filtered on 20 µm sized filter paper to remove sodium acetate.

**Example 3**

Preparation of Poly (EO) Hydroxy! 3-(Methyldiethoxysilyl) Propyl Ether

[0040] PG SF-Allyl E07-OH (191.85 g; from Dow Chemical Company) and sodium acetate (0.05 g; from Fisher Biotech) were loaded in a 500 mL 3-necked round-bottomed flask (RBF) fitted with a crescent-shaped paddle stirring rod, a Claisen adaptor itself fitted

with a water cooled condenser and a 250 mL additional funnel loaded with methyldiethoxysilane (58.67 g from Gelest, Inc), and a thermometer adaptor itself fitted with a thermal couple, all under nitrogen purge. The reaction mixture was heated to 60 °C when 10 wt.% or 6 g of methyldiethoxysilane was dispensed in the RBF immediately followed by the addition of 1% Dow Corning® 2-0707 INT catalyst in IPA (-230 µL or 8 ppm). The exotherm observed instantaneously was 7 °C. The remaining methyldiethoxysilane in the additional funnel was being dispensed into the RBF at -0.88g/min rate while temperature was set at 67 °C and being maintained at -75 °C throughout the addition. When all methyldiethoxysilane was added to the RBF, the temperature was set at 75°C to reflux for an hour to allow the reaction to go to completion. The reaction mixture was cooled down to 60 °C and 159 ppm of residual SiH was obtained by IR at peak 2150 cm<sup>-1</sup>. A second addition of 1% Dow Corning® 2-0707 INT catalyst in IPA (-50 µL or ~ 1.7 ppm) was charged to the reaction mixture, however, no exotherm was detected. The reaction temperature was increased to 80 °C and refluxed for an hour. The residual SiH was measured 126 ppm. On the following day, the product mixture was transferred to a 1 L round-bottomed flask for rotary evaporation. Some material was stripped out while the vacuum pressure was at -3-4 mmHg and the water bath was at 80 °C. This process lasted for two hour and the final product has 13 ppm of SiH left. The final product was pressure-filtered on 20 µm filter paper to remove sodium acetate.

#### **Example 4**

##### *Preparation of Poly (EO) Hydroxy! 3-(Methyldimethoxysilyl) Propyl Ether*

**[0041]** PG SF-Allyl E07-OH (80.58 g; from Dow Chemical Company) and sodium acetate (0.03 g; from Fisher Biotech) were loaded in a 250 mL 3-necked round-bottomed flask (RBF) fitted with a crescent-shaped paddle stirring rod, a Claisen adaptor itself fitted with a water cooled condenser and a 250 mL additional funnel loaded with Dow Corning® Z-6701 Silane (20.06 g), and a thermometer adaptor itself fitted with a thermal couple, all under nitrogen purge. The reaction mixture was heated to 45.6 °C when 10 wt.% or 2 g of Dow Corning® Z-6701 Silane was dispensed in the RBF immediately followed by the addition of 1% Dow Corning® 2-0707 INT catalyst in IPA (-60 µL or 5 ppm). The exotherm observed instantaneously was 0.9 °C. The remaining Dow Corning® Z-6701 Silane in the additional funnel was being dispensed into the RBF at -0.21g/min rate while temperature was set at 50 °C and being maintained at -49-51 °C throughout the addition. When all methyldiethoxysilane was added to the RBF, the temperature was set at 57 °C to reflux for 2.5 hours to allow reaction gone for completion. The reaction mixture

was cooled down to room temperature and 121 ppm of residual SiH was obtained by IR at peak  $2150\text{ cm}^{-1}$ . On the following day, extra PG SF-Allyl E07-OH (5.48 g from Dow Chemical Company) was added to the reaction mixture while holding the reaction at  $57\pm 1^\circ\text{C}$  for 4.5 h, resulting in 20 ppm residual SiH. The Claisen adapter was replaced by a water cooled condenser fitted with a 250 mL round-bottomed flask the day after. The set-up was connected to vacuum for stripping. The product mixture was stripped for 3 h under 10-50 mmHg vacuum pressure at  $80^\circ\text{C}$ . The final residual SiH content measured by IR was still 20 ppm at  $2150\text{ cm}^{-1}$ . The final finished product was pressure-filtered on 20  $\mu\text{m}$  sized filter paper to remove sodium acetate.

#### Example 5

##### Preparation of Poly (EO) Acetate 3-(Methyldimethoxysilyl) Propyl Ether

[0042] PG SF-Allyl E07-Ac (247.77g) and sodium acetate (0.05 g from Fisher Biotech) were loaded in a 500 mL 3-necked round-bottomed flask (RBF) fitted with a crescent-shaped paddle stirring rod, a Claisen adaptor itself fitted with a water cooled condenser and a 250 mL additional funnel loaded with Dow Corning® Z-6701 Silane (52.98 g), and a thermometer adaptor itself fitted with a thermal couple, all under nitrogen purge. The reaction mixture was heated to  $47^\circ\text{C}$  when 10 wt.% or 5 g of Dow Corning® Z-6701 Silane was dispensed in the RBF immediately followed by the addition of 1% Dow Corning® 2-0707 INT catalyst in IPA ( $-270\text{ }\mu\text{L}$  or 8 ppm). The exotherm observed instantaneously was  $1\text{-}2^\circ\text{C}$ . The remaining Dow Corning® Z-6701 Silane in the additional funnel was being dispensed into the RBF at  $-0.79\text{ g/min}$  rate while temperature was set at  $54^\circ\text{C}$  and being maintained below  $58^\circ\text{C}$  throughout the addition. When all Dow Corning® Z-6701 Silane was added to the RBF, the temperature was set at  $54^\circ\text{C}$  to reflux for an hour to allow reaction gone for completion. 540 ppm of residual SiH was obtained by IR at peak  $2150\text{ cm}^{-1}$ . Another hour of reflux was proceeded and the residual SiH was measured 300 ppm. On the following day, the Claisen adapter was replaced by a water cooled condenser fitted with a 250 mL round-bottomed flask. The set-up was connected to vacuum for stripping. The product mixture was stripped for a total of 3 h under 20-80 mmHg vacuum pressure at  $62^\circ\text{C}$ . The final residual SiH content measured by IR was 28 ppm at  $2150\text{ cm}^{-1}$ . The final finished product was pressure-filtered on 20  $\mu\text{m}$  sized filter paper to remove sodium acetate.

#### Example 6

[0043] To a three neck round bottom flask was added 0.20g (2.4mmoles) of sodium acetate and 171.8g (0.29moles) of a polyether containing an allyl end, approximately 12 ethylene oxide units and capped with acetate. Next, 28.2g (0.21 moles) of methyl diethoxy

silane (MDES) was added to the flask. With stirring under N<sub>2</sub>, the mixture was heated to 75°±5°C and then 3ppm of Pt catalyst was added. After a small exotherm (<1.0°±1 °C) the mixture was maintained at 85°±5°C for 6 hours. At this point the reaction was 98.9% complete as measured by SiH consumption via FTIR. The mixture was stripped of volatiles by heating to 120°±5°C/5-1 OmmHg for 4 hours. Finally, the mixture was cooled to room temperature and filtered through Celite that was supported on a Nylon filter to yield 167g (83% yield) of a light yellow oil. Characterization of this material indicated that the desired product had been obtained as evidenced by the single peak in the <sup>29</sup>Si NMR at approximately -5.6ppm.

#### Example 7

[0044] To a three neck round bottom flask was added 0.25g (3.0mmoles) of sodium acetate and 189.3g (97mmoles) of a polyether containing an allyl end, approximately 18 ethylene oxide units and 18 propylene oxide units and capped with acetate. Next, 10.9g (81 moles) of methyl diethoxy silane (MDES) was added to the flask. With stirring under N<sub>2</sub>, the mixture was heated to 75°±5°C and then 4ppm of Pt catalyst was added. After a small exotherm (<1.0°±1 °C) the mixture was maintained at 85°±5°C for 3 hours. At this point the reaction was 99.6% complete as measured by SiH consumption via FTIR. The mixture was stripped of volatiles by heating to 120°±5°C/5-1 OmmHg for 5 hours. Finally, the mixture was cooled to room temperature and filtered through Celite that was supported on a Nylon filter to yield 153g (76% yield) of a light yellow oil. Characterization of this material indicated that the desired product had been obtained as evidenced by the single peak in the <sup>29</sup>Si NMR at approximately -5.6ppm.

#### Example 8

[0045] To a three neck round bottom flask was added 0.25g (3.0mmoles) of sodium acetate and 168.7g (0.31 moles) of a polyether containing an allyl end, approximately 12 ethylene oxide units and was not capped. Next, 31.4g (0.24moles) of methyl diethoxy silane (MDES) was added to the flask. With stirring under N<sub>2</sub>, the mixture was heated to 75°±5°C and then 3ppm of Pt catalyst was added. After a small exotherm (<1.0°±1 °C) the mixture was maintained at 85°±5°C for 3 hours. At this point the reaction was 99.5% complete as measured by SiH consumption via FTIR. The mixture was stripped of volatiles by heating to 120°±5°C/5-1 OmmHg for 4 hours. Finally, the mixture was cooled to room temperature and filtered through Celite that was supported on a Nylon filter to yield 149g (74% yield) of a light yellow oil. Characterization of this material indicated that the desired product had been obtained as evidenced by the single peak in the <sup>29</sup>Si NMR at approximately -5.6ppm.

#### Example 9

[0046] The following tests were conducted to evaluate the performance of the present organosilanes for their ability to improve the water absorption of cellulosic fibers.

**Fiber Treatment Test:** 6 of the 10 cm x 10 cm non-woven 100% cotton fiber weighted 120 gram per square meter (gsm) manufactured by PurCotton™ were used in testing the organosilane of Example 2 (poly (EO) Methyl 3-(Methyldimethoxysilyl) Propyl Ether. A circle with area  $\sim 13 \text{ cm}^2$  was drawn on each fiber sheet, 2 of which were applied the **Example 2** organosilane neat in that whole circle area, 2 other sheets were applied with  $\sim 29.7\%$  the organosilane of **Example 2** in DI water while the last 2 sheets served as control experiment and were untreated. The coated area was then dried at room temperature by blowing air to it for 5 min each. A syringe pump (Model: Cole Parmer 74900 series) was utilized since it could be programmed to dispense liquid at a constant rate and the syringe was filled with DI water. The time for the circle area to fill with liquid by spreading was recorded. It should be recognized that some of the add-on weight to the cloth could include silane + residual moisture that was not removed during the drying process. The results from these tests are summarized below in Table 1.

#### Example 10

[0047] To a 500ml three neck round bottom flask was added 188.9g (98.2mmoles) of a polyether that contains 18 ethylene oxide units, 18 propylene oxide units and is capped with a 3,3-dimethyl-1-propenyl group on one end. The polyether is heated to  $40^\circ \pm 3^\circ \text{C}$  and approximately 5% of total volume of methyldimethoxysilane is added (total volume is 15.7g, 148mmoles) to the reaction vessel via an addition funnel. Next, platinum catalyst is added so that the final concentration is 5ppm in the final mixture, and an exotherm is observed. After the exotherm is complete the remaining methyldimethoxysilane is added from the addition funnel at a rate so that the temperature of the mixture remains below  $50^\circ \text{C}$ . Upon the addition of all the methyldimethoxysilane, the reaction vessel is maintained at  $50^\circ \pm 3^\circ \text{C}$  for 3 hours. Next, the volatiles are removed from the product by increasing the flow of  $\text{N}_2$  through the reaction vessel. A low viscosity liquid is obtained. Analysis by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR and FTIR confirms that the desired material has prepared and the level of unreacted polyether is less than 1% on a molar basis and no residual  $\text{SiH}$  is present.

**Table 1**

| Cloth No. | Cloth Weight (g) | Cloth weight total after treatment and dried (g) | Material Applied on Cloth (g) | Time of wetting-absorption (min'sec") | Remark                                           |
|-----------|------------------|--------------------------------------------------|-------------------------------|---------------------------------------|--------------------------------------------------|
| 1         | 1.16             | 1.55                                             | 0.39                          | 46"45                                 | Example 2 applied neat                           |
| 2         | 1.2              | 1.55                                             | 0.35                          | 45"73                                 | Example 2 applied neat                           |
| 3         | 1.15             | 1.61                                             | 0.46                          | 57"96                                 | Example 2 applied as a 29.7wt % aqueous solution |
| 4         | 1.21             | 1.61                                             | 0.40                          | 59"52                                 | Example 2 applied as a 29.7wt % aqueous solution |
| 5         | 1.16             | n/a                                              | 0.00                          | 1'16"64                               | No treatment                                     |
| 6         | 1.21             | n/a                                              | 0.00                          | 1'11"66                               | No treatment                                     |

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- 5 **[0048]** Similar tests were performed using the organosilane from Example 1 with the same procedure. There were a total of two experiments done for each batch of material in order to ensure the results given were robust. The summary of the entire application screening test is shown in Table 2 below.

10 **Table 2**

| Batch Number                                     | Test 1 (sec) |       | Test 2 (sec) |       | Average Time (sec) | % Average Time Difference |
|--------------------------------------------------|--------------|-------|--------------|-------|--------------------|---------------------------|
| Example 1 applied neat                           | 46.45        | 45.73 | 41.81        | 42.50 | 44.12              | 41                        |
| Example 1 applied neat                           | 40.26        | 40.80 | 44.83        | 46.57 | 43.12              | 42                        |
| Example 1 applied as a 29.7wt % aqueous solution | 57.96        | 59.52 | 47.60        | 46.40 | 52.87              | 29                        |
| Example 1 applied as a 29.7wt % aqueous solution | 47.81        | 46.57 | 49.52        | 50.48 | 48.60              | 35                        |
| Untreated fiber                                  | 76.46        | 71.66 | 75.42        | 74.23 | 74.44              | 0                         |

**[0049]** Embodiments of the invention described and claimed herein are not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are

intended as illustration of several aspects of the disclosure. Any equivalent embodiments are intended to be within the scope of this disclosure. Indeed, various modifications of the embodiments in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

**[0050]** The invention has been described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

**[0051]** As used herein and in the appended claims, the singular forms "a," "an," and "the" include plural reference unless the context clearly dictates otherwise. Thus, for example, a reference to "a reactor" includes a plurality of reactors, such as in a series of reactors. In this document, the term "or" is used to refer to a nonexclusive or, such that "A or B" includes "A but not B," "B but not A," and "A and B," unless otherwise indicated.

**[0052]** Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range of "about 0.1% to about 5%" or "about 0.1% to 5%" should be interpreted to include not just about 0.1% to about 5%, but also the individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range. The statement "about X to Y" has the same meaning as "about X to about Y," unless indicated otherwise. Likewise, the statement "about X, Y, or about Z" has the same meaning as "about X, about Y, or about Z," unless indicated otherwise.

**[0053]** In the methods described herein, the steps can be carried out in any order without departing from the principles of the invention, except when a temporal or operational sequence is explicitly recited. Furthermore, specified steps can be carried out concurrently unless explicit claim language recites that they be carried out separately. For example, a claimed step of doing X and a claimed step of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

The term "about" as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range.

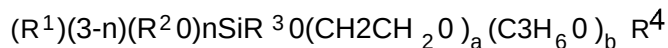
**[0054]** The term "substantially" as used herein refers to a majority of, or mostly, as in at least about 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, or at least about 99.999% or more.

All publications, including non-patent literature (e.g., scientific journal articles), patent application publications, and patents mentioned in this specification are incorporated by reference as if each were specifically and individually indicated to be incorporated by reference.

### Claims

1. A fiber comprising:

an organosilane having the formula:



wherein:

n is 1 or 2;

a ≥ 1, b may vary from 0 to 30, with the proviso a ≥ b;

R<sup>1</sup> is a hydrocarbon group containing 1 to 12 carbon atoms;

R<sup>2</sup> is hydrogen or an alkyl group containing 1 to 6 carbon atoms;

R<sup>3</sup> is a divalent hydrocarbon group containing 2 to 12 carbon atoms; and

R<sup>4</sup> is hydrogen, R<sup>1</sup>, or an acetyl group.

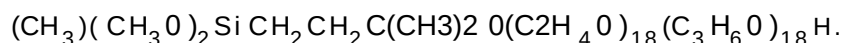
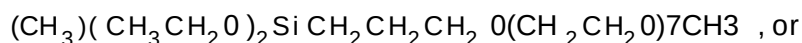
2. The fiber of claim 1 where n is 2.

3. The fiber of any of the above claims where a ranges from 4 to 30.

4. The fiber of any of the above claims where R<sup>1</sup> is methyl and R<sup>2</sup> is methyl or ethyl.

5. The fiber of any of the above claims where R<sup>3</sup> is propylene or -CH<sub>2</sub>CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>-.

6. The fiber of claim 1 where the organosilane has the average formula



7. The fiber of claim 1, wherein the fiber resists pilling.

8. A method for improving at least one of the absorption of moisture, wet strength via anti-fibrillation, and pilling resistance of a surface comprising treating the surface with a composition comprising an organosilane having the formula:



wherein:

n is 1 or 2;

a ≥ 1, b may vary from 0 to 30, with the proviso a ≥ b;

$R^1$  is a hydrocarbon group containing 1 to 12 carbon atoms;  
 $R^2$  is hydrogen or an alkyl group containing 1 to 6 carbon atoms;  
 $R^3$  is a divalent hydrocarbon group containing 2 to 12 carbon atoms; and  
 $R^4$  is hydrogen,  $R^1$ , or an acetyl group.

9. The method of claim 8, wherein the moisture absorption of the surface is improved from about 20% to about 50% relative to a surface that is not treated with the organosilane of claim 16.
10. The method of claims 8-9, wherein the surface comprises a natural fiber.
11. The method of claim 10, wherein the natural fiber comprises cotton, silk, linen, wool, flax, kapok, hemp, flax, ramie, alpaca, cashmere, mohair, sisal, abaca, jute, kenaf, camel hair, etc.; regenerated fibers such as lyocell, rayon, acetate, viscose, cupra, polynosic, high wet modulus rayon, solvent-spun cellulose or combinations or blends thereof.
12. The method of claim 11, wherein the natural fiber comprises cotton.

## INTERNATIONAL SEARCH REPORT

International application No

PCT/US2014/037188

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. D06M13/513 D06M15/647 C03C25/40  
 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 C23C B27K C03C C04B

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

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

EPO-Internal , WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| X         | DATABASE WPI<br>Week 198319<br>Thomson Scienti fic, London, GB;<br>AN 1983-45023K<br>XP0Q2728998,<br>- & JP S58 54080 A (MITSUBISHI RAYON CO<br>LTD) 30 March 1983 (1983-03-30)<br>abstract<br>col umn 1<br>-----<br>- / - - | 1-12                  |



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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search

28 August 2014

Date of mailing of the international search report

09/09/2014

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

Fiocco, Marco

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/US2014/037188

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                       |                       |
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Information on patent family members

International application No

PCT/US2014/037188

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| -----                                     |                     |                             |                               |
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|                                           |                     | WO 2013127775 AI 06-09-2013 |                               |
| -----                                     |                     |                             |                               |