FIG. 1

(57) Abstract: The invention provides a method for treating textile material to inhibit or reduce release of formaldehyde from the textile material. The invention also provides a method for treating textile material without the use of formaldehyde or formaldehydic compounds in the treatment compositions. The resulting textile material is environmentally friendly and can exhibit a high degree of oleophobic, hydrophobic, superoleophobic, superhydrophobic, superhydrophilic, omniphobic, hydrophilic/wicking, abrasion resistance, electrical conductivity, thermal conductivity, anti-fungal and/or anti-bacterial properties textile surfaces. In some cases, the resulting textile material exhibits multivalued oleophobic, hydrophobic, hydrophilic, superoleophobic, superhydrophobic, superhydrophilic and/or omniphobic textile surfaces which can repel soil and/or water at extremely low-surface-tension without sacrificing aesthetic qualities.
TEXTILE PROCESS AND PRODUCT

RELATED APPLICATIONS

[0001] This application claims benefit under 35 U.S.C. § 119(e) of the U.S. Provisional Application No. 62/115,841, filed February 13, 2015, the content of which is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] The present invention relates generally to textile processes and products. Specifically, the present invention provides textile processes and products that are essentially (i.e., completely free of) formaldehyde or formaldehydic compounds or release very little formaldehyde or formaldehydic compounds.

BACKGROUND

[0003] Formaldehyde is a toxic Volatile Organic Compound, which is grouped in the same class of drugs as cyanide and arsenic - deadly poisons. Formaldehyde is commonly used in several textile production processes; for example after treatment of substantive dyeing, hardening of casern fibres, as a wool protection agent, anti mould and above all as a cross linking agent in resin finishing. See, for example, Piccinini, C. Senaldi, C. Summa, European survey on the release of formaldehyde from textiles, European Commission, Directorate-General Joint Research Centre, Institute for Health and Consumer Protection 2007. When added to clothing, it releases formaldehyde fumes. Unfortunately for people, formaldehyde, a known "human carcinogen," is a slow and quiet killer, and little has been done to combat its usage in the fabrics that touch our skin - even in the face of research documenting its relationship to cancer.

[0004] Though this deadly chemical has been around since 1892, the health effects weren't really known until more than a hundred years later when formaldehyde was thrust into the public's consciousness following Hurricane Katrina. Victims of Katrina began complaining of a host of ailments and illnesses that emerged while living in FEMA trailers. If formaldehyde could cause significant health problems in healthy individuals living in FEMA trailers, imagine what it does to all children, including those suffering from cancers including leukemia. A known, recognized, widely-researched carcinogen touching the skin of cancer patients and entering their bodies - while doctors are doing everything in their power to get the cancer to leave their bodies.
Formaldehyde is directly linked to leukemia, so not only is it critical to keep it off the skin of children suffering from cancer, but all children. This is particularly true when children are the most vulnerable. Treatment options are improving, but prevention is much preferred.

As it happens, all apparel - including those for infants and children - contains some level of formaldehyde toxins. Investigations have discovered up to 500 times the safe level of formaldehyde in clothing shipped to brand name clothiers from factories in China and Southeast Asia. Currently, manufacturers add various different formaldehyde toxics to clothing to prevent color fading and wrinkling. The levels of formaldehyde toxins are not regulated, nor are they required to be listed on clothing labels. Consumers are very much in the dark in terms of what clothing is treated with.

The consequences, however, are substantial and far-reaching; indeed possibly a matter of life and death. Further, there is no "safe" level for the various hazardous formaldehyde chemicals - no matter what chemical name they are accorded with - Quaternium-15; 2-bromo-2-nitropropane-1,3-diol; imidazolidinyl urea, diazolidinyl urea, formalin, methanol, methylaldehyde, methylene oxide, morbicid acid, oxymethylene.

In some cases, allergic contact dermatitis (ACD) can be attributed to clothing treated with textile finish resins (TFRs), also named durable press resins or permanent press clothing resins. Under normal and foreseeable use, the majority of these resins can release formaldehyde. TFRs are widely used for cotton, cotton/polyester or wrinkle-resistant linen. (Le Coz C, Clothing. In: Textbook of Contact Dermatitis 3rd edition. Rycroft RJG, Menne T, Frosch PJ, Lepoittevin JP (Eds), pp. 727-749. Springer, Berlin, Heidelberg, Germany) The frequency of ACD due to textile formaldehyde resins has been reported to be between 0.2% and 4.2% after 1990. See, for example, Hovding G., Contact eczema due to formaldehyde in resin-finished textiles, Acta Derm Venereol, 41, 194, 1961; Epstein E, Maibach HI, Formaldehyde allergy, Arch Dermatol, 94, 186, 1966; Fowler IF Jr, Skinner SM, Belsito DV., Allergic contact dermatitis from resins in permanent press clothing: an underdiagnosed cause of generalized dermatitis, Am J Acad Dermatol, 27, 962-968, 1992; Sherertz EF., Clothing dermatitis. Practical aspects for the clinician, Am J Contact Dermat, 3, 55-64, 1992; Fuentes Cuesta MM, Bianco Carmona JG, Herrero Gil D et al, Dermatitis alergica de contacto por textiles, Aiergoi Immunol Clin, 15, 88-92, 2000; and Lazarov A, Trattner A, Abraham D, David M., Frequency of textile
dye and resin sensitization in patients with contact dermatitis in Israel, Contact Dermatitis, 46 (2), 119-120, 2002.

[0009] The process of producing a garment generally includes, using a cotton garment as an example, planting seeds, watering and otherwise tending the crop while reducing the adverse impact of bugs, disease, and weeds on the crop, harvesting the crop, cleaning the cotton fiber from the bales of cotton, producing thread from these individual fibers, weaving these threads into a cloth, bleaching and/or coloring the cloth, applying any additional treatments to the cloth to stabilize the color, provide resistance to wrinkling, repelling water, or provide other value to the processing or user, then cutting the cloth and sewing pieces of processed cloth into a garment, possibly applying additional treatments to the entire garment as a whole, packaging the garment for sale and shipping, and then shipping the garment. As such, the opportunities for intrusion of harmful materials like formaldehyde into the process of producing a garment or other textile-based product are plentiful.

[0010] Accordingly, there is a need in the art for textile materials that are free of formaldehyde or formaldehydic compounds, or textile materials that do not release or release very little formaldehyde or formaldehydic compounds if they are present in the textile material. There is also a need for methods of treating textile material that do not use formaldehyde or formaldehydic compounds and/or can impart oleophobic, hydrophobic, superoleophobic, superhydrophobic, hydrophilic, superhydrophilic and/or omniphobic textile surfaces which can repel soil and water at extremely low-surface-tension. The present invention addresses these needs.

SUMMARY OF THE INVENTION

[0011] The invention is directed to textile processes and the product formed thereby. Generally, the process and the resulting product are characterized in that no formaldehyde or formaldehydic compounds are used in the treatment compositions and a formaldehyde scavenger can be included in at least one of the treatment compositions. In some embodiments, the textile process described herein includes forming a barrier film or coating layer to reduce or inhibit (e.g. lock in) release of formaldehyde or formaldehydic compounds from the treated textile material. The resulting textile material is environmentally friendly and exhibits a high degree of oleophobic, superoleophobic, hydrophobic, superhydrophobic, omniphobic, hydrophilic/wicking, abrasion resistance, electrical conductivity, thermal conductivity, anti-fungal, anti-bacterial and/or de-
icing properties textile surfaces. In some embodiments, the resulting textile material exhibits a high degree of oieophobic, superoleophobic, hydrophobic, superhydrophobic, hydrophiic, superhydrophilic and/or omniphobic textile surfaces which repels soil and water at extremely low-surface-tension without sacrificing aesthetic qualities.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Fig. 1 is a schematic representation of a coated textile material according to an embodiment of the invention.

[0013] Fig. 2 is a schematic representation of a coated textile material according to an embodiment of the invention.

[0014] Fig. 3 is schematic representation of a metal coated textile material according to an embodiment of the invention.

[0015] Fig 4 is a representation of the shape of cotton. As seen cotton has a "bean shape" which means that a simple circle provides for a low surface area estimate for coatings.

[0016] Fig. 5 is a schematic representation of a nanoparticle coated textile material according to an embodiment of the invention.

DETAILED DESCRIPTION

[0017] For convenience, certain terms employed herein, in the specification, examples and appended claims are collected herein. Unless stated otherwise, or implicit from context, the following terms and phrases include the meanings provided below. Unless explicitly stated otherwise, or apparent from context, the terms and phrases below do not exclude the meaning that the term or phrase has acquired in the art to which it pertains. The definitions are provided to aid in describing particular embodiments, and are not intended to limit the claimed invention, because the scope of the invention is limited only by the claims. Further, unless otherwise required by context, singular terms shall include pluralities and plural terms shall include the singular.

[0018] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as those commonly understood to one of ordinary skill in the art to which this invention pertains. Although any known methods, devices, and materials may be used in the practice or testing of the invention, the methods, devices, and materials in this regard are described herein.
[0019] As used herein the term "comprising" or "comprises" is used in reference to compositions, methods, and respective component(s) thereof, that are essential to the invention, yet open to the inclusion of unspecified elements, whether essential or not.

[0020] The singular terms "a," "an," and "the" include plural referents unless context clearly indicates otherwise. Similarly, the word "or" is intended to include "and" unless the context clearly indicates otherwise.

[0021] Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein should be understood as modified in all instances by the term "about." The term "about" when used in connection with percentages may mean ±5% of the value being referred to. For example, about 100 means from 95 to 105.

[0022] Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of this disclosure, suitable methods and materials are described below. The term "comprises" means "includes." The abbreviation, "e.g." is derived from the Latin exempli gratia, and is used herein to indicate a non-limiting example. Thus, the abbreviation "e.g." is synonymous with the term "for example."

[0023] The terms "decrease", "reduced", "reduction", "decrease" or "inhibit" are all used herein generally to mean a decrease by a statistically significant amount. However, for avoidance of doubt, "reduced", "reduction" or "decrease" or "inhibit" means a decrease by at least 10% as compared to a reference level, for example a decrease by at least about 20%, or at least about 30%, or at least about 40%, or at least about 50%, or at least about 60%, or at least about 70%, or at least about 80%, or at least about 90% or up to and including a 100% decrease (e.g. absent level as compared to a reference sample), or any decrease between 10-100% as compared to a reference level.

[0024] The terms "increased", "increase" or "enhance" or "activate" are all used herein to generally mean an increase by a statically significant amount; for the avoidance of any doubt, the terms "increased", "increase" or "enhance" or "activate" means an increase of at least 10% as compared to a reference level, for example an increase of at least about 20%, or at least about 30%, or at least about 40%, or at least about 50%, or at least about 60%, or at least about 70%, or at least about 80%, or at least about 90% or up to and including a 100% increase or any increase between 10-100% as compared to a reference level, or at least about a 2-fold, or at least about a
3-fold, or at least about a 4-fold, or at least about a 5-fold or at least about a 10-fold increase, or any increase between 2-fold and 10-fold or greater as compared to a reference level.

[0025] The term "statistically significant" or "significantly" refers to statistical significance and generally means at least two standard deviation (2SD) away from a reference level. The term refers to statistical evidence that there is a difference. It is defined as the probability of making a decision to reject the null hypothesis when the null hypothesis is actually true.

[0026] The term "microscale" as used herein comprises a surface having a measurable feature in the range of from 1 to 999 μm.

[0027] The term "nanoscale" as used herein comprises a surface having a measurable feature in the range of from 1 to 999 nm.

[0028] The term "multiscale" as used herein comprises a surface having two or more measurable features. For example, a surface having at least one measurable feature which is microscale and at least one measurable feature which is nanoscale.

[0029] The term "pillar" as used herein comprises a measurable surface feature having an aspect ratio of height to narrowest width (or diameter) of greater than 1, greater than 1.5, greater than 2, greater than 3, greater than 4, greater than 5, greater than 10, greater than 15, greater than 20 or in the range of from 1 to 20, 1.5 to 18 or 2 to 15. Pillars can be square, rectangular or cylindrical in cross-sectional shape and may have a uniform cross-sectional shape along at least a portion of their height.

[0030] The term "nanoparticle" as used herein comprises a nanoscale deposit of a homogenous or heterogeneous material. Nanoparticles may be regular or irregular in shape and may be formed from a plurality of co-deposited particles that form a composite nanoscale particle. Nanoparticles may be generally spherical in shape or have a composite shape formed from a plurality of co-deposited generally spherical particles. Exemplary shapes for the nanoparticles include, but are not limited to, spherical, rod, elliptical, cylindrical, disc, and the like. In some embodiments, the nanoparticles have a substantially spherical shape.

[0031] The term textile material is used in a broad sense to encompass any suitable fibrous material which may be woven or non-woven or of any other appropriate construction. The material forming the textile material can be natural fibers, mineral fibers, glass fibers, carbon fibers, fibers composed of synthetic products and/or fibers composed of synthesized polymers. As such, the textile material includes natural materials, synthetic materials, and materials that
contain synthetic fibers. Without limitations, the textile material can be in any size, shape or form.

[0032] As used herein, "natural fibers" refer to fibers which are obtained from natural sources, such as celullosic fibers and protein fibers, or which are formed by the regeneration of or processing of natural occurring fibers and/or products. Natural fibers are not intended to include fibers formed from petroleum products. Natural fibers include fibers formed from cellulose, such as cotton fiber and regenerated cellulose fiber, commonly referred to as rayon, or acetate fiber derived by reacting cellulose with acetic acid and acetic anhydride in the presence of sulfuric acid. Herein, "natural fibers" are intended to include natural fibers in any form, including individual filaments, and fibers present in yarns, fabrics and other textiles, while "individual natural fibers" is intended to refer to individual natural filaments.

[0033] As used herein, "celullosic fibers" are intended to refer to fibers comprising cellulose, and include, but are not limited to, bamboo, cotton, linen, flax, rayon, cellulose acetate, cellulose triacetate, hemp and ramie fibers. Herein, "rayon fibers" is intended to include, but is not limited to, fibers comprising viscose rayon, high wet modulus rayon, cuprammonium rayon, saponified rayon, modal rayon and lyocell rayon. Herein, "protein fibers" are intended to refer to fibers comprising proteins, and include, but are not limited to, wools, such as sheep wool, alpaca, vicuna, mohair, cashmere, guanaco, camel and llama, as well as furs, suedes, silks, and manmade materials.

[0034] As used herein, "synthetic fibers" refer to those fibers that are not prepared from naturally occurring filaments and include, but are not limited to, fibers made from simple components by polymerization, polycondensation or polyaddition. Materials for forming the synthetic fibers include, but are limited to, polyesters, poliamides such asnylons, polycrylics, polyurethanes such as spandex, elastanes, elastodienes, fluoro fibers, acrylics, modacrylics, aramids, polyvinyl chlorides, polyvinylidene chloride, polyethylene, polyproplyenes and vinyls. Synthetic fibers include fibers formed from petroleum products. Synthetic-fiber containing materials are those that contain both the purely synthetic fiber and also natural materials.

[0035] In some embodiments, the textile material can comprise a material selected from the group consisting of polyester, wool, cotton, bamboo, silk, cellulose, nylon, aramid, acetate,
acrylic, jute, sisal, sea grass, coir, polyamide, polyolefin, polyacrylamide, polypropylene, polyaramide, and blends thereof.

[0036] In some embodiments, the textile material is a fibrous material. As used herein, the term "fibrous material" means any material having a ligneous (fibrous) component. Generally, fibrous materials are materials that comprise fibers or materials that are fibers themselves.

[0037] In some embodiments of the various aspects described herein, the textile material can comprise components other than the matrix material of the textile material distributed in the matrix of the textile material. Such materials can include, but are not limited to nanocomposites, nanoparticles, dyes, antibacterial, antifungal agents, metals, metal alloys, carbon nanotubes, graphene, reduced graphene oxide (rGO), nanoclays, metallic fibers and particles (catalysts), and the like.

[0038] In some embodiments, a formaldehyde scavenger can be present or distributed in the textile material. Exemplary formaldehyde scavengers include, but are not limited to, urea, ethylene urea 4,5-dihydroxyl ethylene urea, ammonium phosphate monobasic and ammonium phosphate dibasic, FREETEX® HFSE, and tannin. Additional formaldehyde scavengers amenable to the present invention include those described, for example, in US Patent No. 5,194,674 and US Patent Publication No. 2009/0014034, the contents of which are incorporated herein by reference in their entirety. In some embodiments, chlorine bleach can be used to break down or scavange the formaldehyde.

[0039] In some embodiments, a material having antibacterial or antifungal properties can be present or distributed in the textile material. Exemplary materials having antibacterial or antifungal properties include, but are not limited to, TiO₂, quaternary ammonium salts, silver and silver containing compounds, zinc and zinc containing compounds, copper and copper containing compounds, quaternary ammonium containing materials such as BARDAC/BARQUAT® from Lonza, quaternary siianes such as DC5700® from Dow Corning, polyhexamethylene biguanide available from Zeneca, lialammes from Halosource, chitosan, and derivatives thereof, as well various other materials.

[0040] In some embodiments, nanoparticles or microparticles can be present or distributed in the textile material.
In some embodiments, the textile material comprises a dye distributed in the textile material. As used herein, the term "dye" means substances which impart color to a substrate by selective absorption of light.

In some embodiments, the textile material comprises a brightener component distributed in the textile material. Brightener components useful in the present invention include one or more optical brighteners or whiteners. Typically, the terms "optical brighteners" and "whiteners" are used interchangeably and are taken to mean organic compounds that absorb the invisible ultraviolet (UV) portion of the daylight spectrum and convert this energy into the longer-wavelength visible portion of the spectra.

Commercial optical brighteners include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents," M. Zahradmk, published by John Wiley & Sons, New York (1982).

Examples of optical brighteners useful in the present invention are those identified in the Wixon U.S. Pat. No. 4,790,856. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include; Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Arctic White CC and Arctic White CWD, the 2-(4-styryl-phenyl)-2H-naptho[1,2-d]oxazoles; 4,4'-bis(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the amino-coumarins. Specific examples of these brighteners include 4-methyl-7-diethyl-amino coumarin; 1,2-bis(benzimidazol-2-yl)ethylene; 1,3-diphenyl-pyrazolmes; 2,5-bis(benzoaxazol-2-yl)thiophene; 2-styryl-naphth[1,2-d]oxazole; and 2-(stilben-4-yl)-2H-naptho[1,2-d]triazole. Additional known brighteners are disclosed in the Hamilton U.S. Pat. No. 3,646,015.

In some embodiments, the textile material is a fiber. As used herein, the term "fiber" refers to any slender, elongated structure that can be carded, combed, or otherwise formed into a thread. Examples include "staple fibers", a term that is well-known in the textile art. A reference to "fiber" of "fibers" may mean or include individual fibers or a plurality or bulk of fibers as the situation requires. A plurality of fibers may comprise fibers of different compositions or may be substantially uniform in composition. Thus, by way of illustration, a reference to "natural fiber" or "synthetic fiber" may mean and may include a single fiber of such
type, or may mean any quantity or plurality of such fibers and they may be comprised in threads, felts, yarns, fabrics materials etc., ail as will be apparent from the context.

[0046] The fiber can be a synthetic fiber or a natural or organic fiber. As one of skill in the art is well aware, smoothness of the outer surfaces is significantly varied between different fibers. Accordingly, the outer surface of the fiber can be smooth or rough. By way of example only, manmade fibers, such as polyester fibers, usually have a smooth outer surface. In contrast, natural fibers, such as cotton, usually have a rough outer surface. One consequence of the roughness of the outer surface is that rough surfaces take more fluid to completely cover the surface per unit diameter.

[0047] Without limitation, the fiber can have desired cross-sectional shape, including but not limited to, round, star, elliptical, the shape of cotton shown in Fig. 4, or other geometrical or non-geometrical shape. Without wishing to be bound by a theory, cross-sectional shape of natural fibers, such as shape of cotton fiber is a less efficient shape for coating and increases the fluid intake. Further, the cross-sectional diameter or size of the fiber can range from a few microns to hundreds of millimeters.

[0048] In some embodiments, the textile material is a thread. As used herein, the term "thread" refers to continuous or discontinuous elongated strands formed by carding or otherwise joining together one or more different kinds of fibers. In embodiments threads may be incorporated into yarns or other structures comprising a plurality of threads, before being woven to form fabrics. In some embodiments, the thread comprises two or more different types of fibers.

[0049] As used herein, the term "yarn" refers to a structure comprising a plurality of strands that have been twisted, spun or otherwise joined together to form the yarn and may include spun yarns, continuous filament yarns, and yarns of core spun construction. Yarns according to the invention may be manufactured using virtually any yarn-forming process known in the art, including but not limited to, by spinning or stretch broken spinning.

[0050] In some embodiments, the textile material is a fabric. As used herein, the term "fabric" is to be understood in its widest meaning. The term "fabric" may be used for all structures composed of fibers which have been manufactured according to a surface-forming method. Fabrics include materials where one or more different types of yarns, threads, filaments, or fibers that have been woven, knitted, felted, wrapped, spun, co-mingled, coated, coextruded,
braided, entangled, applied or otherwise assembled into a desired material. Generally, the fabric has a structure which comprises a series of meshes or openings and filament bundles which define the mesh boundaries, such as woven, knitted, knotted, interwoven or tufted structures. Without limitations, the term "fabric" is intended to include woven fabrics, yarn sheets, knitted fabrics and non-woven fabrics. Further, the fabrics may be constructed from a combination of fibers, threads or yarns. Fabrics comprising different fibers, threads or yarns are also referred to as fabric blends herein.

[0051] In some embodiments, the textile material is a cloth. As used herein, the term cloth refers to any textile fabric woven, nonwoven, felted, knitted or otherwise formed from any filament or fiber or plurality of filaments or fibers, including but not limited to thread yarn, monofilaments, and ribbons. Further, the term cloth is intended to include within its scope not only woven, knitted, non-woven, and felted materials, but also sheet materials.

[0052] In some embodiments, the textile material is a garment. As used herein, the term "garment" refers to any item that is worn by a user to cover or protect some region of the user's body from weather or other factors in the environment outside the body. Exemplary garments, include, but are not limited to, coats, jackets, pants, hats, gloves, shoes, socks, shirts, etc... It is noted that the term "garment" is intended to cover clothing for human or animal use.

[0053] The disclosure provides textile materials that are essentially free of formaldehyde or formaldehydic compounds or release formaldehyde or formaldehydic compounds at very low rates or amounts relative to textile materials known in the art.

[0054] As used herein, the term "essentially free" means that the no more than trace amounts of the indicated component may be present. Generally, "essentially free" means that the indicated component is well below 0.05%, preferably below 0.01%, and more preferably below 0.005%. Most preferably no amount of the indicated component can be detected with standard analytical methods used for detecting said component.

[0055] One approach for providing textile materials that are essentially free of formaldehyde or formaldehydic compounds is to use compositions and process that are essentially free of formaldehyde or formaldehydic compounds in preparing the textile materials. However, this can be expensive and time consuming since many of the compositions and process currently in use require use of preservative, such as formaldehyde. Compositions that are free of preservatives,
such as formaldehyde, have shorted shelf and recycling life. As such, these compositions need to be changed more often, thereby increasing the cost.

[0056] In one aspect, the invention provides a method for treating a textile material for reducing the amount of formaldehyde or formaldehydic compounds present in the textile material. Generally, the method comprises washing the textile material with a composition that is essentially free of formaldehyde or formaldehydic compounds. For example, soap and water can be used to remove oils from textile materials. In some embodiments, the method comprises contacting the textile material with a composition comprising a formaldehyde or formaldehydic compound scavenger before the wash step. In some embodiments, the method comprises contacting the textile material with a composition comprising a compound that neutralizes or binds with formaldehyde or formaldehydic compound present in the textile material. In one example, the method comprises contacting the textile material with chlorine bleach.

[0057] Instead of washing out or neutralizing the formaldehyde or formaldehydic compounds present in the textile fabric, the textile fabric can be treated to inhibit or reduce the release or diffusion of the formaldehyde or formaldehydic compounds from the textile material. In the prior art, barrier films or coating layers are used to reduce or inhibit the rate or amount of an undesired material into substrate. Barrier films or coating layers are also used in the art to retain a desired material in a substrate. For example, one needs to keep out oxygen and biological material from food when a long shelf life is for the food is required. In one instance, Hybrid Plastics created a fine sausage casing which keeps out CO$_2$ using a polyhedral oligomeric silsesquioxanes (POSS)-filled polymer - Nanoreinforced® Polyamide 6. See for example, hybridplastics.com/wp-content/uploads/2015/04/Hybrid-Plastics%C2%AE-Packaging-Case-Study.pdf. In another example, one needs to keep the surface of the outer layer of glass (cladding) of an optical fiber from becoming etched by exposure to oxygen in the air while keeping the optical fiber flexible. This can be accomplished by coating the outer layer of the optical fiber with a buffer coating of gold, carbon, acrylic, urethane, or polyimide. In another example, metalized Mylar is commonly used to keep helium balloons to keep them afloat when the metal layer acts as a barrier film. In still another example, nanoclays are used to make helium-filled pockets for tennis shoes mimicking Nike Air Jordan's (air pockets). Montmorillonite nanoclays are also used as barrier materials in several applications including for

[0058] Inventors have now discovered inter alia that a barrier film or coating on a surface of the textile material lock in, reduce, or inhibit the release of an undesired material, e.g., formaldehyde, from the textile material. Thus, in the instant invention, the barrier film or the coating layer is used to lock in, reduce, or inhibit the release of an undesired material, e.g., formaldehyde, from the textile material. The prior art appears to be completely silent on taking such an approach. Accordingly, in another aspect the invention provides a method for reducing or inhibiting the release or diffusion out of a molecule from the textile material. Generally, the method comprises contacting the textile material with a composition to form a barrier film or coating layer on a surface of the textile material. Without limitation, the contacting of the textile material with the composition can be accomplished by any art-known method. For example, the contacting can be, but is not limited to, spraying, painting, rinsing, washing, dipping in the composition, and the like.

[0059] In some embodiments, the barrier film or the coating layer is only present on a part of the surface or the textile material. In some other embodiments, the textile material is encapsulated in the barrier film or the coating layer. As used herein, the term "encapsulation" means that the whole surface of the textile material is covered with the barrier film or the coating layer.

[0060] In some embodiments, the barrier film or the coating can impart a desired characteristic or property to the textile surface. Exemplary characteristics or properties include, but are not limited to, oleophobic, hydrophobic, superoleophobic, superhydrophobic, omniphobic, hydrophiiic/wicking, superhydrophytic, abrasion resistance, electrical conductivity, thermal conductivity, anti-fungal and/or anti-bacterial properties.

[0061] Generally, any material that can inhibit or reduce the release or diffusion of an unwanted molecule from the textile material can be used for forming the barrier film or coating layer. Generally, the material used to form the barrier film or the coating layer is a polymeric material or a material capable of forming a polymer. Accordingly, in some embodiments, the barrier film or the coating layer is made from a material selected from the group consisting of carbohydrate polymers, proteins, silk fibroin, polydimethylsiloxane, polyimide, polyethylene, polypropylene, terephthalate, polymethylmethacrylate, urethanes (such as polyurethane),
polyvinylchloride, polystyrene polysulfone, polycarbonate, polymethylpentene, polypropylene, a polyvinylidene fluoride, polysilicon, polytetrafluoroethylene, polysulfone, acrylics; fluoropolymers, polyesters; polyimides; POSS* butadiene styrene, polyacrylonitrile, polybutadiene, poly(butylene terephthalate), poly(ether sulphone), poly(ether ether ketones), poly(ethylene glycol), styrene-acrylonitrile resin, poly(trimethylene terephthalate), polyvinyl butyral, polyvinylidenedifluoride, poly(vinyl pyrrolidone), and any combination thereof.

[0062] Additional, suitable polymers which can be used for forming the barrier film or the coating layer include, but are not limited to, one or a mixture of polymers selected from the group consisting of carbohydrate polymers; silk; glycosaminoglycan; fibrin; poly-ethyleneglycol (PEG); C2 to C4 polyalkylene glycols (e.g., propylene glycol); polyhydroxy ethyl methacrylate; polyvinyl alcohol; polyacrylamide; poly (N-vinyl pyrrolidone); poly glycolic acid (PGA); poly lactic-co-glycolic acid (PLGA); poly e-carbolactone (PCL); poiyethylene oxide; poly propylene fumarate (PPF); poly acrylic acid (PAA); hydrolysed polyacrylonitrile; polytetrafluoroethylene, polyethylene amine; polyanhydrides; polyhydroxybutyric acid; polyorthoesters; polysiloxanes; poly caprolactone; poly(lactic-co-glycolic acid); poly(lactic acid); poly(glycolic acid); alginic acid; esters of alginic acid; pectinic acid; esters of pectic acid; carboxy methyl cellulose; hyaluronic acid; esters of hyaluronic acid; heparin; heparin sulfate; chitosan; carboxymethyl chitosan; clutin; pullulan; gellan; xanthan; collagen; carboxymethyl starch; carboxymethyl dextran; chondroitin sulfate; cationic guar; cationic starch as well as salts and esters thereof, and and copolymers prepared from the monomers of the polymer listed herein.

[0063] In some embodiments, the barrier film or the coating layer is made from a biocompatible material. As used herein, the term "biocompatible material" refers to any-polymeric material that does not deteriorate appreciably and does not induce a significant immune response or deleterious tissue reaction, e.g., toxic reaction or significant irritation, over time when implanted into or placed adjacent to the biological tissue of a subject, or induce blood clotting or coagulation when it comes in contact with blood. Suitable biocompatible materials include derivatives and copolymers of a polyimides, poiy(ethylene glycol), polyvinyl alcohol, polyethyleneimine, and polyvinylamine, polyacrylates, poiyamides, polyesters, polycarbonates, and polystyrenes.

[0064] In some embodiments, the barrier film or the coating layer is made from a material selected from the group consisting of acrylics; fluoropolymers, polyesters; polyimides; POSS*. 

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polymers (silesquioxanes); urethanes (such as polyurethanes); biologically-compatible polymers, such as, polycarbonates, polymers based on propylene (such as polypropylenes), and polymers based on ethylene (such as polyethylenes); ultra-high molecular weight polyethylene (UHMWPE); and any combinations thereof. Zhu and Han, Polymer (2008) 48: 3624-3631, content of which is incorporated herein by reference in its entirety, describes a hydrophobic fluoropolymer coating that is amenable to the present invention. Many POSS* polymers are commercially available from Sigma Aldrich. Bakshi et al., JOM July 2007, page 50, content of which is incorporated herein by reference in its entirety, describe the nanomechanical and nanoscratch properties of MW CNT-reinforced ultrahigh-Molecular Weight Polyethylene coatings. In some embodiments, the barrier film or the coating layer comprises acrylic, or nanoclay filled acrylic. In some embodiments, the barrier film or the coating layer comprises a non-fluoropolymer. Non-fluoropolymers, such as polyurethanes, are available from DuPont.

In some embodiments, the barrier film or the coating layer is made from two or more different materials. In some embodiments, at least one of the material in forming the barrier film or the coating layer is a fluoropolymer. As used herein, the term "fluoropolymer" refers to a polymer comprising recurring units derived from at least one fluorinated monomer. As used herein, the term "at least one fluorinated monomer" means that the polymer may comprise recurring units derived from one or more than one fluorinated monomers. Exemplary fluoropolymers amenable to the invention are described, for example, in US Patent No. 7,829,477.

It is also possible to form the barrier film or the coating layer with a harder material. This is what the optical fiber industry does to protect the core glass fiber when it applies a cladding layer of glass over the core glass. Use of a hard but sufficiently flexible coating material allows for additions of other useful properties at the coating level. Thus, in some embodiments, the barrier film or the coating layer is a nanocomposite dielectric coating. Nanocomposite dielectric coatings are described, for example in US Patent No. 8,470,459, content of which is incorporated herein by reference in its entirety.

Jason Benkoski (Johns Hopkins University), "Passive cooling with UV-resistant siloxane coatings in direct sunlight," 250th National Meeting & Exposition of the American Chemical Society (ACS) in Boston, August 17, 2015, describes a glass-based paint that reflects light off metal surfaces to keep them cool and protects those surfaces from corrosion accelerated
by the harsh rays of the sun. Use of such glass/silica paint can also be useful for controlling the 
wear er's temperature in certain circumstances. Thus, in some embodiments, the barrier film or 
the coating layer comprises a glass/silica based paint.

[0068] The barrier film or the coating layer can be of any desired thickness. In some 
embodiments, the barrier film or the coating can have a thickness of a few nanometers to a few 
millimeters. For example, the barrier film or the coating thickness can range from about 0.1 nm 
to about 1000 nm. It is noted that the barrier film or the coating thickness can be based on the 
material used for the barrier film or the coating. For example, when the barrier film or the 
coating comprises a metal or is metallic the thickness can be under 25 microns. When the 
barrier film or the coating comprises a polymer or is polymeric the thickness can range from 
about 5 microns to about 100 microns. It is noted that the thickness can be varied as desired.

[0069] Generally, the barrier film or the coating is very, very thin and does not show up on a 
simple light microscope. However, the barrier film or the coating may be seen as a film bridging 
the gaps between threads in a woven substrate as shown in Fig. 1. At the thread level, the barrier 
film or the coating can be a thin or ultrathin coating on the shape, e.g., cylindrical, of the fiber. 
An exemplary embodiment of coated fiber is shown schematically in Fig. 2.

[0070] Metal films including gold, as well as carbon films, have been used for many years as 
barrier films in many industries including the optical fiber industry where they virtually 
eliminate the attack by oxygen from the air on the glass surface of the optical fiber's cladding 
layer. The wire and cable industry also uses metallic coatings to reduce corrosion of underlying 
metals. While the use of metal and carbon films in the prior art is directed to protecting the 
coated surface, there is no description in the art teaching or suggesting the use of metal or carbon 
films to inhibit or reduce release of undesired molecules from the coated surface. Thus, in some 
embodiments, the barrier film or the coating layer comprises a metal coating layer on a surface 
of the barrier film or the coating layer.

[0071] As used herein, the term "metal coating" means applying to a surface of the barrier 
film or the coating layer a metal. Without limitations, any metal can be used for forming the 
metal coating layer. Exemplary metals include, but are not limited to gold, silver, copper, nickel, 
iron, cobalt, zinc, titanium, platinum, palladium, aluminum, tin, lead, and other metals or any 
combination of metals to make a metal alloy. Metal coating layer can formed using known
metal coating or metal plating processes such as spraying, vapor deposition, powder coating, immersion processes, solution dipping processes, electroless plating and electroplating.

[0072] In some embodiments, the barrier film or the coating layer comprises a metal coating layer on a surface of the barrier film or the coating layer. An exemplary embodiment of this is shown schematically in Fig. 3. As used herein, carbon coating generally includes two to four covalently linked carbon (C), hydrogen (H), silicon (Si), and oxygen (O) atoms.

[0073] Like the barrier film or the coating layer, the metal coating layer can be of any desired thickness. In some embodiments, the metal coating can have a thickness of a few nanometers to a few millimeters. For example, the metal coating thickness can range from about 0.1 nm to about 1000µm. The metal coating thickness can be of the same thickness as the barrier film or the coating layer, larger than the thickness of the barrier film or the coating layer, or smaller than the thickness of the barrier film or the coating layer. In some embodiments, the metal coating thickness is about from 5 microns to about 15 microns.

[0074] In some embodiments, the barrier film or the coating layer comprises a carbon coating layer on a surface of the barrier film or the coating layer. As used herein, carbon coating generally includes two to four covalently linked carbon (C), hydrogen (H), silicon (Si), and oxygen (O) atoms.

[0075] Like the barrier film or the coating layer, the carbon coating layer can be of any desired thickness. In some embodiments, the carbon coating can have a thickness of a few nanometers to a few millimeters. For example, the carbon coating thickness can range from about 0.1 nm to about 1000µm. The carbon coating thickness can be of the same thickness as the barrier film or the coating layer, larger than the thickness of the barrier film or the coating layer, or smaller than the thickness of the barrier film or the coating layer.

[0076] In some embodiments, the matrix of the barrier film or the coating layer can comprise materials other than the matrix material distributed in the matrix material. Such materials can include, but are not limited to nanocomposites, nanoparticies, dyes, antibacterial or antifungal agents, metals, metal alloys, and the like.

[0077] In some embodiments, the barrier film or the coating layer comprises nanoclays, carbon based materials, e.g., CNTs or graphene platelets, dispersed in the matrix material of the barrier film or the coating layer. Without wishing to be bound by theory, inclusion of nanoclays, CNTs, platelets, graphene platelets and particles in the barrier film or coating layer can provide
an arduous path for gas or liquid molecules as they outgas from the textile material. Without wishing to be bound by a theory, this can be considered biomimicry when, for example, you combine a polymer film with layered hard platelets like nanoclays as is done in producing abalone shells (using hard salts and soft living proteins) creating impact resistant and flexible structures.

[0078] In some embodiments, the barrier film or the coating layer comprises more than one layer, e.g., two, three, four, five, six, seven, eight, nine, ten or more layers. The different layers can be the same or different. By "different" in this context is meant that two layers differ from each other by at least one aspect. For example, the two layers can differ from each other based on the matrix material, components distributed in the matrix material, thickness of the layers, density of the layers, functional properties of the layers, etc... The layers can be individual layers or the same material, e.g., Integran's NANOBATE CoP plating and NANO-Copper plating product.

[0079] In some embodiments, the barrier film or the coating layer comprises particles, such as nanoparticles. In some embodiments, the nanoparticles form features such as microscale, nanoscale, multiscale or pillars on the surface of the textile material. In some embodiments, the nanoparticles form localized deposits on surface of the textile material that act as pillars. In some embodiments, the nanoparticles form features, such as those shown in Fig. 5 on the surface of the textile material.

[0080] Generally, the barrier film or the coating layer can inhibit or reduce the release or diffusion out of the undesired molecule, e.g., formaldehyde or formaldehydic compounds from the treated textile material by at least 10% (e.g., at least 15%, at least 20%, at least 25%, at least 30%, at least 35%, at least 40%, at least 45%, at least 50%, at least 55%, at least 55%, at least 60%, at least 65%, at least 70%, at least 75%, at least 80%, at least 85%, at least 90%, at least 95%, or at least 99% and upto and including 100%, i.e., complete inhibition or reduction) relative to release or diffusion from an untreated control textile material. In some embodiments, the treated textile material releases no formaldehyde or formaldehydic compounds or only trace amounts that are below the detection limit of the method employed for detecting the release of formaldehyde or formaldehydic compounds.

[0081] European Ecolabel and Oeko-Tex Standard 100 have set limits for formaldehyde that vary depending on textile categories. In particular, Ecolabel set limits of 30 mg/kg for
formaldehyde released from textiles in direct contact with the skin and 300 mg/kg for textiles which have no direct contact with the skin. Oeko-Tex Standard 100 set limits of 75 mg/kg for for formaldehyde released from textiles in direct contact with the skin and 300 mg/kg for textiles which have no direct contact with the skin. In addition, Oeko-Tex Standard 100 established that textiles for babies up to two years old should release less than 20 mg/kg. Thus, in some embodiments, less than 30 mg/kg (e.g., 30 mg/kg, 25 mg/kg, 20 mg/kg, 15 mg/kg, 10 mg/kg, 5 mg/kg or less) formaldehyde is released from the treated textile material.

[0082] Several colorimetric procedures are available in the art for the detection of trace amounts of formaldehyde. These colorimetric procedures can detect formaldehyde concentrations in the range of parts per million (ppm). The procedures commonly employ Schiffs reagent or Edgriwe's reagent as the indicator. Schiffs reagent, which is prepared from rosaniline and bisulfite in concentrated hydrochloric acid, and Edgriwe's reagent, which consists of chloraotropic acid in strong sulfuric acid, both require strong acid. For the determination of percent levels of formaldehyde, the sodium sulfite and sodium bisulfite methods have been used. In these methods, the reaction of a sodium sulfite or sodium bisulfite reagent with formaldehyde generates an equal molar amount of sodium hydroxide. The amount of formaldehyde is estimated from the amount of acid required to titrate the generated sodium hydroxide. For a more thorough description of the sodium sulfite and sodium bisulfite methods, see IF. Walker, "Quantitative Analysis of Formaldehyde," in Formaldehyde, 3rd ed., Reinhold Publishing Corporation, New York, NY, pp. 486-488 (1964), content of which is incorporated herein by reference in its entirety.

[0083] Organic nitrogen compounds, such as amines, amides, ureides, amino acids, and proteins having hydrogen bonded to the nitrogen, also can react with formaldehyde to provide a useful assay for formaldehyde content. For example, formaldehyde reacts with lower amino acids, such as alanine, asparagine, and glycine in an aqueous solution. The aqueous solutions of these lower amino acids have a slightly acidic or neutral pH. In the presence of formaldehyde, however, the amino acids react as strong acids. The concentration of formaldehyde can be determined by end point titration of the amino acid-formaldehyde solution with an alkaline solution. Further description of the reaction of formaldehyde with organic nitrogen containing compounds, and more particularly amino acids, can be found in IF. Walker, "Reaction with Amines, Amides and Nitriles," in Formaldehyde, 3rd ed., Reinhold Publishing Corporation, New
Dye color leaching from the textile material during processing or washing is a big concern in the textile industry. The methods disclosed herein can be used to reduce or inhibit the release of dyes from textile material. In one example, textile material in the form of cotton thread was treated with an acrylic based fluoropolymer from Clariant to form a barrier film or coating layer. The release of dyes from the textile material was significantly reduced when compared to non-coated textile material.

Specifically, red dye treated cotton thread was wound onto a spool for further treatment. Normally, a special chemical bath of color fixative would then be applied to minimize loss of the red dye into the later expensive treatment fluids for producing softness to the touch, resistance to wrinkle development, repelling water, etc. However, according to an embodiment of the invention, this step was skipped and a modified Clariant-branded acrylic-based fluoropolymer fluid was applied under heat and pressure. The immediate result was a reduction in the redness of the recovered treatment fluid. This process and chemistry provided a barrier film with both water repellant and fixative benefits with application of one fluid reducing material, labor, and machine-time costs.

In another aspect, the invention provides a method for treating a textile material with a composition that is essentially free of formaldehyde or formaldehydic compounds. Generally, the method comprises contacting a textile material with a composition that is essentially free of formaldehyde or formaldehydic compounds. In some embodiments, the composition imparts superoleophobic, superhydrophobic, omniphobic, hydrophilic/wicking, abrasion resistance, electrical conductivity, thermal conductivity, anti-fungal and/or anti-bacterial characteristics to the textile material.

The finishing composition, i.e., the composition for forming the barrier film or the coating layer or the composition used for imparting a desired characteristic or functionality to the textile material, can be applied to the textile material in accordance with any of the conventional techniques known in the art. For example, the contacting of the textile material with the composition can be, but is not limited to, spraying, painting, rinsing, washing, dipping in the composition, and the like.
[0088] In one embodiment, the treatment composition can be applied to the textile material by saturating the textile material in a trough and squeezing the saturated textile material through pressure rollers to achieve a uniform application (padding process). Herein "wet pick-up" refers to the amount of treatment composition applied to and/or absorbed into the textile material based on the original weight of the textile material. "Original weight of the textile material" or simply "weight of the textile material" refers to the weight of the textile material prior to its contact with the treatment composition. For example, 50% pick-up means that the textile material picks up an amount of treatment solution equal to about 50% of the textile material's original weight. Preferably the wet pick-up is at least about 20%, preferably from about 50% to 100%, more preferably from about 65% to about 80%, by weight of the textile material for many applications. It is noted that, for fluorocarbon treatments of materials to be labeled "organic," 3-7% pick-up is preferred to maintain the label. Other application techniques that can be employed include kiss roll application, engraved roll application, printing, foam finishing, vacuum extraction, spray application or any process known in the art. Generally, these techniques provide lower wet pick-up than the padding process. The concentration of the components in the solution can be adjusted to provide the desired amount of barrier film or the coating layer on the original weight of the textile material.

[0089] In some embodiments, the composition is applied in an amount to insure a moisture content of more than about 10% by weight, preferably more than about 30% by weight, on the textile material.

[0090] In some embodiments, the textile material can be pretreated with a textile pre-treatment preparation technique known in the art. Suitable preparation techniques include brushing, singeing, de-sizing, scouring, mercerizing, and bleaching. For example, the textile material can be treated by brushing which refers to the use of mechanical means for raising surface fibers that will be removed during singeing. The textile material then be singed using a flame to burn away fibers and fuzz protruding from the fabric surface. The textile material can be de-sized, which refers to the removal of sizing chemicals such as starch and/or polyvinyl alcohol, which are put on yarns prior to weaving to protect individual yarns. The textile material can be scoured, which refers to the process of removing natural impurities such as oils, fats and waxes and synthetic impurities such as mill grease from the textile material. Mercerization refers to the application of high concentrations of sodium hydroxide (or optionally liquid ammonia) and
optionally high temperatures, steam, and tension to a fabric to alter the morphology of fibers, particularly cotton fibers. Fabrics may be mercerized to improve fabric stability, moisture retention and uptake, chemical reactivity, tensile strength, dye affinity, smoothness, and luster. Fabrics may also be compressively stabilized (e.g., SANFORIZED®) by manipulation/compaction of the fabric in the presence of heat and steam. Finally, bleaching refers to the process of destroying any natural color bodies within the natural fiber. A typical bleaching agent is hydrogen peroxide.

[0091] After treatment, the textile material can optionally be washed to remove residual materials or to apply additional technologies/treatments to the textile material. Post-washing of the textile material can occur before or after construction of the end-product. Washing can occur via continuous or batch processes.

[0092] The finish composition can comprise, in addition to the material for forming the barrier film or the coating layer or the material for imparting a desired characteristic or functionality to the textile material, additional ingredients to enhance the characteristics of the final finished textile material. Exemplary such ingredients include, but are not limited to, wetting agents, brighteners, softening agents, stain repellant agents, color enhancing agents, anti-abrasion additives, water repellency agents, UV absorbing agents and fire retarding agents.

[0093] The invention also provides the textile material treated with the methods disclosed herein. In some embodiments, the textile material is in the form of a wearable, i.e., an article of clothing. In some embodiments, the textile material, e.g., the article of clothing is worn against the skin.

[0094] After contacting with the composition, the treatment process can further comprise contacting the substrate with a composition comprising a formaldehyde scavenger. Exemplary formaldehyde scavengers include, but are not limited to, urea, ethylene urea 4,5-dihydroxyl ethylene urea, ammonium phosphate monobasic and ammonium phosphate dibasic, FREETEX® HFSE, and tannin. Additional formaldehyde scavengers amenable to the present invention include those described, for example, in US Patent No. 5,194,674 and US Patent Publication No. 2009/0014034, the contents of which are incorporated herein by reference in their entirety.

[0095] The treatment process can further comprise one or more wash steps. In some embodiments, the substrate undergoes a washing step before contacting with the composition that is free of formaldehyde or formaldehydic compounds. In some embodiments, the substrate
undergoes a washing step before contacting with the composition that is free of formaldehyde or formaldehydic compounds.

[0096] Without limitation, the treatment process can be at any appropriate temperature, e.g., room-temperature (e.g., about 16°C to about 30°C), a cold temperature (e.g. about 0°C to about 16°C), or an elevated temperature (e.g., about 30°C to about 95°C). Further, different steps of the treatment process can be carried out at different temperatures.

[0097] Generally, contacting of the composition with the substrate is for sufficient duration to impart a desired level of oleophobic, hydrophobic, hydrophilic, superoleophobic, superhydrophobic, superhydrophilic and/or omniphobic characteristics to the substrate. Accordingly, the contacting can be from anywhere from few seconds to minutes, hours, days, weeks or months.

[0098] Suitable compositions that can impart superoleophobic, superhydrophobic and/or omniphobic characteristics to a surface include those described, for example, in U.S. Patent No. 8,580,027, the contents of which are incorporated herein by reference in their entirety.

[0099] It is noted that not the whole of the textile material needs to undergo the treatments described herein. For example, it can be desirable to only treat a part of the textile material. This can provide textile material having different surface properties.

[00100] Two standard methods are available for measuring the release of formaldehyde from textiles: the water extraction method (EN ISO 14184-1) and the vapour absorption method (EN ISO 14184-2). The first method (EN ISO 14184-1) is based on the extraction of a weighed amount of sample material (approx. 1.0 g) with water at 40°C for one hour (an oscillating water bath was used). The extract is then filtered and treated with acetylacetone (Nash reactive), with which formaldehyde reacts to give a yellow compound (3,5-diacetyi-l,4-dihydrolutidine). The color development is obtained in half an hour at 40°C. The absorbance of the reaction product is measured at 412 nm and the quantification of formaldehyde is performed with the use of external standards.

[00101] The second method (EN ISO 14184-2) is based on the absorption in water of formaldehyde vapour released by a weighed amount of sample material (approx. 1.0 g) suspended over water in a sealed jar. The jar is placed in an oven at 49°C for 20 hours. The quantification of formaldehyde in the aqueous solution is performed, as in the previous method, by a colorimetric reaction with Nash reagent.
Over the course of the last century, experiments have revealed that the wax on the lotus leaf surface, by itself, is weakly hydrophilic, even though the lotus leaf is known to be superhydrophobic. Conventional understanding suggests that a surface of such a waxy composition should not be able to support superhydrophobicity and high contact angles between a liquid and the surface. As disclosed herein, the unexpected superhydrophobicity is related to the presence of "reentrant texture" (that is, a multivalued surface topography) on the surface of the lotus leaf. The inventors used their understanding of this multivalued surface topology to enable the development of superoleophobic surfaces (i.e., surfaces that repel soil and water at extremely low-surface-tension liquids, such as various fluoroalkanes), where essentially no naturally oleophobic materials exist. The invention further provides general design parameters for "breathability," that enable the evaluation of the robustness of the composite interface on textile surface depending on the usage and amount of "waterproofness and breathability." Based on design parameters of a textile's "weave," airflow can be regulated. For example, the more open weave a fabric has, the more "breathable" it will be in transporting water away from the body, although axiomatically that also means less waterproofness as there is a direct tradeoff between airflow and not letting water in.

Surface roughness and apparent contact angles are important elements for textile surfaces "staying dry" and not wetting themselves.

The engineering of liquid-repellent surfaces typically involves the manipulation of two key surface parameters: surface energy and physical roughness. The overall free energy of the system determines whether a given liquid fully wets or creates a composite interface with a particular textured surface. In contrast to a fully wetted interface, the composite interface typically leads to high contact angles and low roll-off angles (corresponding to low contact-angle hysteresis). Studies show that a series of rough or textured substrates within the fabric, with progressively decreasing surface energy, or increasing equilibrium contact angles (Θ), exhibit a transition from a fully wetted state to a composite interface, equating the critical value of the equilibrium contact angle (Θc) this transition. Contact angles above Θc lead to a lower overall free energy for the composite interface than for the corresponding fully wetted interface (enabling the localized trapping of air) underneath liquid droplets on the fabric which, through dimensionless design parameters and the independent control of the surface chemical and topographic features, allow for the development of textured surfaces that can support both an extremely robust
composite interface and high contact angles with any liquid in the creation of a superhydrophobic or superoleophobic textured surface.

[00105] Measuring the contact angle $\Theta$ is one way to characterize wetting of surfaces. The contact angle $\Theta$ is affected both by the chemical nature of the surface and by its roughness. Affinity of a flat surface towards a certain liquid is defined in terms of the "flat" (or intrinsic, or Young's) contact angle:

$$\cos(\Theta_{\text{flat}}) = \frac{\gamma_{SL} - \gamma_{SL}}{\gamma_{LA}}$$

(1)

[00106] where $\gamma$ is the surface energy (or surface tension), subscript $S$ stands for solid, $L$ for liquid and $A$ for air. The solid-liquid surface energy can be estimated via the other two as follows:

$$\gamma_{SL} = \gamma_{SA} + \gamma_{LA} - 2\sqrt{\gamma_{SA}\gamma_{LA}}$$

(2)

[00107] The surface is called (hydro-, oleo-, etc.) -phobic if the contact angle is greater than 90°, and -philic otherwise. For water (surface energy $\gamma_{LA} = 73$ mJ m$^{-2}$) the best non-wetting situation on a flat surface is achieved if it is terminated with -CF$_3$ groups, which brings its surface energy down to $SA \approx 6$ mJ m$^{-2}$. The value of intrinsic (Young's) contact angle for water on such a surface is $\theta_{\text{flat}} \approx 120^\circ$

[00108] By contrast, most oils have very low surface energies (e.g. $\gamma_{LA} = 27.6$ mJ m$^{-2}$ for hexadecane, $\gamma_{\nu} = 23.8$ mJ m$^{-2}$ for decane). Consequently, even on the chemically least energetic -CF$_3$ terminated surface, the intrinsic (Young's) contact angle for typical oil such as hexadecane is $\theta_{\text{flat}} \approx 78^\circ$. In other words, flat surfaces are intrinsically oleophilic, according to Young's contact angle, no matter what the chemical nature is of the flat surface. This circumstance has profound consequences on the design of superoleophobic surfaces.

[00109] As used herein, the term "oleophobic" comprises surfaces having a contact angle for an organic liquid of greater than 90°. As used herein the term "superoleophobic" comprises surfaces having a contact angle for an organic liquid of greater than 150°. Such organic liquids may comprise hydrocarbon liquids having a surface energy $\gamma_{LA} < 30$ mJ m$^{-2}$. Such liquid hydrocarbons may be characterized as hydrophobic and may be liquid at ambient temperature and pressure. Such liquids may comprise aliphatic hydrocarbons having from 6 to 14 carbon
atoms, for example octane, decane or hexadecane. A preferred organic liquid for the purposes of defining superoleophobicity herein is hexadecane.

[00110] As used herein, the term "hydrophobic" comprises surfaces having a contact angle for water of greater than 90°. As used herein, the term "superhydrophobic" as used herein comprises surfaces having a contact angle for water of greater than 150°.

[00111] The area fraction, f, of the surface can be important for providing desirable superoleophobic properties. It can be desirable to provide the textile fabric surface with an area fraction in the range of from 0.01 to 0.20, or from 0.01 to 0.15, or from 0.01 to 0.10, or from 0.05 to 0.10, or from 0.02 to 0.09, or from 0.03 to 0.08, or from 0.04 to 0.07, or from 0.05 to 0.06.

[00112] As used herein, the term "hydrophilic" comprises surfaces having a contact angle for water of less than 90°. As used herein, the term "superhydrophilic" comprises surfaces having a contact angle for water of less than 1°.

[00113] The term "anti-icing" as used herein refers to the process of preventing ice from bonding to or forming on a surface. It will be understood that the term "anti-icing" refers to the prevention of the formation of ice in the first place whereas the term "de-icing" refers to the reduction, or elimination, of ice after it has begun to form.

[00114] The term "reentrant" as used herein comprises a surface feature that has a first portion with a first width and a second portion with a second width, the first width greater than the second width. One example of a re-entrant surface feature is provided by a plurality of nanoparticles aggregated atop a micropillar such that a composite top is formed having a diameter larger than that of the pillar. Re-entrant features preferably have a convex upper surface. Re-entrant surface features may resemble "mushroom caps", "bean sprouts", "hoodoos", or a variety of other similar commonly known shapes when seen in side view. The terms "reentrant" and "multivalued" as they refer to a surface topology are used interchangeably herein.

[00115] Accordingly, in some embodiments, the textile process treatment disclosed herein imparts a reentrant texture to the textile fabric surface feature that has a first portion with a first width and a second portion with a second width, the first width greater than the second width. One example of a re-entrant surface feature is provided by a plurality of nanoparticles aggregated atop a micropillar such that a composite top is formed having a diameter larger than that of the
pillar. Re-entrant features preferably have a convex upper surface. Re-entrant surface features may resemble "mushroom caps", "bean sprouts", "hoodoos", or a variety of other similar commonly known shapes when seen in side view. The terms "reentrant" and "multivalued" as they refer to a surface topology are used interchangeably herein.

[00116] In some embodiments, the reentrant texture comprises microscale features or nanoscale scale features. In some embodiments, the reentrant texture comprises a combination of microscale and nanoscale features, i.e., the reentrant texture is a multiscale surface. In some embodiments, the reentrant texture comprises features that appear to be pillars. In some embodiments, the reentrant texture comprises features that are multiscale pillars and/or hierarchical features.

[00117] In some embodiments, the reentrant texture comprises features or shape formed from a plurality of co-deposited generally spherical particles, such as nanoparticles.

[00118] Exemplary embodiments of the various aspects disclosed herein can be described by one or more of the following numbered paragraphs:

1. A method for inhibiting or reducing the release or diffusion of a molecule present in textile material, the method contacting a textile material with a composition comprising a barrier film or a coating layer forming material, thereby forming a barrier film or a coating layer on surface of the textile material.

2. The method of paragraph 1, wherein the molecule is formaldehyde or a formaldehydic compound.

3. The method of paragraph 1 or 2, wherein said forming the barrier film or the coating layer is in absence of formaldehyde or formaldehydic compounds.

4. The method of any of paragraphs 1-3, wherein the textile material is a fibrous material.

5. The method of any of paragraphs 1-4, wherein the textile material is selected from the group consisting of fiber, thread, yarn, cloth, fabric, fabric blend or garment.

6. The method of any of paragraphs 1-5, wherein the textile material comprises a synthetic material.

7. The method of any of paragraphs 1-6, wherein the textile material comprises a natural material.
The method of any of paragraphs 1-7, wherein the textile material is selected from the group consisting of cotton, cellulose, wool, silk, rayon, nylon, aramid, acetate, acrylic, jute, sisal, sea grass, coir, polyamide, polyester, polyolefin, polyacrylonitrile, polypropylene, polyaramide, and blends thereof.

The method of any of paragraphs 1-8, wherein the textile material is a thread and the thread comprises two or more different types of fibers.

The method of any of paragraphs 1-9, wherein the textile material further comprises a material dispersed in the matrix of the textile material.

The method of any of paragraphs 1-10, wherein the barrier film or the coating layer is made from a polymeric material or a nanocomposite material.

The method of any of paragraphs 1-11, wherein the barrier film or the coating layer comprises acrylic, polyester, polyimide, POSS, urethane, biologically-compatible polymer, SiCoN, or any combinations thereof.

The method of any of paragraphs 1-12, wherein the barrier film or the coating layer comprises ultra-high molecular weight polyethylene (UHMWPE) or propylene based polymer.

The method of any of paragraphs 1-13, wherein the barrier film or the coating layer comprises a non-fluoropolymer.

The method of paragraph 14, wherein the non-fluoropolymer is a urethane based polymer.

The method of any of paragraphs 1-15, wherein the barrier film or the coating layer comprises at least two different materials.

The method of paragraph 16, wherein at least one of the at least two different material is a fluoropolymer.

The method of any of paragraphs 1-17, wherein the barrier film or the coating layer comprises a material dispersed in the barrier film or the coating layer.

The method of paragraph 18, wherein the material is nanoclay, CNTs, platelet, graphene platelet, particles, or any combinations thereof.

The method of any of paragraphs 1-19, wherein the barrier film or the coating layer comprises a metal coating layer or carbon coating on a surface of the barrier or the coating film.
21. A method for treating a textile material to form a oleophobic, hydrophobic, superoleophobic, superhydrophobic, omniphobic, hydrophilic/wicking, abrasion resistance, electrical or thermal conductive, anti-fungal, anti-bacterial, or anti-icing textile surface, the method comprising contacting a textile material with a composition that is free of formaldehyde or formaldehydic compounds.

22. The method of any of paragraphs 1-21, further comprising contacting the textile material with a composition comprising formaldehyde scavenger.

23. The method of any of paragraphs 1-22, further comprising a step of washing the textile material.


25. A textile material comprising a barrier film or a coating layer on surface of the textile material, wherein the barrier film or the coating film inhibits or reduces the diffusion of a molecule present in textile material by at least 10% relative to a textile material lacking the barrier film or the coating film.

26. The textile material of paragraph 25, wherein the molecule is formaldehyde or a formaldehydic compound.

27. The textile material of paragraph 25 or 26, wherein said forming the barrier film or the coating layer is in absence of formaldehyde or formaldehydic compounds.

28. The textile material of any of paragraphs 25-27, wherein the textile material is a fibrous material.

29. The textile material of any of paragraphs 25-28, wherein the textile material is selected from the group consisting of fiber, thread, yarn, cloth, fabric, fabric blend or garment.

30. The textile material of any of paragraphs 25-29, wherein the textile material comprises a synthetic material.

31. The textile material of any of paragraphs 25-30, wherein the textile material comprises a natural material.

32. The textile material of any of paragraphs 25-31, wherein the textile material is selected from the group consisting of cotton, cellulose, wool, silk, rayon, nylon, aramid, acetate, acrylic, jute, sisal, sea grass, coir, polyamide, polyester, polyolefin, polyacrylamide, polypropylene, polyaramide, and blends thereof.
33. The textile material of any of paragraphs 25-32, wherein the textile material is a thread and the thread comprises two or more different types of fibers.

34. The textile material of any of paragraphs 25-33, wherein the textile material further comprises a material dispersed in the matrix of the textile material.

35. The textile material of any of paragraphs 25-34, wherein the barrier film or the coating layer comprises a polymeric material or a nanocomposite material.

36. The textile material of any of paragraphs 25-35, wherein the barrier film or the coating layer comprises acrylic, polyester, polyimide, polyhedral oligomeric silsesquioxanes, urethane, biologically-compatible polymer, SiCoN nanocomposites, glass/silica paint or any combinations thereof.

37. The textile material of any of paragraphs 25-36, wherein the barrier film or the coating layer comprises ultra-high molecular weight polyethylene (UHMWPE).

38. The method of any of paragraphs 25-37, wherein the barrier film or the coating layer comprises a non-fluoropolymer.

39. The method of paragraph 38, wherein the non-fluoropolymer is polyurethane.

40. The textile material of any of paragraphs 25-39, wherein the barrier film or the coating layer comprises at least two different materials.

41. The textile material of paragraph 40, wherein at least one of the at least two different material is a fluoropolymer.

42. The textile material of any of paragraphs 25-41, wherein the barrier film or the coating layer further comprises a material dispersed in the barrier film or the coating layer.

43. The textile material of paragraph 42, wherein the material is nanoclay, platelet, graphene platelets, particles, or any combinations thereof.

44. The textile material of any of paragraphs 25-43, wherein the barrier film or the coating layer comprises a metal coating layer on a surface of the barrier or the coating film.

[00119] All patents and other publications identified in the specification and examples are expressly incorporated herein by reference for all purposes. These publications are provided
solely for their disclosure prior to the filing date of the present application. Nothing in this regard should be construed as an admission that the inventors are not entitled to antedate such disclosure by virtue of prior invention or for any other reason. All statements as to the date or representation as to the contents of these documents is based on the information available to the applicants and does not constitute any admission as to the correctness of the dates or contents of these documents.

[00120] Although preferred embodiments have been depicted and described in detail herein, it will be apparent to those skilled in the relevant art that various modifications, additions, substitutions, and the like can be made without departing from the spirit of the invention and these are therefore considered to be within the scope of the invention as defined in the claims which follow. Further, to the extent not already indicated, it will be understood by those of ordinary skill in the art that any one of the various embodiments herein described and illustrated can be further modified to incorporate features shown in any of the other embodiments disclosed herein.
CLAIMS

What is claimed is:

1. A method for inhibiting or reducing the release or diffusion of a molecule present in textile material, the method contacting a textile material with a composition comprising a barrier film or a coating layer forming material, thereby forming a barrier film or a coating layer on surface of the textile material.

2. The method of claim 1, wherein the molecule is formaldehyde or a formaldehydic compound.

3. The method of claim 1 or 2, wherein said forming the barrier film or the coating layer is in absence of formaldehyde or formaldehydic compounds.

4. The method of any of claims 1-3, wherein the textile material is a fibrous material.

5. The method of any of claims 1-4, wherein the textile material is selected from the group consisting of fiber, thread, yarn, cloth, fabric, fabric blend or garment.

6. The method of any of claims 1-5, wherein the textile material comprises a synthetic material.

7. The method of any of claims 1-6, wherein the textile material comprises a natural material.

8. The method of any of claims 1-7, wherein the textile material is selected from the group consisting of cotton, cellulose, wool, silk, rayon, nylon, aramid, acetate, acrylic, jute, sisal, sea grass, coir, poiyamide, polyester, poiyoiefin, polyaerylamide, polypropylene, polyaramide, and blends thereof.

9. The method of any of claims 1-8, wherein the textile material is a thread and the thread comprises two or more different types of fibers.

10. The method of any of claims 1-9, wherein the textile material further comprises a material dispersed in the matrix of the textile material.

11. The method of any of claims 1-10, wherein the barrier film or the coating layer is made from a polymeric material or a nanocomposite material.

12. The method of any of claims 1-11, wherein the barrier film or the coating layer comprises acrylic, polyester, polyimide, POSS, urethane, biologically-compatible polymer, SiCoN, or any combinations thereof.
13. The method of any of claims 1-12, wherein the barrier film or the coating layer comprises ultra-high molecular weight polyethylene (UHMWPE) or a propylene based polymer.
14. The method of any of claims 1-13, wherein the barrier film or the coating layer comprises a non-fluoropolymer.
15. The method of claim 14, wherein the non-fluoropolymer is a urethane based polymer.
16. The method of any of claims 1-15, wherein the barrier film or the coating layer comprises at least two different materials.
17. The method of claim 16, wherein at least one of the at least two different material is a fluoropolymer.
18. The method of any of claims 1-17, wherein the barrier film or the coating layer comprises a material dispersed in the barrier film or the coating layer.
19. The method of claim 18, wherein the material is nanoclay, CNTs, platelet, graphene platelet, particles, or any combinations thereof.
20. The method of any of claims 1-19, wherein the barrier film or the coating layer comprises a metal coating layer or carbon coating on a surface of the barrier or the coating film.
21. A method for treating a textile material to form a oleophobic, hydrophobic, superoleophobic, superhydrophobic, omniphobic, hydrophilic/wicking, abrasion resistance, electrical or thermal conductive, anti-fungal, or anti-bacterial textile surface, the method comprising contacting a textile material with a composition that is free of formaldehyde or formaldehydic compounds.
22. The method of any of claims 1-21, further comprising contacting the textile material with a composition comprising formaldehyde scavenger.
23. The method of any of claims 1-22, further comprising a step of washing the textile material.
24. A textile material treated by the method any of claims 1-23.
25. A textile material comprising a barrier film or a coating layer on surface of the textile material, wherein the barrier film or the coating film inhibits or reduces the diffusion of a molecule present in textile material by at least 10% relative to a textile material lacking the barrier film or the coating film.
26. The textile material of claim 25, wherein the molecule is formaldehyde or a formaldehydic compound.
27. The textile material of claim 25 or 26, wherein said forming the barrier film or the coating layer is in absence of formaldehyde or formaldehydic compounds.

28. The textile material of any of claims 25-27, wherein the textile material is a fibrous material.

29. The textile material of any of claims 25-28, wherein the textile material is selected from the group consisting of fiber, thread, yarn, cloth, fabric, fabric blend or garment.

30. The textile material of any of claims 25-29, wherein the textile material comprises a synthetic material.

31. The textile material of any of claims 25-30, wherein the textile material comprises a natural material.

32. The textile material of any of claims 25-31, wherein the textile material is selected from the group consisting of cotton, cellulose, wool, silk, rayon, nylon, aramid, acetate, acrylic, jute, sisal, sea grass, coir, polyamide, polyester, polyolefin, polyacrylamide, polypropylene, polyaramide, and blends thereof.

33. The textile material of any of claims 25-32, wherein the textile material is a thread and the thread comprises two or more different types of fibers.

34. The textile material of any of claims 25-33, wherein the textile material further comprises a material dispersed in the matrix of the textile material.

35. The textile material of any of claims 25-34, wherein the barrier film or the coating layer comprises a polymeric material or a nanocomposite material.

36. The textile material of any of claims 25-35, wherein the barrier film or the coating layer comprises acrylic, polyester, polyimide, polyhedral oligomeric silsesquioxanes, urethane, biologically-compatible polymer, SiCoN nanocomposites, glass/silica paint or any combinations thereof.

37. The textile material of any of claims 25-36, wherein the barrier film or the coating layer comprises ultra-high molecular weight polyethylene (UHMWPE).

38. The method of any of claims 25-37, wherein the barrier film or the coating layer comprises a non-fluoropolymer.

39. The method of claim 38, wherein the non-fluoropolymer is polyurethane.
40. The textile material of any of claims 25-39, wherein the barrier film or the coating layer comprises at least two different materials.

41. The textile material of claim 40, wherein at least one of the at least two different material is a fluoropolymer.

42. The textile material of any of claims 25-41, wherein the barrier film or the coating layer further comprises a material dispersed in the barrier film or the coating layer.

43. The textile material of claim 42, wherein the material is nanoclay, platelet, graphene platelets, particles, or any combinations thereof.

44. The textile material of any of claims 25-43, wherein the barrier film or the coating layer comprises a metal coating layer on a surface of the barrier or the coating film.
FIG. 1

FIG. 2

SUBSTITUTE SHEET (RULE 26)
FIG. 3

Textile material

Barrier film/coating layer

Metallic layer

FIG. 4

SUBSTITUTE SHEET (RULE 26)
FIG. 5
INTERNATIONAL SEARCH REPORT

International application No. PCT/US 16/17892

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B32B 27/12; D06M 13/00; D06M 15/00; D06M 15/507; D06M 15/59; D06M 15/564 (2016.01)

CPC - B32B 27/12; D06M 13/00; D06M 15/00; D06M 15/507; D06M 15/59; D06M 15/564

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)

IPC(8) - B32B 27/12; D06M 13/00; D06M 15/00; D06M 15/507; D06M 15/59; D06M 15/564 (2016.01)

CPC - B32B 27/12; D06M 13/00; D06M 15/00; D06M 15/507; D06M 15/59; D06M 15/564

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

USPC - 427/288; 442/85; 442/96; 8/1 15.51; 8/1 15.6

Patent Literature and Non-Patent Literature

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


C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 2004/010214 A1 (BOYLAN) 27 May 2004 (27.05.2004) para [0010], [0013], [0027], [0052], [0062], [0098], Table 5</td>
<td>1-3, 21, 25-26 and 27</td>
</tr>
<tr>
<td>X</td>
<td>US 5,1,12,652 A (GREENE) 12 May 1992 (12.05.1992) the entire document</td>
<td>1-2, 25-26</td>
</tr>
<tr>
<td>X</td>
<td>US 4,524,093 A (DEVRY) 18 June 1985 (18.06.1985) the entire document</td>
<td>1-2, 25-26</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

* 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
  "Z" document member of the same patent family

Date of the actual completion of the international search: 30 March 2016

Date of mailing of the international search report: 16 MAY 2016

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-8300

Authorized officer: Lee W. Young

PCT I/Pool: 571-272-4300
PCT O/S: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 2015)
## Box No. II  Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

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

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

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

3. Claims Nos.: 4-20, 22-24, 28-44
   - because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

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

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

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

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

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.