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(54) WATERFROOF APERTURED SURFACES OR MATERIALS USING NANOPARTICLE HYDROPHOBIC TREATMENTS

PERFORIERTE WASSERDICHTE OBERFLÄCHEN ODER MATERIALIEN MIT BEARBEITUNG HYDROPHOBER NANOPARTIKEL

MATÉRIAUX OU SURFACES À OUVERTURES IMPERMÉABLES UTILISANT DES TRAITEMENTS HYDROPHOBES DE NANOPARTICULES

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(56) References cited:
EP-A1- 1 674 609
DE-A1-102010 028 662
GB-A- 2 452 568
US-A1- 2004 142 168
US-A1- 2004 142 168
US-A1- 2006 008 618
US-A1- 2008 075 900
US-A1- 2008 096 001

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Description

BACKGROUND OF THE INVENTION

[0001] This application relates generally to the field of waterproofing, and more particularly to the field of waterproofing normally permeable apertured surfaces or materials, and even more particularly to the field of waterproofing materials using nanotechnology coatings or chemical compositions and treatments.

[0002] Many common materials are not waterproof, either because their material of composition absorbs liquids or because of apertures present in the material that are of sufficient size to allow penetration of water or other liquids. Some materials, such as common woven fabrics for example, are often composed of materials which absorb liquids and which contain apertures as a result of the weaving process. It has long been known to treat such materials with waterproofing materials, such as for example waxes, polymer coatings or PTFE-based SCOTCHGARD brand water repellent. Recently, advances in nanotechnology have produced coatings or solutions which impart extreme hydrophobic properties to the materials to which they are applied by providing specialized nanoparticles in the coatings or solutions. The term hydrophobic is used for surfaces having water contact angels greater than about 120 degrees, and the term superhydrophobic is used for surfaces having water contact angles of greater than about 150 degrees. The nanoparticle technology often provides oleophobic and other nonaqueous liquid barriers as well as creating a hydrophobic barrier.

[0003] Examples of various hydrophobic and superhydrophobic compositions and treatment methodologies are provided in U.S Patent Publication Nos. 2013/0109261, 2012/0009396, 2010/0314575, 2012/0045954, and 2006/0029808, and also in U.S. Patent Nos. 8,007,638, 6,103,379, 6,645,569, 6,743,467, 7,985,451, 8,187,707, 8,202,614, 7,998,554, 7,989,619, 5,042,991, 8,361,176, 8,258,206 and 6,723,378, and also in International Publication No. WO2013/058843 as well as in German Patent application DE 10 2010 028 662 A1. An example of a commercially available superhydrophobic coating is sold under the brand ULTRA EVER DRY by UltraTech International, Inc.

[0004] In materials such as woven fabrics having relatively small apertures between the intersecting threads or yarns, i.e., the apertures are smaller than the widths of the intersecting members, it has proven relatively easy to create waterproof surfaces using known waterproofing technology. Problems will arise however when the apertures are excessively large in relation to the diameters of the threads. Similar problems occur in screens or meshes, or materials that have inherent apertures that are of sufficient size to allow water passage directly or by wicking through the material. Another problem arises due to intrusion of connecting members or the like passing through the material, such as occurs for example with stitching or lacing passed through fabrics or leather.

[0005] It is an object of this invention to provide waterproof apertured materials or surfaces composed of intersecting members and a method for waterproofing such apertured materials or surfaces, using nanoparticle hydrophobic coatings or treatments, wherein the apertures defined by intersecting members are of greater width than the individual intersecting members. It is a further object to provide such waterproof materials or surfaces wherein the aperture size is sufficient such that the material or surface only minimally interferes with the passage of air or wind through the material or surface.

[0006] It is a further object to provide a method for waterproofing materials or surfaces having intrusive or breeching members passing through the waterproof material or surface, wherein the intrusive members are treated with a nanoparticle hydrophobic coating or treatment.

SUMMARY OF THE INVENTION

[0007] The invention comprises a method of providing waterproof apertured materials or surfaces using hydrophobic nanoparticle compositions and treatments, and preferably superhydrophobic compositions and treatments, and the materials or surfaces resulting therefrom, wherein apertures of a size that would normally render the surface or material water-permeable may be provided in the surface or material, and further wherein intrusive or breeching members, such as stitching threads, laces, strings, shoestrings or the like, may pass through a waterproof surface or material without reducing the impermeability to water.

[0008] For open or unfilled apertures, the method comprises determining the extent of the hydrophobic field that extends beyond the physical edge of a particular treated material to determine the allowable size of the aperture, such that the extended hydrophobic field present on the material surrounding the aperture will be sufficient to prevent surface wetting and water permeability by fully overlapping the aperture or by presenting a reduced area effective aperture that is small enough to preclude passage of water.

[0009] Expressed in other terms, the invention embodies a method of manufacturing an apertured waterproof mesh material comprised of intersecting members, the method comprising the steps of treating said intersecting members with a nanoparticle hydrophobic or superhydrophobic composition to create a hydrophobic field extending beyond said intersecting members; determining the extent of said hydrophobic field; interweaving intersecting members to form a mesh material having apertures wider than the width of each of said intersecting members, such that said hydrophobic field extends a sufficient distance into said apertures to preclude passage of water through said apertures.

[0010] Additionally, it is a method wherein said intersecting members are treated prior to said interweaving step; or wherein said intersecting members are treated

after said interweaving step; and/or wherein said step of interweaving intersecting members produces apertures of a size such that said hydrophobic fields of said intersecting members adjacent said apertures extend completely across said apertures; and/or wherein said step of interweaving intersecting members produces apertures of a size such that said hydrophobic fields of said intersecting members adjacent said apertures extend partially into said apertures a sufficient distance to define effective apertures that preclude passage of water through said apertures.

[0011] Also, the invention embodies an apertured waterproof mesh material produced by the above method.

[0012] Not according to the invention, for filled apertures extending through waterproof materials that receive breeching members, such as for example apertures produced by stitching or to receive a lace or similar elongated member, the breeching member is first treated with a nanoparticle hydrophobic composition, such that wicking through the breeching member is precluded and the aperture is effectively blocked by the hydrophobic field, thereby maintaining liquid impermeability of the waterproof material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013]

Figure 1 is an illustration of an apertured material composed of intersecting members having been treated to produce a hydrophobic surface and showing the extended hydrophobic field sufficient to maintain liquid impermeability.

Figure 2 illustrates a breeching member extending through a waterproof material.

DETAILED DESCRIPTION OF THE INVENTION

[0014] With reference to the drawings, embodiments of the invention will now be described in detail. In general, the embodiments of the invention disclose a method of manufacturing an apertured mesh material composed of intersecting members defining apertures of sufficient size to be permeable to water, and treating said intersecting members before or after the step of intersecting the members with a nanoparticle hydrophobic, including superhydrophobic, composition that creates a hydrophobic field extending beyond the intersecting members and across and into the apertures, whereby the overlapping or adjacent hydrophobic fields preclude passage of water through said normally permeable apertures. For purposes of this disclosure, the term "mesh" or "mesh material" shall refer to and include a material, such as a fabric, screen or the like, composed of intersecting elongated members, such as threads, yarns, strings, wires, cables, rods or the like.

[0015] For purposes of this disclosure, hydrophobic or superhydrophobic compositions and treatments suitable for this invention shall include but not be limited to the compositions and treatments disclosed in U.S Patent Publication Nos. 2013/0109261, 2012/0009396, 2010/0314575, 2012/0045954, and 2006/0029808, and also in U.S. Patent Nos. 8,007,638, 6,103,379, 6,645,569, 6,743,467, 7,985,451, 8,187,707, 8,202,614, 7,998,554, 7,989,619, 5,042,991, 8,361,176, 8,258,206 and 6,723,378, and also in International Publication No. WO2013/058843.

[0016] As shown in Figure 1, an apertured mesh material or surface 10 is manufactured by interweaving a plurality of intersecting members 11, such as for example thread members combing to create a fabric. The intersecting members 11, and therefore the apertured mesh material 10 as well, is treated with a nanoparticle hydrophobic composition through either a coating process or an absorption process. For example, intersecting members 11 may be treated with a nanoparticle hydrophobic composition sold under the brand name ULTRA EVER DRY. The intersecting members 11 may be treated prior to the step of intersecting the members 11 to form the mesh material 10, or the intersecting members 11 may be inter woven together first to form the apertured material 10 and then treated. The treatment step does not physically block any portions of or reduce the actual size of the apertures 13.

[0017] The intersecting members 11 are interwoven to produce apertures 13 of a size that are permeable to water. More preferably, the apertures 13, which are generally square or rectangular in configuration, have width dimensions greater than the cross-sectional widths of the intersecting members 11, i.e., greater than the diameters of generally cylindrical intersecting members 11 for example. Apertures of such size are typically provided in mesh materials 10 that are designed to permit significant flow of air through the mesh material 10.

[0018] Application of the nanoparticle hydrophobic or superhydrophobic composition to the intersecting members 11 creates a hydrophobic field 12 (taken herein to include superhydrophobic fields as well) that extends beyond the actual physical edges of each of the intersecting members 11. The extent of the extended hydrophobic field 12 must be measured and known, as it is this extent that determines the maximum permissible size for an aperture 13. Properly chosen, the combination of the hydrophobic fields 12 associated with the portions of the intersecting members 11 defining an aperture 13 will combine, either because of overlapping or being sufficiently adjacent, to create a hydrophobic barrier either fully across the aperture 13 or sufficiently across the aperture 13 to create an effective aperture 14 sufficiently small in dimensions so as to preclude passage of water through the aperture 13, thereby producing a mesh material that is liquid impermeable. The extent of the hydrophobic field 12 will vary dependent upon the material of composition of the intersecting members 11 and the strength of the particular nanoparticle hydrophobic or superhydrophobic composition chosen. The hydrophobic

can be measured for a particular intersecting member 11 can be measured by treating the intersecting member 11 and then varying the size of the interwoven aperture 13 to determine the maximum allowable size for the aperture 13 to remain waterproof.

[0019] In this manner, mesh materials such as fabrics, screens or the like may be manufactured that are water impermeable while still allowing passage of air through the apertures 13. The method thus comprises determining the extent of the hydrophobic field 12 that extends beyond the physical edge of a particular treated intersecting member 11 to determine the allowable maximum size of the aperture 13, such that the extended hydrophobic field 12 extending from the intersecting members 11 surrounding the aperture 13 will be sufficient to prevent surface wetting and water permeability by fully overlapping and extending across the aperture 13 or by extending sufficiently into the aperture 13 to create an effective aperture 14 of reduced area that is inherently small enough to preclude passage of water.

[0020] In a second example (not according to the invention), an aperture 13 may be present in a waterproof material 16 for the purpose of receiving a breeching or member 15. The material 16 which may be naturally liquid impermeable or treated as discussed or referenced above, the breeching member 15 passing through either a pre-made hole or bore, such as a shoelace, tie or string passing through a pre-cut hole or a grommet in a leather material, or a hole or bore made during construction, such as a stitching thread passing through a fabric. In many instances the presence of the breeching member 15 in the aperture 13 may render the material 16 permeable to liquids, especially if the breeching member 15 is composed of a material susceptible to wicking, such as a shoelace or thread. To maintain liquid impermeability, the breeching member 15 is treated with a nanoparticle hydrophobic or superhydrophobic composition that creates a hydrophobic field 12, as shown in Figure 2, such that the combination of the nanoparticle hydrophobic or superhydrophobic treatment and the hydrophobic field 12 preclude passage of liquid through the aperture 13 whether by wicking or capillary effect. More preferably, the material 16 is also treated with the nanoparticle hydrophobic or superhydrophobic composition such that the hydrophobic fields 12 will overlap to better seal the aperture 13.

[0021] While the terms "nanoparticle hydrophobic or superhydrophobic treatment and composition" have been used herein, it is to be understood that some of the nanoparticle hydrophobic or superhydrophobic treatments and compositions will also render the treated material impermeable to almost all liquids and oils, such that the effect is hydrophobic, liquid-phobic and oleophobic. The allowable presence of apertures in the liquid impermeable material, whether the apertures are present due to weaving manufacture, needling, apertures inherent in the material, apertures required for functionality of the object (e.g., a shoe), etc., enables surfaces, materials, coverings, garments or the like to be created, for example, that allow air passage through the material while maintaining impermeability. Such materials can be utilized for normal or protective clothing, shoes, covers, tents, canopies, umbrellas, etc. In addition to providing materials that are not wetted, the invention also provides such materials that may be termed "self-cleaning", in that the material is not susceptible to common liquid stains and is more easily cleaned of solid or particulate matter. Most preferably even the inherently waterproof materials are treated so as to be hydrophobic.

[0022] It is contemplated that equivalents and substitutions for certain elements set forth above may be obvious to those of skill in the art, and therefore the true scope and definition of the invention is to be as set forth in the following claims. The examples and embodiments described above and in the drawings are not meant to be limiting.

Claims

1. A method of manufacturing an apertured waterproof mesh material (10) comprised of intersecting members (11), the method comprising the steps of:

   treating said intersecting members (11) with a nanoparticle hydrophobic or superhydrophobic composition to create a hydrophobic field (12) extending beyond said intersecting members (11);
   the method being **characterised by** determining the extent of said hydrophobic field (12);
   interweaving intersecting members (11) to form a mesh material (10) having apertures (13) wider than the width of each of said intersecting members (11), such that said hydrophobic field (12) extends a sufficient distance into said apertures (13) to preclude passage of water through said apertures (13).

2. The method of claim 1, wherein said intersecting members (11) are treated after said interweaving step.

3. The method of claim 1, wherein said step of interweaving intersecting members (11) produces apertures (13) of a size such that said hydrophobic fields (12) of said intersecting members (11) adjacent said apertures (13) extend partially into said apertures (13) a sufficient distance to define effective apertures (14) that preclude passage of water through said apertures (13).

4. An apertured waterproof mesh material (10) produced by the process of claim 1.

5. The method of claim 1, wherein said step of treating

said intersecting members (11) with said nanoparticle hydrophobic or superhydrophobic composition to create a hydrophobic field (12) does not physically reduce the size of or block said apertures (13).

Patentansprüche

1. Verfahren zum Herstellen eines wasserdichten Netzmaterials (10) mit Öffnungen, bestehend aus sich schneidenden Elementen (11), wobei das Verfahren die folgenden Schritte umfasst:

   Behandeln der sich schneidenden Elemente (11) mit einer hydrophoben oder superhydrophoben Zusammensetzung aus Nanopartikeln, um ein hydrophobes Feld (12) zu erzeugen, das sich über die sich schneidenden Elemente (11) hinaus erstreckt;
   wobei das Verfahren gekennzeichnet ist, indem das Ausmaß des hydrophoben Feldes (12) bestimmt wird;
   Verflechten von sich schneidenden Elementen (11), um ein Netzmaterial (10) mit Öffnungen (13) auszubilden, die breiter sind als die Breite jedes der sich schneidenden Elemente (11), derart dass sich das hydrophobe Feld (12) um einem ausreichenden Abstand in die Öffnungen (13) erstreckt, um den Durchgang von Wasser durch die Öffnungen (13) zu verhindern.

2. Verfahren nach Anspruch 1, wobei die sich schneidenden Elemente (11) nach dem Verflechtungsschritt behandelt werden.

3. Verfahren nach Anspruch 1, wobei der Schritt des Verflechtens von sich schneidenden Elementen (11) Öffnungen (13) einer solchen Größe produziert, dass sich die hydrophoben Felder (12) der sich schneidenden Elemente (11), die an die Öffnungen (13) angrenzen, teilweise um einen ausreichenden Abstand in die Öffnungen (13) erstrecken, um effektive Öffnungen (14) zu definieren, die den Durchgang von Wasser durch die Öffnungen (13) verhindern.

4. Wasserdichtes Netzmaterial (10) mit Öffnungen, produziert nach dem Vorgang nach Anspruch 1.

5. Verfahren nach Anspruch 1, wobei der Schritt des Behandelns der sich schneidenden Elemente (11) mit der hydrophoben oder superhydrophoben Zusammensetzung aus Nanopartikeln, um ein hydrophobes Feld (12) zu erzeugen, die Größe der Öffnungen (13) nicht physikalisch verringert oder diese blockiert.

Revendications

1. Procédé de fabrication d'un matériau maillé imperméable à ouverture (10) constitué d'éléments entrecroisés (11), le procédé comprenant les étapes consistant à :

   traiter lesdits éléments entrecroisés (11) au moyen d'une composition hydrophobe ou superhydrophobe de nanoparticules afin de créer un champ hydrophobe (12) s'étendant au-delà desdits éléments d'intersection (11) ;
   le procédé étant **caractérisé par**
   la détermination de l'étendue dudit champ hydrophobe (12) ;
   des éléments entrecroisés entrelacés (11) pour former un matériau maillé (10) ayant des ouvertures (13) plus larges que la largeur de chacun desdits éléments entrecroisés (11), de telle sorte que ledit champ hydrophobe (12) s'étend sur une distance suffisante dans lesdites ouvertures (13) pour empêcher le passage d'eau à travers lesdites ouvertures (13).

2. Procédé selon la revendication 1, dans lequel lesdits éléments entrecroisés (11) sont traités après ladite étape d'entrelaçage.

3. Procédé selon la revendication 1, dans lequel ladite étape consistant à entrelacer des éléments d'intersection (11) produit des ouvertures (13) d'une taille telle que lesdits champs hydrophobes (12) desdits éléments d'intersection (11) adjacents auxdites ouvertures (13) s'étendent partiellement dans lesdites ouvertures (13) à une distance suffisante pour définir des ouvertures efficaces (14) qui empêchent le passage d'eau à travers lesdites ouvertures (13).

4. Matériau maillé imperméable à ouverture (10) produit par le procédé selon la revendication 1.

5. Procédé selon la revendication 1, dans lequel ladite étape de traitement desdits éléments d'intersection (11) au moyen de ladite composition hydrophobe ou superhydrophobe de nanoparticules afin de créer un champ hydrophobe (12) ne réduit pas physiquement la taille desdites ouvertures (13), ni ne les bloque.

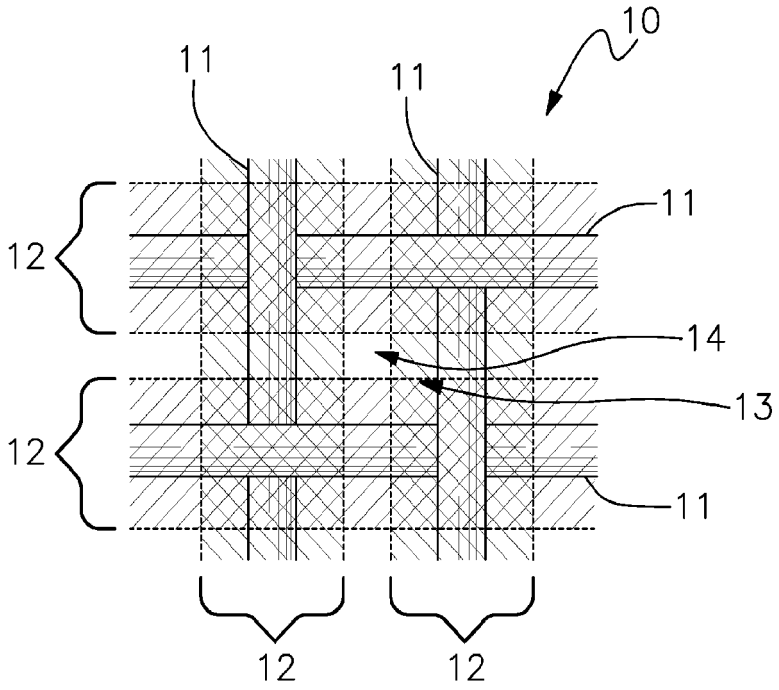

Fig. 1

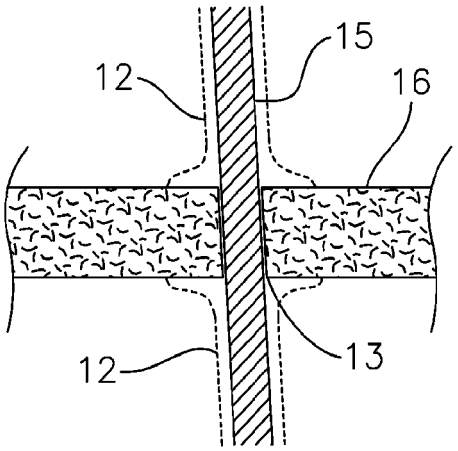

Fig. 2

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 20130109261 A **[0003] [0015]**
- US 20120009396 A **[0003] [0015]**
- US 20100314575 A **[0003] [0015]**
- US 20120045954 A **[0003] [0015]**
- US 20060029808 A **[0003] [0015]**
- US 8007638 B **[0003] [0015]**
- US 6103379 A **[0003] [0015]**
- US 6645569 B **[0003] [0015]**
- US 6743467 B **[0003] [0015]**
- US 7985451 B **[0003] [0015]**
- US 8187707 B **[0003] [0015]**
- US 8202614 B **[0003] [0015]**
- US 7998554 B **[0003] [0015]**
- US 7989619 B **[0003] [0015]**
- US 5042991 A **[0003] [0015]**
- US 8361176 B **[0003] [0015]**
- US 8258206 B **[0003] [0015]**
- US 6723378 B **[0003] [0015]**
- WO 2013058843 A **[0003] [0015]**
- DE 102010028662 A1 **[0003]**