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(54) A PROCESS FOR PREPARING OF COTTON TEXTILES HAVING SELF-CLEANING AND WASHING RESISTANT PROPERTIES

(57) The invention relates to a process for the preparation of self-cleaning wash-resistant and air-permeable superhydrophobic and oleophobic cotton textiles. The coating is applied to the surface of the cotton textile and results in sliding angles for water that are lower than 10 degrees, even after 10 washings. The coatings consist of differently sized premade siloxane particles and particles grown *in-situ* in the presence of cotton textiles. The *in-situ* preparation of siloxane particles provides a bi-hierarchical surface roughness and a good connection between the siloxane particles and the textile, which is further strengthened by the use of fluorinated alkoxy silanes. The combination of the proposed solution enables improved wash-resistant properties for the coatings.

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Description

Field of invention

[0001] The invention relates to a process for the preparation of self-cleaning wash-resistant and air-permeable superhydrophobic and oleophobic cotton textiles, The coating is applied *in-situ* to the surface of the cotton textile. This resulted in water sliding angles smaller than 10 degrees even after ten washings.

Background of the invention

[0002] Cotton fibres are natural cellulosic fibres that are widely used as a raw material for the manufacturing of various textile products. Their attractiveness is directly related to the chemical structure and morphological characteristics of the cellulosic fibres. These fibres are pleasant to the touch and exhibit a hydrophilic character to ensure product comfort, respiratory activity, and aesthetic appearance, The fibres are biodegradable, which, in terms of ecology and sustainable development, is their major advantage over synthetic fibres.

[0003] Cotton fibres have been gaining attention as components in the production of specialized high-tech textiles; this is due to their advantages and successfully outcompeting ecologically less acceptable synthetic fibres. Such high-tech materials include bio-mimetic self-cleaning textiles, which must ensure simultaneous wetting resistances for a variety of polar and non-polar liquids, in addition to air and water vapour permeabilities. These requirements can only be achieved by careful chemical modifications of the cellulosic fibre surface.

[0004] The use of textiles that are easy on the skin and, at the same time, offer the user welfare and protection against the environment arc very common in everyday life. Such fabrics are on the one hand suitable for sports and leisure (e.g., obstacle courses, mountaineering, cross-country running, downhill skiing, motocrossing, mountain biking) and, on the other hand, serve as protective technical textiles. Technical textiles are used by professionals who frequently encounter water and soilage (e.g., butchers, plumbers, hairdressers, bricklayers, fine mechanics or firefighters). All of the mentioned users are also likely to be physically active, which results in sweating and may also stain the textiles. In such cases, it is recommended that the textile allows for the passage of body sweat, so that end users are not completely drenched with sweat for long periods.

[0005] Superhydrophobicity and oleophobicity are basic properties of a solid surface that are dependent on the chemical composition and the surface roughness of a substrate. Chemical composition determines surface free energy and, consequently, surface wettability. Micro-and nanostructured surfaces can further influence wettability, if the roughness is inappropriate.

[0006] EP 2,589,578 A1 patent application shows that a reduction in surface wettability can be achieved by the derivatives of catechols. In addition to a low surface free energy, the fluorinated catechol derivatives have been known to form vesicles (70 nm) or capsules with a hollow core 200 to 1000 nm in size, which increase microstructure. This combination of features enables the preparation of surfaces, such as carbon nanotubes, iron oxide nanoparticles and mesoporous silica, with water-repellent properties.

[0007] In US Patent Application 20020192385A1 Jenkner et al. describe a method for the application of hydro- and oleophobic fluorinated coatings on polymeric substrates pre-treated by physical methods (plasma, corona discharge, and electromagnetic radiation). In the next step, fluorinated silanes are applied to the activated surface with bonding promoters (metal oxides).

[0008] U.S. Patent 7,732,497 B2 discloses the use of pre-prepared surface-treated particles for the preparation of a liquid repellent layer. A minimum of two particle sizes are used, and at least one particle surface is further functionalized by alkyl chains.

[0009] US 7,985,475 B2 patent describes the preparation of superhydrophobic coatings by placing well-defined silicon nano-fibres on a surface coated with exogenous hydrophobic or amphiphilic materials. In the patent, fluorinated molecules are also used to achieve hydrophobic properties.

[0010] U.S. Patent 8,541,056 B2 discloses the preparation of water-repellent textiles by mechanical abrasion. The previously abraded substrates are coated with colloidal dispersions of various metal oxides (commercial products) and cross-linked using isocyanate compounds, which usually form at the end of polyurethane bonds.

[0011] The preparation of water-repellent textiles is also possible by integrating fumed SiO_2 particles with the fibres through the use of binders without formaldehyde, as indicated in US patent application 20110287245. Alkali metal salts of phosphorous are used as a catalyst for polymerization, which allows the matrix and the cellulose fibres to bond together. A method for preparing water-repellent coatings also includes the use of SiO_2 particles prepared from dimethyldichlorosilanes and coated with polycarboxylic acids.

[0012] US patent application 20110250422A1 discloses the use of a porous matrix built from fluorosilanes for the preparation of hydro- and oleophobic coatings. The main significance of the coating, given the pore size and the distribution of pores by volume, is its suitable surface roughness in combination with a low surface free energy that are provided by the building blocks of the porous structures. The coatings can also be used to reduce adhesion, which provides the surfaces with a self-cleaning effect.

[0013] Bae et al. (Colloid Interface Sci., 337 (2009) 170-175) prepare a water-repellent layer on textiles, mainly because of their good qualities, such as tenderness, comfort, biodegradability, and low cost, as well as the possibility of applying the layer to casual wear. To produce the aforementioned textile coatings, the authors combine SiO_2 particles with a chemical-based low-cost water repellent. By using this method, they obtain a static contact angle for water of 140°. Oil repellent properties, which are acquired by measuring the static contact angles for a series of n-alkanes (C6-C25), are not specified.

[0014] The preparation of cotton textiles with high static contact angles for water (up to 150°) and n-hexadecane (near 120°) is possible with surface finishes prepared from alkoxy-functionalized PDMS in combination with perfluorinated alkoxy silanes. This low surface free energy of these coatings prevents the adhesion of bacteria to the surface, thereby imparting passive antimicrobial properties to cotton textiles (VilČnik A. et al Langmuir, 25 (2009) 5869-5880). Ma et al. (J. Colloid Interface Sci., 392 (2013) 194-200) report on the use of a single-stage emulsion to prepare monodisperse polysiloxane spherical particles surface-functionalized with a variety of organic groups. In addition to water-repellency, the authors analyse the influence of the organic groups on the properties of the coatings, e.g., thermal stability, The purpose of generating particles on the surface of cotton was to imitate the surface structure of a lotus leaf.

[0015] Stöber et al. (J. Colloid Interface Sci., 26 (1968) 62-69) previously reported on the mechanism of amorphous SiO_2 particle formation and proposed a series of chemical reactions that resulted in the controlled growth of uniformly sized spherical particles.

[0016] Though modified cotton fabrics provide high contact angles for water and oil, it is necessary to wash technical cotton textiles for hygienic reasons. However, we do not want to lose the superhydrophobic, oleopllohic, and self-cleaning properties that prevent the retention of various emulsions on the surface of cotton fabrics during the washing process. According to the literature, there are no reports on washing resistant cotton textiles prepared by SiO_2 spherical particles, nor is there mention of the *in-situ* modification of cotton by SiO_2 particles for the production of the aforementioned textiles.

[0017] The present invention relates to a process that enables the preparation of wash-resistant, air-permeable superhydrophobic, oleophobic, and self-cleaning coatings from a variety of organic-modified silanes. In the first stage of the process, *in-situ* monodisperse particles of SiO_2 are formed with the use of silanes. In the next stage, the formed particles are chemically bonded to the surface of cotton textiles, which acquire a low surface energy. An appropriate surface roughness, resulting from the chemical bonding between the SiO_2 spherical particles and the cotton fibre surface, is maintained on the cotton even after four washing cycles according to ISO 105-C06: 1994 (E), which is equivalent to twenty washings in a household washing machine. The SiO_2-cotton chemical links are further consolidated by the porous structure of hardened perfluoro-modified silanes. The process enables the preparation of finishes for cotton-based textiles and products that require durable superhydrophobic and oleophobic properties in combination with a highly breathable textile, which provides air and water vapour (perspiration) permeation.

Summary of the invention

[0018] According to the invention, the preparation of wash-resistant textiles is conducted using a wet process without compounds that release toxic formaldehyde. The process allows the chemical bonding of spherical SiO_2 particles to the cotton fibre surface, providing an appropriate surface roughness to the fabrics and is responsible for the following characteristics:

- superhydrophobicity, as determined by obtaining static contact angles for water (a 5 μL water droplet) between 160 and 170° for the finished surface of textiles and remaining as such after several consecutive washings;
- superoleophobicity, by measuring static contact angles for n-hexadecane (a droplet of n-hexadecane with a volume of 1 μL) on the textile and showing contact angles between 130 and 150°, which are maintained even after repeated washings;
- self-cleaning property, by measuring a tilt angle, which is the inclination needed for a water droplet to remove dirt from the textile surface, between 2 and 10° to a horizontal surface and exhibiting angles of less than 10° after ten household washings cycles;
- air permeability, as determined by the standard BS EN ISO 9237: 1999 after four washing cycles, which are conducted according to the standard ISO 105-C06: 1994 (E) and is the equivalent of twenty washings in a household washing machine;
- washing fastness, as exhibited by the rough surface of textiles, which are retained after washing (ISO 105-C06: 1994 (E));
- and thermal stability, as evidenced by the absence of degradation even after prolonged exposure to an elevated temperature (120 °C/30 min).

[0019] The described wash-resistant properties can be achieved only with the use of the proposed process. In the first step, we apply pre-prepared siloxane particles, which are spherical SiO_2 particles. In the second step, the spherical SiO_2 particles grow *in-situ* over the cotton fibre surface and form a network, thus, enabling the formation of chemical bonds between amorphous SiO_2 particles and the cotton fibre surface. These chemical bonds further consolidate in the third step and form a network with a water- and oil-repellent layer derived from a water-based precursor.

Detailed description

[0020] According to the present invention, it is possible to produce wash-resistant, respiratory active textiles with superhydrophobic, highly oleophobic and self-cleaning properties. These textiles have a passive antibacterial protection and can be used for clothing, as in the above-described case. Superhydrophobic and oleophobic properties are derived from the roughness of a suitable double nano- and microstructured textile surface. Double roughness is achieved by applying pre-manufactured spherical SiO_2 particles to the surface of the textile, in the first step, and is supplemented by the *in-situ* formation of spherical SiO_2 particles on the surface of the textile, in the second step. According to the proposed process, the pre-manufactured spherical SiO_2 particles are responsible for the increase in the surface roughness, whereas the application of *in-situ* SiO_2 particles in the second step is unavoidable because of the lack of a chemical connection between the spherical SiO_2 particles and the cotton fibre surface. Non-bonded spherical SiO_2 particles are removed from the surface of the textile with the first washing. This disadvantage, which is inherent to the classical single step process, is eliminated by a second step. This step consists of covering and soaking the entire surface, i.e., the spherical SiO_2 particles and the fibres, with a solution of tetraethoxysilane (TEOS), base, water and alcohol, during which the *in-situ* formation of spherical SiO_2 particles with a size between 50 and 200 nm occurs. At the same time, the formation of a thin porous coating allows the chemical bonding of spherical SiO_2 particles, deposited in the first step, to the surface of cotton. The spherical SiO_2 particles from the first step are used directly from the solution in which they have been prepared to avoid the problem of particle agglomeration, which is probable when dried particles are re-dispersed. Water- and alcohol-based dispersions in the proposed invention are characterized by a high content of cross-linked polysilsesquioxanes. Nanometre-sized siloxane spheres are responsible for the formation of a thin film of comparable thickness.

[0021] The invention is presented in detail by the figures below:

Figure 1: Scanning electron microscopy (SEM) images of cotton fibres without modification.

Figure 2: SEM images of cotton fibres modified with 200 nm SiO_2 particles.

Figure 3: SEM images of cotton fibres, modified by the operative procedure CO/AP600+IS150-FAS, after one washing cycle according to the standard ISO 105-C06: 1994 (E), which is equivalent to five washings in the household washing machine.

Figure 4: SEM images of cotton fibres, modified by the operative procedure CO/AP60+IS150-FAS, after two washing cycles according to the standard ISO 105-C06: 1994 (E), which is equivalent to ten washings in a household washing machine.

Figure 5: SEM images of cotton fibres, modified by the operative procedure CO/AP60+IS150-FAS, after three washing cycles in accordance with ISO 105-C06: 1994 (E), which is equivalent to fifteen washings in a household washing machine.

Figure 6: SEM images of cotton fibres, modified by the operative procedure CO/AP60-HS150-FAS, after four washing cycles according to the standard ISO 105-C06: 1994 (E), which is equivalent to twenty washings in a household washing machine.

Figure 7: The static contact angles, θ, for water on cotton textiles functionalized by different implementation procedures (sample) and after a number of washings (W) according to ISO 105-C06: 1994(E).

Figure 8: The static contact angles, θ, for n-hexadecane on cotton textiles functionalized by different implementation procedures (sample) and after a number of washings (W) according to ISO 105-C06: 1994 (E).

Figure 9: The tilt angles for water, α on cotton textiles functionalized by different implementation procedures (sample) and after different washings.

[0022] A process for the preparation of the wash-resistant, vapour permeable, self-cleaning, and highly hydrophobic and oleophobic cotton textiles involves the following steps:

- the cotton fabrics are modified in advance with pre-prepared siloxane particles,;
- the siloxane particles are applied by an *in-situ* sol-gel method, wherein the whole surface of the textile is covered with the same bi-hierarchical roughness through the formation of a thin porous coating, which enables the chemical bonding of siloxane particles, deposited in the first step, to the surface of cotton fabrics;
- the rough cotton surface is further consolidated by application of a sol-gel coating prepared from hydrophobic and oleophobic silanes.

Modifying the cotton fabrics with the pre-prepared spherical SiO_2 particles

[0023] The aqueous/alcoholic dispersions of SiO_2 particles, i.e., colloidal dispersions based on tetraethoxysilane, include pre-prepared monodisperse spherical SiO_2 particles. It is desirable that at least 95% of the particles in the dispersion are the same size. Preferably, the siloxane particle and SiO_2 particle size is 200 - 1000 nm. The weight ratio of alcohol:TEOS:NH_3:water is 46:2:1:5. Preparation of the particles is not the subject of the patent. According to the invention, the dispersion of SiO_2 particles is 10% by weight and is used in the first step of the process for the cotton modification, i.e., for the application of the first coating on the cotton fibre surface. The ratio of the weight of the aqueous alcoholic dispersion of SiO_2 particles and the weight of the textiles should be 1:15. After application of the dispersion of SiO_2 particles, a padder is used to squeeze the excess dispersion from the textiles while passing the textile sample between two rollers at a pressure of 0.4 bar; the fabric is then air dried at room temperature for 10 min. The advantage of the first layer is that the deposited SiO_2 particles are well separated from each other, which enables a high surface roughness of the textile. The exact parameters are very important to avoid loss of the SiO_2 particles from the surface. SiO_2 particles are preferably prepared from tetraethoxysilane, so their surface is full of free-OH bonds, which will enable chemical linking between the SiO_2 particles and the cotton fibres of the textile in the next stage.

In-situ growth of spherical SiO_2 particles on the surface of modified SiO_2 particles and fibres

[0024] It is known that the *in-situ* growth of particles by a sol-gel method allows greater coating density after a suitable thermal treatment. In the second step, the cotton fibre surface, modified by spherical SiO_2 particles, is coated by a second layer of siloxane particles. These are spherical SiO_2 particles 50 - 200 nm in size, which are made *in-situ* by the sol-gel growth method from a colloidal nucleus dispersion. The weight ratio of alcohol:TEOS:NH_3:water is in this case 30:5:2:5. This coating enables the chemical bonding of SiO_2 particles, which were deposited on the cotton fibre surface in the first step. The reactivity of the substrate, which consists of cellulosic OH groups and surface OH groups on the spherical SiO_2 particles from the first layer, facilitates the connection to particles from the second step of the process. Simultaneously, the colloidal dispersion at the concentration described for the *in-situ* process generates uniform spherical SiO_2 particles that are sized 50 - 200 nm. The *in-situ* deposited SiO_2 spherical particles give the cotton fibre surface a double roughness, or a bi-hierarchical roughness, and at the same time secures the SiO_2 particles deposited in the first step. For the second step of the process, it is important to apply two to three times more particles, compared with the amount applied in the first step. Therefore, the smaller SiO_2 particles that are produced during the *in-situ* growth completely cover the textile surface. The weight ratio between the pre-manufactured siloxane particles used in the first step and the *in-situ* siloxane particles prepared in the second step is between 1:2 and 1:3.

Consolidation of the rough surface of the textile by silanes

[0025] In the third step, the biomimetic surface of the textile, which has already hardened, is coated again with a thin layer of hydrophobic and oleophohic silanes, preferably from hydrolysed fluorosilane (FAS), bis [(ureapropyl) triethoxysilane] bis(propyl)-terminiran-polydimethylsiloxane (PDMSU) or a mixture of FAS and PDMSU. A 10% aqueous/alcohol solution of silane is used for the coating. This layer allows further consolidation of the biomimetic surface from the first two steps and grants the textile surface superhydrophobic, high oleophobic and self-cleaning properties. The thickness of such a thin layer may not exceed 150 mn. Hardening of the surface is possible due to the covalent bonding between the free-OH groups present on the surface of the porous coating applied in the second step and the OH groups of the hydrolysed silane. Thermal curing of the coating results in an increased density and stability, as well as an increased washing fastness.

[0026] Hydrophobic and oleophobic silanes, which are used for the hardening of the rough surfaces, are selected from the groups of perfluoroalkyl-trialkoxysilanes, perfluoroalkyl-alkyldialkoxysilanes, perfluoroalkyl-dialkylalkoxysilanes, perfluoroalkyl-trihalosilanes, perfluoroalkyl-alkyldihalosilanes, perfluoroalkyl-dialkylhalosilanes and (trialkoxysilyl)alkyl terminated polydimethylsiloxane.

[0027] The formation of individual layers with a specific particle size depends on the properties of the applied colloidal dispersions but is preferably within the conditions set out below. Various alcohols, such as methanol, ethanol, isopropanol, and butanol, should be used in the preparation of colloidal dispersions. These solvents affect the growth and size of the particles. According to the invention, additional organic-modified silanes may also be used for the preparation of SiO_2 particles in the first and second steps, such as methyltriethoxysilane, vinyltriethoxysilane, and aminopropyltriethoxysilane. Monodisperse SiO_2 particles provide a uniform roughness over the entire surface of the textile. Application can be performed by the exhaustion method, dipping, or sputter deposition.

[0028] Cotton fibres already possess their own roughness (Figure 1), but because of their chemical composition (cellulose), they are extremely hydrophilic. The surface roughness is improved by the proposed process, as shown in Figure 2. High washing fastness is provided by the *in-situ* growth of particles in the second layer and by further consolidation of the fluorosilane coating. The final coating maintains its properties after the first washing cycle, according to the standard ISO 105-C06: 1994 (E), and is equivalent to five washings in a household washing machine (Figure 3). It is slightly changed after four washing cycles (Figures 4 to 6).

[0029] The modified textile displays high hydrophobic and oleophobic properties after twenty washings with static contact angles for n-hexadecane higher than 130°. The results that indicate the preservation of the superhydrophobicity and oleophobicity are disclosed in Figures 7 and 8. These figures show the static contact angles for water and n-hexadecane as a function of the number of washing cycles, according to the standard ISO 105-C06: 1994 (E), (1 W = 5x washing in a household washing machine) for the various embodiments of the invention. The extremely low sliding angles for the modified textile (Figure 9) allow rolling of the droplets and the simultaneous removal of dirt from the surface, demonstrating the self-cleaning properties.

Examples:

[0030] The reaction conditions for the preparation of SiO_2 particles from tetraethoxysilane (TEOS 98%, Aldrich) in alcohol are as follows:

- reaction temperature, T = 60 °C;
- concentration (TEOS) = 0.2 - 1.1 mol/L;
- concentration (NH_3) = 0.3 - 1.1 mol/L;
- concentration (H_2O) = 6 - 10 mol/L;
- reaction time = 1 - 3 h.

CO/AP200-FAS

[0031] A bottle (250 mL) was filled with 130 g of ethanol and 8 g of TEOS. The solution was well mixed and allowed to stand for an additional 10 min at room temperature (RT). In the second step, a mixture of ammonia (4 g (25%)) and water (20 g) was added to the prepared solution of EtOH and TEOS. The solution was re-mixed and left for 3 h at RT. The prepared solution was used for finishing the cotton fabric. After soaking the textile in the above described reaction mixture, the fabric was squeezed with an 85% spin effect and air dried. In final step, the application of a 10% FAS solution was followed by the impregnating procedure with full soaking, squeezing with an 85% spin effect, drying at 100 °C and curing at 150 °C for 5 min.

CO/AP200+IS150-FAS

[0032] In a bottle, a solution of 130 g ethanol and 8 g of TEOS was well mixed and allowed to stand for an additional 10 min at room temperature. Ammonia (4 g) in water (20 g) was then added to the prepared solution, which was re-mixed and left for 3 11 at RT. Cotton fabric was treated in the next step by the above-described dispersion. The soaked fabric was squeezed with an 85% spin effect and air dried. The as-prepared cotton fabrics were added to a mixture of 2-propanol (100 g) and TEOS (20 g), mixed well, and left for 10 min at 50 °C. Then, a solution of ammonia (4 g) in water (20 g) was added to the TEOS solution, which was re-mixed again and left for 1 h at 50 °C. The immersed cotton textile was taken out of the reaction mixture, rinsed with water three times and dried at room temperature. This was followed by applying a 10% FAS solution, performing the impregnating procedure with full soaking, squeezing with an 85% spin effect, drying at 100 °C and curing at 150 °C for 5 min.

CO/AP60+IS150-FAS

[0033] The solution of 130 g ethanol and 15 g of TEOS was mixed well in the bottle and allowed to stand for 10 min at 40 °C. Then, ammonia (4 g) in water (20 g) was added to the prepared solution, which was re-mixed and left for additional 1 h at 40 °C. Cotton fabric was treated in the next step by the above described dispersion. The soaked fabric was squeezed with an 85% spin effect and air dried. The as-prepared cotton fabrics were added, in the next step, to the mixture of 2-propanol (100 g) and TEOS (20 g), mixed well, and left for 10 min at 50°C, Then, a solution of ammonia (4 g) in water (20 g) was added to the TEOS solution, which was re-mixed again and left for 1 h at 50 °C. The immersed cotton textile was taken out from the reaction mixture, rinsed with water three times and dried at room temperature. This was followed by applying a 10% FAS solution, performing the impregnating procedure with full soaking, squeezing with an 85% spin effect, drying at 100 °C and curing at 150 °C for 5 min.

CO/AP600+IS150-FAS

[0034] The solution, of 120 g ethanol and 20 g of TEOS was mixed well in the bottle and allowed to stand for 10 min at 50 °C. Then, ammonia (7 g) in water (20 g) was added to the prepared solution, which was re-mixed and left for an additional 1 h at 50 °C. Cotton fabric was treated in the next step by the above described dispersion. The soaked fabric was squeezed with an 85% spin effect and air dried. The as-prepared cotton fabric was added, in the next step, to the mixture of 2-propanol (100 g) and TEOS (20 g), mixed well, and left for 10 min at 50 °C. Then, a solution of ammonia (7 g) in water (20 g) was added to the TEOS solution, which was re-mixed again and left for 1 h at 50 °C. The immersed cotton textile was taken out from the reaction mixture, rinsed with water three times and dried at room temperature. This was followed by applying a 10% FAS solution, performing the impregnating procedure with full soaking, squeezing with an 85% spin effect, drying at 100 °C and curing at 150 °C for 5 min.

CO/AP600+IS150-PDMSU-FAS

[0035] In a bottle, a solution of 120 g ethanol and 20 g of TEOS was mixed well and allowed to stand for 10 min at 50 °C. Then, ammonia (7 g) in water (20 g) was added to the prepared solution, which was re-mixed and left for an additional 1 h at 50 °C. The cotton fabric was treated in the next step by the above described dispersion. The soaked fabric was squeezed with an 85% spin effect and air dried. The as-prepared cotton fabric was added, in the next step, to the mixture of 2-propanol (100 g) and TEOS (20 g), mixed well, and left for 10 min at 50 °C. Then, a solution of ammonia (7 g) in water (20 g) was added to the TEOS solution, which was re-mixed again and left for 1 h at 50 °C. The immersed cotton textile was taken out of the reaction mixture, rinsed with water three times and dried at room temperature. This was followed by applying a 10% PDMSU-FAS solution, performing the impregnating procedure with full soaking, squeezing with an 85% spin effect, drying at 100 °C and curing at 150 °C for 5 min.

Claims

1. A process for the preparation of self-cleaning wash-resistant, air permeable, superhydrophobic, oleophobic and self-cleaning cotton textiles, which includes the following steps:

   - cotton fabrics are modified in advance with pre-prepared siloxane particles ;
   - the siloxane particles are applied by an *in-situ* sol-gel method, wherein the whole surface of the textile is covered with the same bi-hierarchical roughness through the formation of a thin porous coating, which enables the chemical bonding of siloxane particles, deposited in the first step, to the surface of cotton fabrics;
   - the rough cotton surface is further consolidated by application of a sol-gel coating prepared from hydrophobic and oleophobic silanes.

2. The process according to claim 1 **characterized in that** the modification of planar woven fabrics in the first step is carried out using aqueous/alcoholic dispersions of siloxane particles 200 - 1000 nm in size, wherein at least 95% of the siloxane particles in the dispersion are of the same size, the concentration of dispersed siloxane particles is 10% by weight, and the ratio of the weight of the dispersed siloxane particles and the mass of the textile is 1:15.

3. The process according to claim 1 **characterized in that** the deposition of siloxane particles with an *in-situ* sol-gel process is carried out using dispersions of siloxane particles 50 - 200 nm in size, wherein the layer of siloxane particles is grown *in-situ* on the surface of textile fibres from a colloidal dispersion, which surrounds the textile and forms a coating with the siloxane particles in the structure.

4. The process according to claim 1 and 3 **characterized in that** the chemical bonding of the siloxane particles deposited in the first step with the surface of cotton fabrics is enabled by the reactivity of the free-OH groups on the siloxane particles and the textiles.

5. The process according to claims 1 to 4 **characterized in that** for the preparation of siloxane particles in the first and second step organic-modified silanes are used, such as tetraethoxy ortosilane, methyltriethoxysilane, vinyltriethoxysilane or aminopropyltriethoxysilane, preferably tetraethoxy ortosilane.

6. The process according to claims 1 to 5 **characterized in that** the weight ratio of the previously prepared siloxane particles in the first step and the siloxane particles prepared *in-situ* during the second step is between 1:2 and 1:3.

7. The process according to claims 1 to 6 **characterized in that** for the hardening of a roughened surface hydrophobic and oleophobic silanes are used which are selected from perfluoroalkyl-trialkoxysilanes, perfluoroalkyl-alkyldialkoxysilanes, perfluoroalkyl-dialkylalkoxysilanes, perfluoroalkyl-trihalosilanes, perfluoroalkyl-alkyldihalosilanes, perfluoroalkyl-dialkylhalosilanes, and (trialkoxysilyl)alkyl terminated polydimethylsiloxanes.

8. The process according to claims 1 to 7 **characterized in that** the thickness of the thin layer of the hydrophobic and oleophobic silanes may not exceed 150 nm.

9. The process according to claims 1 to 8 **characterized in that** the coating of individual layers on the surface of cotton fabrics is applied by exhaustion method, by dipping, or by sputter deposition.

10. Woven fabrics obtained by the process according to claims 1 to 9 **characterized in that** they display high hydrophobic and oleophobic properties after twenty washings with static contact angles for n-hexadecane higher than 130°.

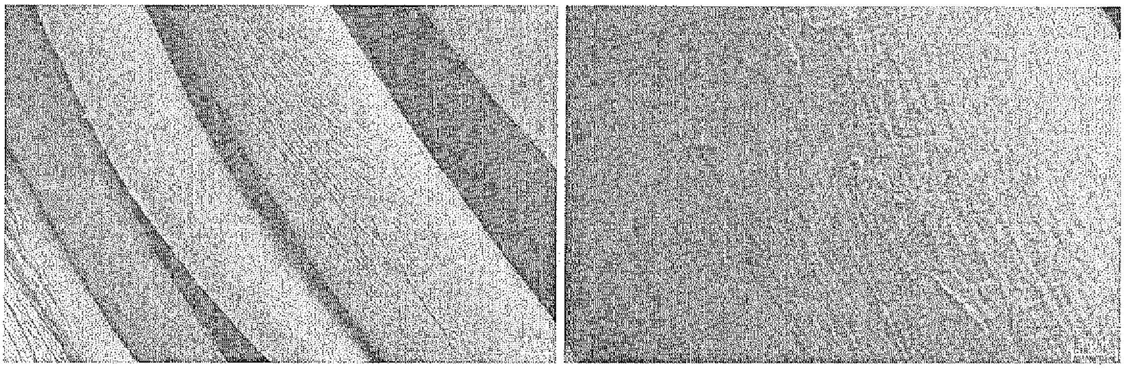
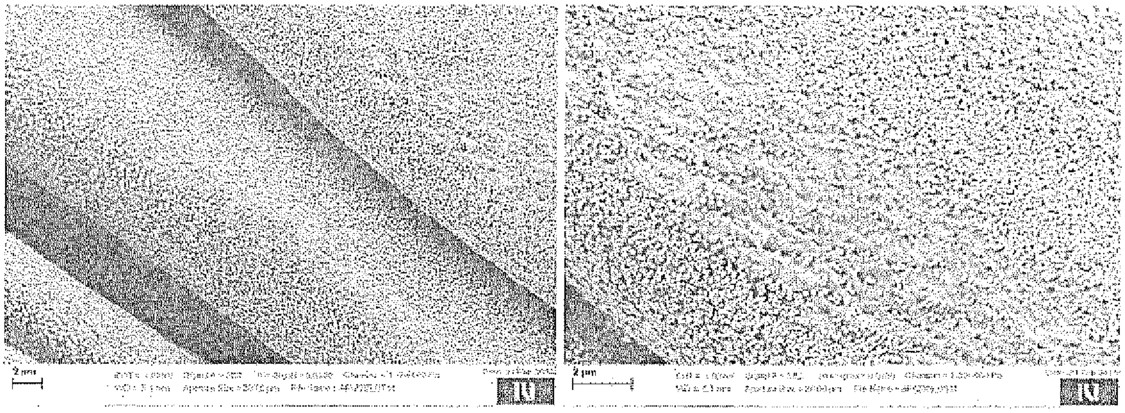


Figure 1



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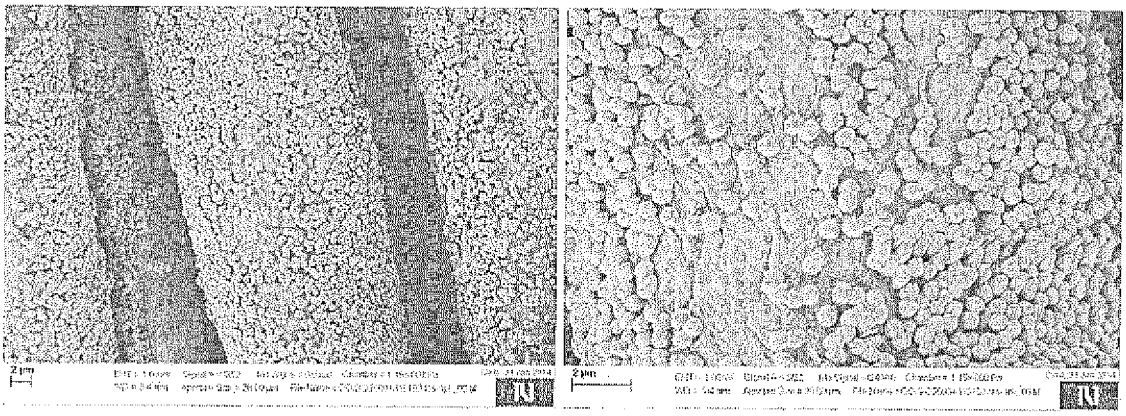

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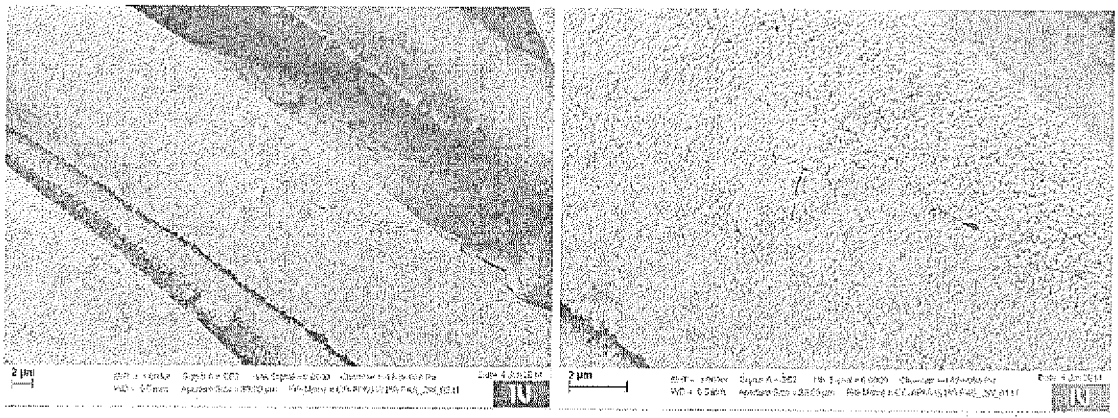

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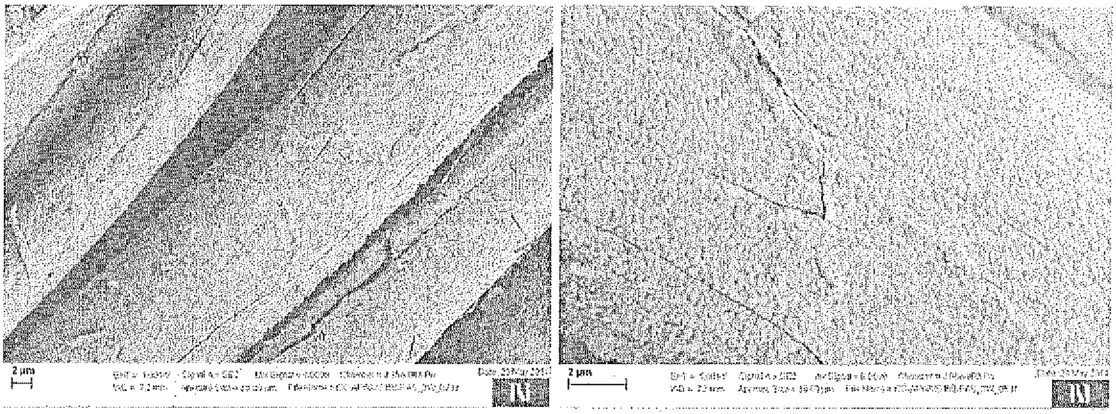

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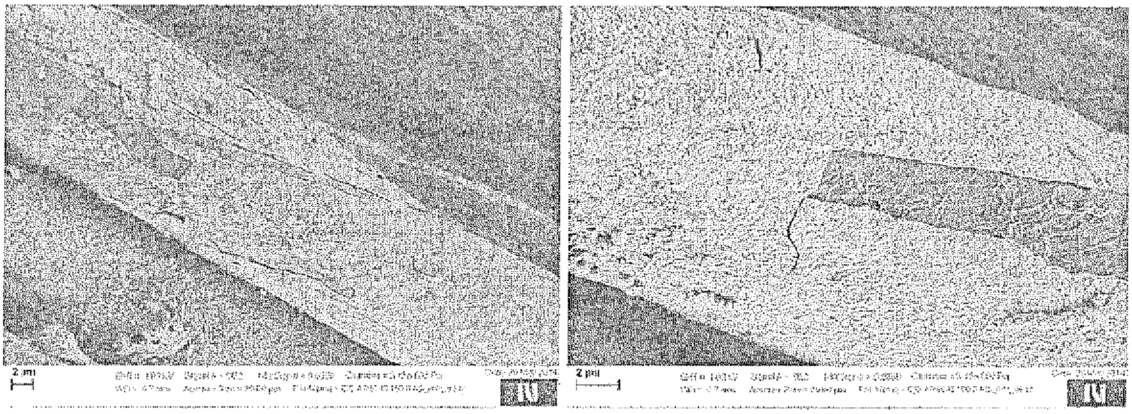

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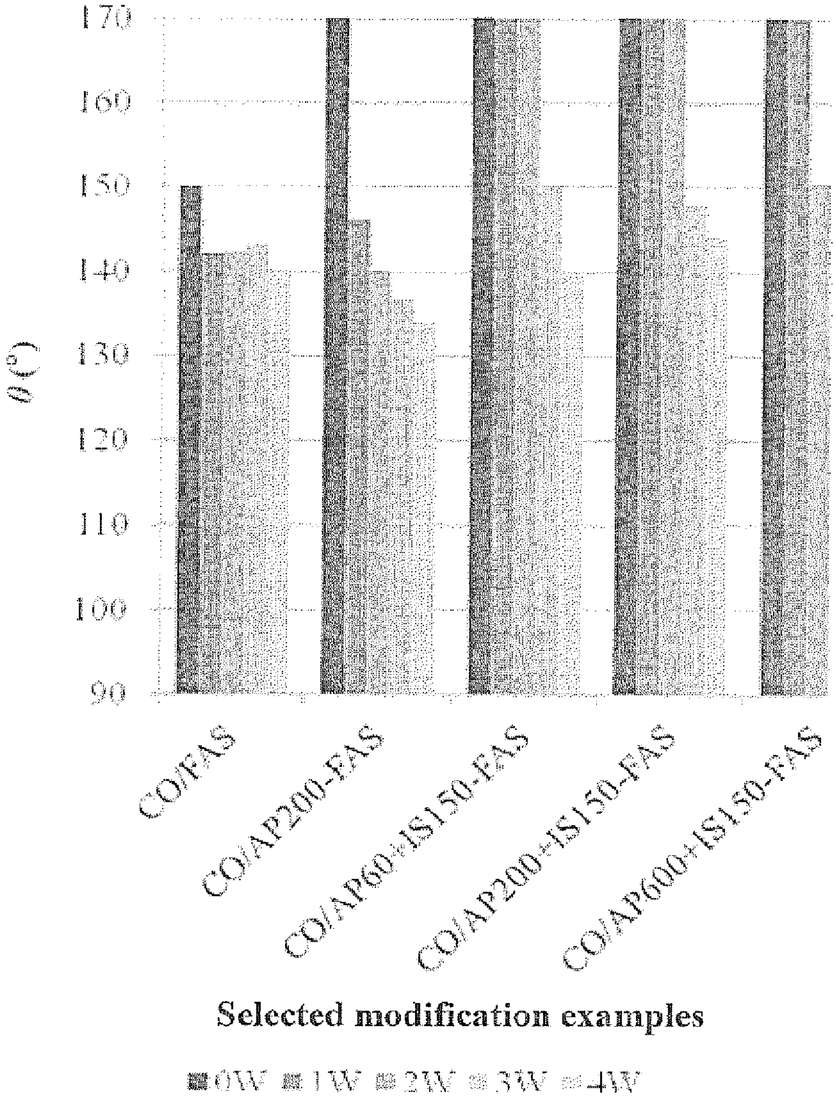
170
160
150
140
130
120
110
100
90
θ (°)
CO/FAS
CO/AP200-FAS
CO/AP60+IS150-FAS
CO/AP200+IS150-FAS
CO/AP600+IS150-FAS
Selected modification examples
0W
1W
2W
3W
4W

Figure 7

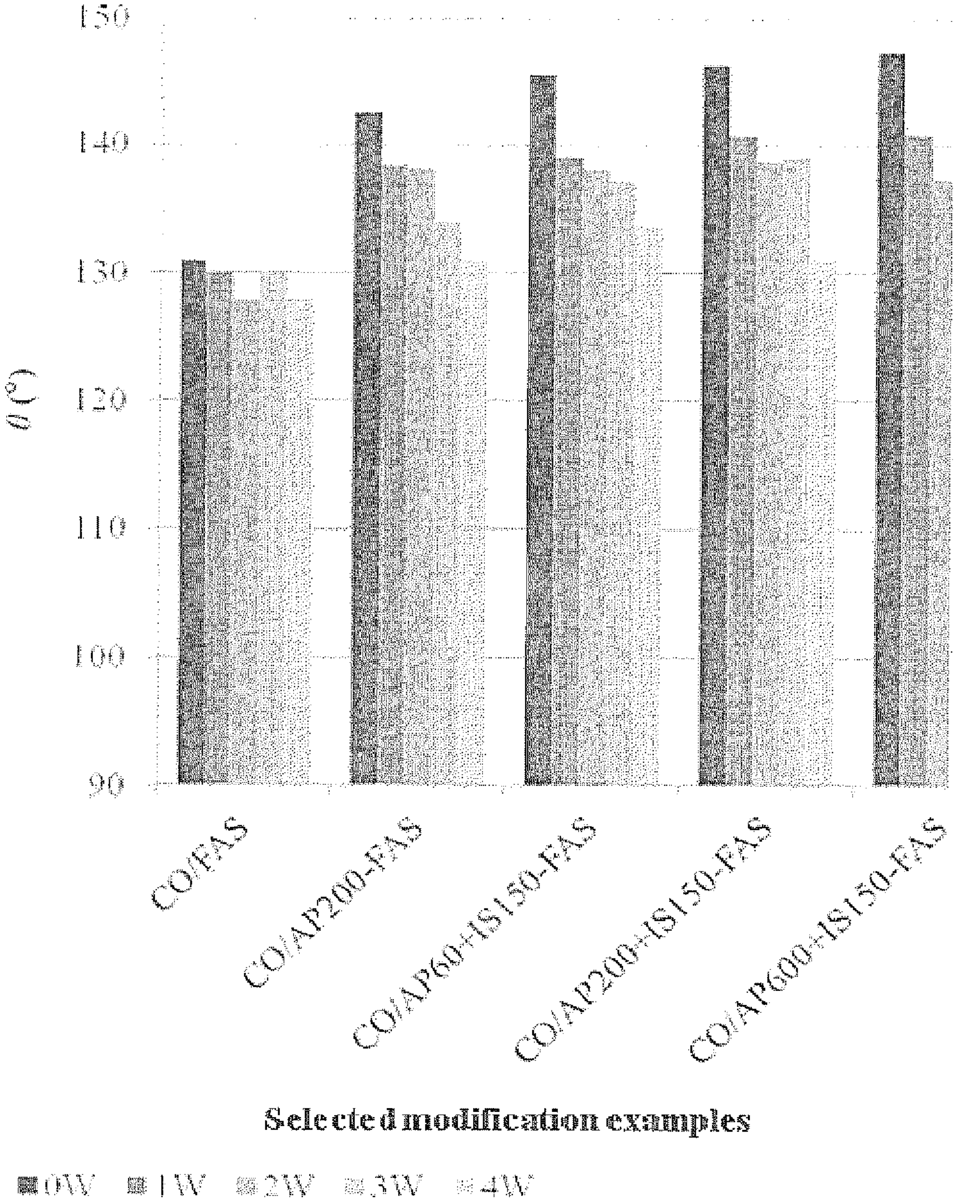
150
140
130
120
110
100
90
θ (°)
CO/FAS
CO/AP200-FAS
CO/AP60+IS150-FAS
CO/AP200+IS150-FAS
CO/AP600+IS150-FAS
Selected modification examples
0W
1W
2W
3W
4W

Figure 8

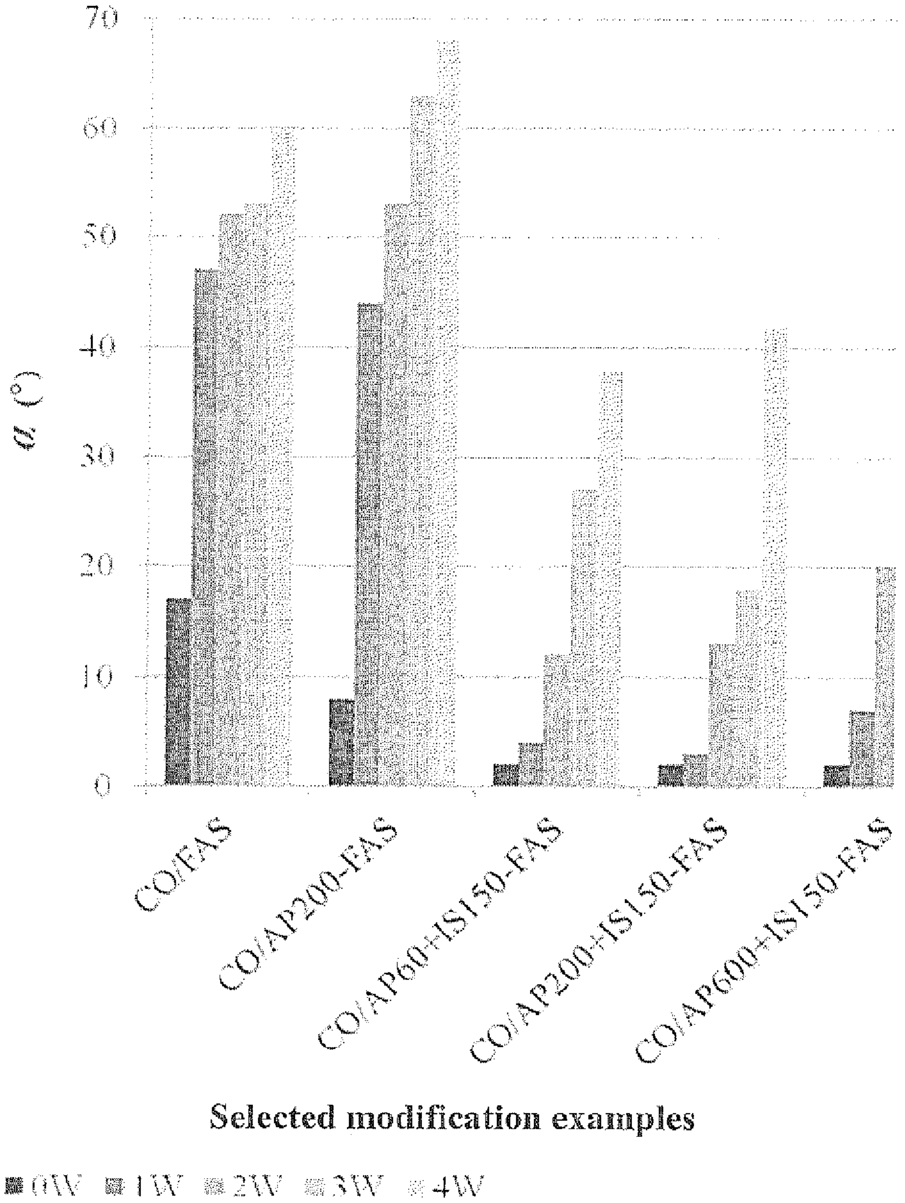
70
60
50
40
30
20
10
0
α (°)
CO/FAS
CO/AP200-FAS
CO/AP60+IS150-FAS
CO/AP200+IS150-FAS
CO/AP600+IS150-FAS
Selected modification examples
0W
1W
2W
3W
4W

Figure 9

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EUROPEAN SEARCH REPORT

Application Number
EP 15 46 8007

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	LENG BOXUN ET AL: "Superoleophobic Cotton Textiles", LANGMUIR, AMERICAN CHEMICAL SOCIETY, NEW YORK, NY; US, vol. 25, no. 4, 22 January 2009 (2009-01-22), pages 2456-2460, XP002601745, ISSN: 0743-7463, DOI: 10.1021/LA8031144 * page 2457 - page 2460 * -----	1-10	INV. D06M11/79 D06M23/08 ADD. D06M101/06
A	H. F. HOEFNAGELS ET AL: "Biomimetic Superhydrophobic and Highly Oleophobic Cotton Textiles", LANGMUIR, vol. 23, no. 26, 27 September 2007 (2007-09-27), pages 13158-13163, XP55243993, NEW YORK, NY; US ISSN: 0743-7463, DOI: 10.1021/la702174x * page 13158 - page 13159 * * page 13162 - page 13163 * -----	1-10	TECHNICAL FIELDS SEARCHED (IPC)
A	JUN LIANG ET AL: "Transformation of hydrophilic cotton fabrics into superhydrofobic surfaces for oil/water separation", THE JOURNAL OF THE TEXTILE INSTITUTE, TAYLOR & FRANCIS, vol. 104, no. 3, 10 August 2012 (2012-08-10), pages 305-311, XP001581545, ISSN: 0040-5000, DOI: HTTP://DX.DOI.ORG/10.1080/00405000.2012.721207 * page 305 - page 306 * ----- -/--	1-10	D06M

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	25 January 2016	Menard, Claire

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

Application Number
EP 15 46 8007

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	BAE G Y ET AL: "Superhydrophobicity of cotton fabrics treated with silica nanoparticles and water-repellent agent", JOURNAL OF COLLOID AND INTERFACE SCIENCE, ACADEMIC PRESS, NEW YORK, NY, US, vol. 337, no. 1, 22 April 2009 (2009-04-22), pages 170-175, XP027597754, ISSN: 0021-9797, DOI: 10.1016/J.JCIS.2009.04.066 [retrieved on 2009-05-03] * page 171 - page 172 * -----	1-10	
			TECHNICAL FIELDS SEARCHED (IPC)
	The present search report has been drawn up for all claims		

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D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

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- US 20020192385 A1 **[0007]**
- US 7732497 B2 **[0008]**
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- **MA et al.** *J. Colloid Interface Sci.,* 2013, vol. 392, 194-200 **[0014]**
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