



(43) International Publication Date
5 November 2015 (05.11.2015)

- (51) International Patent Classification:
D06M 15/277 (2006.01) **D04H 13/00** (2006.01)
- (21) International Application Number:
PCT/IB2015/053124
- (22) International Filing Date:
29 April 2015 (29.04.2015)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
14/268,071 2 May 2014 (02.05.2014) US
- (71) Applicant: **KIMBERLY-CLARK WORLDWIDE, INC.**
[US/US]; 2300 Winchester Road, Neenah, WI 54956 (US).
- (72) Inventors: **GOEDERS, Karen, Meloy**; 2300 Winchester Road, Neenah, WI 54956 (US). **FORTHOFFER, Marsha, R.**; 1400 Holcomb Bridge Road, Bldg. 200, Roswell, GA 30076 (US).
- (74) Agent: **FIELDHACK, Randall, W.**; 2300 Winchester Road, Neenah, WI 54956 (US).

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

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

Published:

— with international search report (Art. 21(3))

(54) Title: HYDROPHOBIC TREATMENT ON HYDROPHILIC NONWOVEN

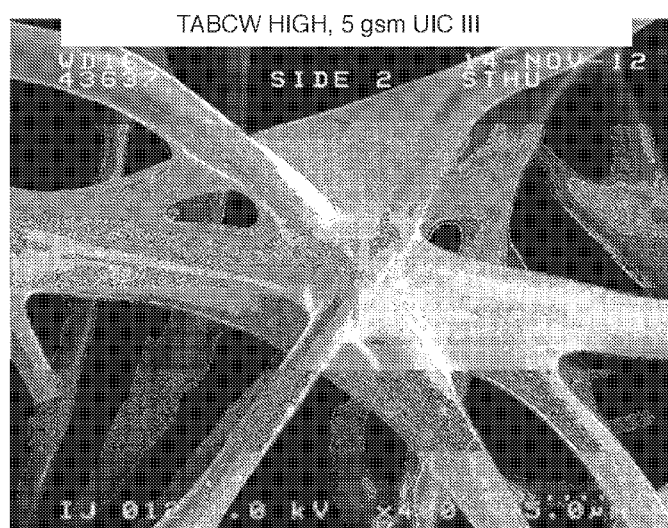


FIG. 6

(57) Abstract: A liquid-impermeable barrier material includes a hydrophilic nonwoven web having two surfaces, the nonwoven web including fibers; and a hydrophobic composition disposed on a surface, wherein the barrier material is breathable. The barrier material exhibits a positive hydrohead value. The hydrophobic composition can include a hydrophobic component selected from the group consisting of fluorinated polymers, perfluorinated polymers, and mixtures thereof. The barrier material can include a hydrophilic surface opposite the surface having the hydrophobic composition. The nonwoven web can include tissue, cellulose, or other suitable material. A barrier material has a hydrophobic surface and includes a hydrophilic nonwoven substrate treated with a composition including a hydrophobic component and water.



HYDROPHOBIC TREATMENT ON HYDROPHILIC NONWOVEN

BACKGROUND

The present disclosure relates to hydrophilic, breathable materials that exhibit hydrophobic
5 properties when treated with certain compositions. Currently, hydrophobic, breathable materials are generally made using hydrophobic polymeric films. Such materials tend to be hydrophobic throughout the thickness of the material, which might not be desired in many cases. Such materials also tend to be less cost effective. Although various formulated dispersions capable of coating a surface to make that surface hydrophobic exist, these tend not to be water-based. These tend to require the use of organic solvents.

10 Disposable absorbent products (e.g., diapers, feminine hygiene products, incontinence products, etc.) are subjected to one or more liquid insults, such as of water, urine, menses, or blood, during use. Many commercially available diapers allow water vapor to pass through the diaper and into the environment to lessen the amount of moisture held against the skin and reduce the chance of skin irritation and rash due to skin overhydration. To allow the passage of vapor through the diaper and into the
15 environment while holding liquid, a "breathable" outer cover is often employed that is formed from a nonwoven web laminated to a film.

SUMMARY

As a result, a new material is needed that is both cost-effective and does not rely on organic
20 solvents. For a multitude of safety, health, economic, and environmental issues, it is also important that the dispersion be fully aqueous-based when regarding commercial scale production, as this will decrease concerns associated with the use of organic solvents. The present disclosure relates to the use of a hydrophobic chemistry applied to a hydrophilic fibrous material to create liquid barrier properties in an otherwise wettable nonwoven by creating a film-like structure between the fibers. This yields a hydrophilic
25 substrate that acts like a film while still being air permeable and exceeding the breathability seen in standard breathable outer cover films.

The present disclosure provides a liquid-impermeable barrier material including a hydrophilic nonwoven web having two surfaces, the nonwoven web including fibers; and a hydrophobic composition disposed on a surface, wherein the barrier material is breathable. The barrier material exhibits a positive
30 hydrohead value. The hydrophobic composition can include a hydrophobic component selected from the group consisting of fluorinated polymers, perfluorinated polymers, and mixtures thereof. The barrier

material can include a hydrophilic surface opposite the surface having the hydrophobic composition. The nonwoven web can include tissue, cellulose, or other suitable material.

The present disclosure also provides a barrier material having a hydrophobic surface, the barrier material including a hydrophilic nonwoven substrate treated with a composition including a hydrophobic component and water.

BRIEF DESCRIPTION OF THE FIGURES

The foregoing and other features and aspects of the present disclosure and the manner of attaining them will become more apparent, and the disclosure itself will be better understood by reference to the following description, appended claims and accompanying drawings, where:

Figure 1 illustrates the contact angle exhibited by various hydrophobic treatments;

Figure 2 illustrates the roll off angle exhibited by the various hydrophobic treatments of Fig. 1;

Figure 3 illustrates the hydrohead values exhibited by a hydrophilic HYDROKNIT brand towel with various hydrophobic treatments;

Figure 4 illustrates scanning electron microscope micrographs of hydrophilic HYDROKNIT brand towels with various hydrophobic treatments;

Figure 5 illustrates scanning electron microscope micrographs of SMS with various hydrophobic treatments; and

Figures 6 illustrates a scanning electron microscope micrograph of TABCW (through air dried bonded carded web) fibers with UIC III hydrophobic treatment.

Repeat use of reference characters in the present specification and drawings is intended to represent the same or analogous features or elements of the present disclosure. The drawings are representational and are not necessarily drawn to scale. Certain proportions thereof might be exaggerated, while others might be minimized.

DETAILED DESCRIPTION

All percentages are by weight of the total composition unless specifically stated otherwise. All ratios are weight ratios unless specifically stated otherwise.

5 The term "hydrophobic," as used herein, refers to the property of a surface to repel water with a water contact angle from about 90° to about 120°.

The term "hydrophilic," as used herein, refers to surfaces with water contact angles well below 90°.

As used herein, the term "breathability" refers to the water vapor transmission rate (WVTR) of an area of film. Breathability is measured in grams of water per square meter per day. For purposes of the present disclosure, a film is "breathable" if it has a WVTR of at least 800 grams per square meter per 24
10 hours as calculated using the MOCON test method, which is described in detail below.

Various methods can significantly increase the water vapor transmission rate ("WVTR") of a film, which is the rate at which water vapor permeates through a material as measured in units of grams per meter squared per 24 hours ($\text{g}/\text{m}^2/24 \text{ hrs}$). For example, the film can exhibit a WVTR of about 500
15 grams/ m^2 -24 hours or more, in some aspects about 1,000 grams/ m^2 -24 hours or more, in some aspects about 2,000 grams/ m^2 -24 hours or more, and in some aspects, from about 3,000 to about 15,000 grams/ m^2 -24 hours. The high void volume can also lower the density of the film. For example, the film can have a density of about 1.4 grams per cubic centimeter (" g/cm^3 ") or less, in some aspects about 1.1 g/cm^3 or less, in some aspects from about 0.4 g/cm^3 to about 1.0 g/cm^3 , and in some aspects, from about 0.5 g/cm^3 to about 0.95 g/cm^3 .

20 As used herein, the term "nonwoven web" or "nonwoven fabric" means a web having a structure of individual fibers or threads that are interlaid, but not in an identifiable manner as in a knitted web. Nonwoven webs have been formed from many processes, such as, for example, meltblowing processes, spunbonding processes, air-laying processes, coforming processes and bonded carded web processes. The basis weight of nonwoven webs is usually expressed in ounces of material per square yard (osy) or
25 grams per square meter (gsm) and the fiber diameters are usually expressed in microns, or in the case of staple fibers, denier. It is noted that to convert from osy to gsm, multiply osy by 33.91.

As used herein the term "spunbond fibers" refers to small diameter fibers of molecularly oriented polymeric material. Spunbond fibers can be formed by extruding molten thermoplastic material as fibers from a plurality of fine, usually circular capillaries of a spinneret with the diameter of the extruded fibers
30 then being rapidly reduced as in, for example, U.S. Patent No. 4,340,563 to Appel et al., and U.S. Patent No. 3,692,618 to Dorschner et al., U.S. Patent No. 3,802,817 to Matsuki et al., U.S. Patent Nos. 3,338,992

and 3,341,394 to Kinney, U.S. Patent No. 3,502,763 to Hartman, U.S. Patent No. 3,542,615 to Dobo et al, and U.S. Patent No. 5,382,400 to Pike et al. Spunbond fibers are generally not tacky when they are deposited onto a collecting surface and are generally continuous. Spunbond fibers are often about 10 microns or greater in diameter. However, fine fiber spunbond webs (having an average fiber diameter less than about 10 microns) can be achieved by various methods including, but not limited to, those described in commonly assigned U.S. Patent No. 6,200,669 to Marmon et al. and U.S. Patent No. 5,759,926 to Pike et al.

Meltblown nonwoven webs are prepared from meltblown fibers. As used herein the term "meltblown fibers" means fibers formed by extruding a molten thermoplastic material through a plurality of fine, usually circular, die capillaries as molten threads or filaments into converging high velocity, usually hot, gas (e.g. air) streams that attenuate the filaments of molten thermoplastic material to reduce their diameter, which can be to microfiber diameter. Thereafter, the meltblown fibers are carried by the high velocity gas stream and are deposited on a collecting surface to form a web of randomly dispersed meltblown fibers. Such a process is disclosed, for example, in U.S. Patent No. 3,849,241 to Buntin.

Meltblown fibers are microfibers that can be continuous or discontinuous, are generally smaller than 10 microns in average diameter (using a sample size of at least 10), and are generally tacky when deposited onto a collecting surface.

As used herein, the term "polymer" generally includes, but is not limited to, homopolymers, copolymers, such as for example, block, graft, random and alternating copolymers, terpolymers, etc. and blends and modifications thereof. Furthermore, unless otherwise specifically limited, the term "polymer" shall include all possible geometrical configurations of the molecule. These configurations include, but are not limited to isotactic, syndiotactic and random symmetries.

As used herein, the term "multicomponent fibers" refers to fibers or filaments that have been formed from at least two polymers extruded from separate extruders but spun together to form one fiber.

Multicomponent fibers are also sometimes referred to as "conjugate" or "bicomponent" fibers or filaments. The term "bicomponent" means that there are two polymeric components making up the fibers. The polymers are usually different from each other, although conjugate fibers can be prepared from the same polymer, if the polymer in each component is different from one another in some physical property, such as, for example, melting point, glass transition temperature or the softening point. In all cases, the polymers are arranged in substantially constantly positioned distinct zones across the cross-section of the multicomponent fibers or filaments and extend continuously along the length of the multicomponent fibers or filaments. The configuration of such a multicomponent fiber can be, for example, a sheath/core

arrangement, wherein one polymer is surrounded by another, a side-by-side arrangement, a pie arrangement or an "islands-in-the-sea" arrangement. Multicomponent fibers are taught in U.S. Patent No. 5,108,820 to Kaneko et al.; U.S. Patent No. 5,336,552 to Strack et al.; and U.S. Patent No. 5,382,400 to Pike et al. For two component fibers or filaments, the polymers can be present in ratios of 75/25, 50/50, 25/75 or any other desired ratios.

As used herein, the term "multiconstituent fibers" refers to fibers that have been formed from at least two polymers extruded from the same extruder as a blend or mixture. Multiconstituent fibers do not have the various polymer components arranged in relatively constantly positioned distinct zones across the cross-sectional area of the fiber and the various polymers are usually not continuous along the entire length of the fiber, instead usually forming fibrils or protofibrils that start and end at random. Fibers of this general type are discussed in, for example, U.S. Patent Nos. 5,108,827 and 5,294,482 to Gessner.

As used herein, the term "substantially continuous fibers" is intended to mean fiber that have a length that is greater than the length of staple fibers. The term is intended to include fibers that are continuous, such as spunbond fibers, and fibers that are not continuous, but have a defined length greater than about 150 millimeters.

As used herein, the term "staple fibers" means fibers that have a fiber length generally in the range of about 0.5 to about 150 millimeters. Staple fibers can be cellulosic fibers or non-cellulosic fibers. Some examples of suitable non-cellulosic fibers that can be used include, but are not limited to, polyolefin fibers, polyester fibers, nylon fibers, polyvinyl acetate fibers, and mixtures thereof. Cellulosic staple fibers include for example, pulp, thermomechanical pulp, synthetic cellulosic fibers, modified cellulosic fibers, and the like. Cellulosic fibers can be obtained from secondary or recycled sources. Some examples of suitable cellulosic fiber sources include virgin wood fibers, such as thermomechanical, bleached and unbleached softwood and hardwood pulps. Secondary or recycled cellulosic fibers can be obtained from office waste, newsprint, brown paper stock, paperboard scrap, etc., can also be used. Further, vegetable fibers, such as abaca, flax, milkweed, cotton, modified cotton, cotton linters, can also be used as the cellulosic fibers. In addition, synthetic cellulosic fibers such as, for example, rayon and viscose rayon can be used. Modified cellulosic fibers are generally composed of derivatives of cellulose formed by substitution of appropriate radicals (e.g., carboxyl, alkyl, acetate, nitrate, etc.) for hydroxyl groups along the carbon chain.

As used herein, the term "pulp" refers to fibers from natural sources such as woody and non-woody plants. Woody plants include, for example, deciduous and coniferous trees. Non-woody plants include, for example, cotton, flax, esparto grass, milkweed, straw, jute, hemp, and bagasse.

As used herein, "tissue products" are meant to include facial tissue, bath tissue, towels, hankies, napkins and the like. The present disclosure is useful with tissue products and tissue paper in general, including but not limited to conventionally felt-pressed tissue paper, high bulk pattern densified tissue paper, and high bulk, uncompacted tissue paper.

5 The present disclosure relates to a surface of a hydrophilic substrate, or the substrate itself, exhibiting hydrophobic characteristics when treated with certain compositions. The hydrophobicity can be applied either over the entire surface, patterned throughout or on the substrate material, and/or directly penetrated through the z-directional thickness of the substrate material.

10 Materials such as diaper outercover spunbond-film laminate or surgical gown SMS are currently used to prevent liquid from penetrating through the material and onto the user or into the user's environment. These materials use film or meltblown as the barrier materials to prevent fluid penetration. Many hydrophilic materials are currently used in various applications, the materials including those such as coform and HYDROKNIT brand towel for wipes as well as cellulosic tissues for facial and bath tissues. These materials are absorptive and thus not useful as barriers to fluids. Tissue-based materials tend to be
15 less expensive than polymeric laminates and films.

 There is interest in using naturally hydrophilic materials in new ways. For example, a surface wet wipe made of a cellulosic basesheet such as coform or airlaid that can maintain dryness on one side while being wet on the other can offer hand protection to the user. A tissue that has a barrier to fluid on one side could allow a one-ply bath tissue to perform like a multi-ply bath tissue by reducing fluid wet through or
20 could allow a facial tissue to better protect the user by reducing the amount of fluid that penetrates through the tissue to the user's hand. Additionally, when considering alternative and possibly lower cost or lower tier diaper outer cover options, there is a need to consider ways to create barriers to liquid on otherwise hydrophilic materials like HYDROKNIT brand towel and tissue substrates.

 The development described here is the use of a hydrophobic chemistry applied to a hydrophilic
25 nonwoven material to create liquid barrier properties to an otherwise wettable nonwoven by way of creating a film-like structure between the nonwoven fibers.

Hydrophobic Component

 The hydrophobic component is a hydrophobic polymer that is dispersible in water to form the basic
30 elements of the hydrophobic properties of the present disclosure. In general, a hydrophobic component of this disclosure can include, but is not limited to, fluorinated or perfluorinated polymers. However, due to

low degree of water dispersibility, the fluorinated or perfluorinated polymer can need to be modified by introducing a comonomer onto their molecular structure. Suitable comonomers include, but are not limited to, ethylenically unsaturated monomers including functional groups that are capable of being ionized in water. One example is ethylenically unsaturated carboxylic acid, such as acrylic acid. The amount of the comonomer within the hydrophobic component is determined by balancing two properties: hydrophobicity and water dispersibility. One example of the hydrophobic component of this disclosure is a commercially available modified perfluorinated polymer compound available from DuPont as a water-based product under the trade name CAPSTONE STC-100. Due to its low surface energy, the polymer contributes to the hydrophobicity. Additionally, the polymer molecules can be modified to contain groups, such as amines, that can become charged upon pH reduction and alter the dynamics of hydrophobicity within the liquid dispersion. In such a case, the polymer can stabilize in water through partial interaction. Surfactants that are introduced into the composition can also behave as dispersants of the polymer, thereby also altering some of the hydrophobic mechanics.

The solid components of the present disclosure can be present in an amount from about 1.0% to about 3.0%, by weight of the solution. Such an amount is suitable for spray applications where higher concentrations of polymer can lead to either viscoelastic behavior, resulting in either clogging of the spray nozzle or incomplete atomization and fiber formation, or dramatic increases in dispersion viscosity and thus nozzle clogging. It should be noted that this range is not fixed and that it is a function of the materials being utilized and the procedure used to prepare the dispersion. When a higher amount of the polymer is used, the surface structure is less desirable as it lacks the proper texture to be hydrophobic. When a lower amount of the polymer is used, the binding is less desirable as the coating behaves more so as a removable powder coating.

Non-Organic Solvent

The formulation used in treating the surface of the present disclosure eliminates the use of an organic solvent by carefully selecting the appropriate combination of elements to impart the hydrophobic characteristics. Preferably, the non-organic solvent is water. Any type of water can be used; however, demineralized or distilled water can be opted for use during the manufacturing process for enhanced capabilities. The use of water helps to reduce the safety concerns associated with making commercial scale formulations including organic solvents. For example, due to the high volatility and flammability of most organic solvents, eliminating such use in the composition reduces production safety hazards. Additionally, production costs can be lowered with the elimination of ventilation and fire prevention

equipment necessitated by organic solvents. Raw material costs can be reduced in addition to the transportation of such materials as an added advantage to utilizing the non-organic solvent formulation to arrive at the present disclosure.

5 Additionally, because water is considered a natural resource, surfaces treated with solvents including water as its base can be considered healthier and better for the environment. The formulation used to treat the surface of the present disclosure includes greater than about 95%, greater than about 98%, or about 99% water, by weight of the dispersion composition.

Other Ingredients

10 Binders

The hydrophobic polymers within the formulation of the present disclosure play a dual role in acting both as a hydrophobic component and a binder. Polymers such as Dupont's CAPSTONE STC-100 promote adhesion, as compared to the fluorinated polymer alone, so that an additional binder within the composition is not necessary. If a water-dispersible hydrophobic polymer is used wherein an additional
15 binder is needed, it is preferred that the binder is selected from water-dispersible acrylics, polyurethane dispersions, acrylic copolymers, or acrylic polymer precursors (which can cross link after the coating is cured).

The amount of the binder present within the formulation of the present disclosure can vary. A binder can be included in an effective amount of up to about 2.0% by weight of the total dispersion
20 composition.

Stabilizing Agent

The formulation within the present disclosure can be additionally treated with a stabilizing agent to promote the formation of a stable dispersion when other ingredients are added to it. The stabilizing agent can be a surfactant, a polymer, or mixtures thereof. If a polymer acts as a stabilizing agent, it is preferred
25 that the polymer differ from the hydrophobic component used within the base composition previously described.

Additional stabilizing agents can include, but are not limited to, cationic surfactants such as quaternary amines; anionic surfactants such as sulfonates, carboxylates, and phosphates; or nonionic surfactants such as block copolymers containing ethylene oxide and silicone surfactants. The surfactants
30 can be either external or internal. External surfactants do not become chemically reacted into the base

polymer during dispersion preparation. Examples of external surfactants useful herein include, but are not limited to, salts of dodecyl benzene sulfonic acid and lauryl sulfonic acid salt. Internal surfactants are surfactants that do become chemically reacted into the base polymer during dispersion preparation. An example of an internal surfactant useful herein includes 2, 2-dimethylol propionic acid and its salts.

5 In some aspects, the stabilizing agent used within the composition to treat the surface of the present disclosure can be used in an amount ranging from greater than zero to about 60%, by of the hydrophobic component. For example, long chain fatty acids or salts thereof can be used from about 0.5% to about 10% by weight based on the amount of hydrophobic component. In other aspects, ethylene-
10 acrylic acid or ethylene-methacrylic acid copolymers can be used in an amount up to about 80%, by weight based of hydrophobic component. In yet other aspects, sulfonic acid salts can be used in an amount from about 0.01% to about 60 % by weight based on the weight of the hydrophobic component. Other mild acids, such as those in the carboxylic acid family (e.g., formic acid), can also be included in order to further stabilize the dispersion. In an aspect that includes formic acid, the formic acid can be present in amount that is determined by the desired pH of the dispersion wherein the pH is less than about 6.

15 Additional Fillers

The composition used to treat the surface of the present disclosure can further include one or more fillers. The composition can include from about 0.01 to about 600 parts, by weight of the hydrophobic component, for example, polyolefin and the stabilizing agent. In certain aspects, the filler loading in the composition can be from about 0.01 to about 200 parts by the weight of the hydrophobic component, for
20 example, polyolefin, and the stabilizing agent. It is preferred that such filler material, if used, be hydrophilic. The filler material can include conventional fillers such as milled glass, calcium carbonate, aluminum trihydrate, talc, antimony trioxide, fly ash, clays (such as bentonite or kaolin clays for example), or other known fillers. Untreated clays and talc are usually hydrophilic by nature.

Substrate

25 The substrate of the present disclosure can be treated such that it is superhydrophobic throughout the z-directional thickness of the material and is controlled in such a way that only certain areas of the material are superhydrophobic. Such treatment can be designed to control which areas of the material can or cannot be penetrated by wetness, thereby controlling where liquid can flow.

Suitable substrates of the present disclosure can include a nonwoven fabric, woven fabric, knit
30 fabric, or laminates of these materials. The substrate can also be a tissue or towel, as described herein. Materials and processes suitable for forming such substrate are generally well known to those skilled in the

art. For instance, some examples of nonwoven fabrics that can be used in the present disclosure include, but are not limited to, spunbonded webs, meltblown webs, bonded carded webs, air-laid webs, coform webs, spunlace nonwoven web, hydraulically entangled webs, and the like. In each case, at least one of the fibers used to prepare the nonwoven fabric is a thermoplastic material containing fiber. In addition, nonwoven fabrics can be a combination of thermoplastic fibers and natural fibers, such as, for example, cellulosic fibers (softwood pulp, hardwood pulp, thermomechanical pulp, etc.). Generally, from the standpoint of cost and desired properties, the substrate of the present disclosure is a hydrophilic nonwoven fabric.

If desired, the nonwoven fabric can also be bonded using techniques well known in the art to improve the durability, strength, hand, aesthetics, texture, and/or other properties of the fabric. For instance, the nonwoven fabric can be thermally (e.g., pattern bonded, through-air dried), ultrasonically, adhesively and/or mechanically (e.g. needled) bonded. For instance, various pattern bonding techniques are described in U.S. Patent No. 3,855,046 to Hansen; U.S. Patent No. 5,620,779 to Levy, et al.; U.S. Patent No. 5,962,112 to Haynes, et al.; U.S. Patent No. 6,093,665 to Sayovitz, et al.; U.S. Design Patent No. 428,267 to Romano, et al.; and U.S. Design Patent No. 390,708 to Brown.

The nonwoven fabric can be bonded by continuous seams or patterns. As additional examples, the nonwoven fabric can be bonded along the periphery of the sheet or simply across the width or cross-direction (CD) of the web adjacent the edges. Other bond techniques, such as a combination of thermal bonding and latex impregnation, can also be used. Alternatively and/or additionally, a resin, latex or adhesive can be applied to the nonwoven fabric by, for example, spraying or printing, and dried to provide the desired bonding. Still other suitable bonding techniques are described in U.S. Patent No. 5,284,703 to Everhart, et al., U.S. Patent No. 6,103,061 to Anderson, et al., and U.S. Patent No. 6,197,404 to Varona.

In another aspect, the substrate of the present disclosure is formed from a spunbonded web containing monocomponent and/or multicomponent fibers. Multicomponent fibers are fibers that have been formed from at least two polymer components. Such fibers are usually extruded from separate extruders but spun together to form one fiber. The polymers of the respective components are usually different from each other although multicomponent fibers can include separate components of similar or identical polymeric materials. The individual components are typically arranged in substantially constantly positioned distinct zones across the cross-section of the fiber and extend substantially along the entire length of the fiber. The configuration of such fibers can be, for example, a side-by-side arrangement, a pie arrangement, or any other arrangement.

When used, multicomponent fibers can also be splittable. In fabricating multicomponent fibers that are splittable, the individual segments that collectively form the unitary multicomponent fiber are contiguous along the longitudinal direction of the multicomponent fiber in a manner such that one or more segments form part of the outer surface of the unitary multicomponent fiber. In other words, one or more segments are exposed along the outer perimeter of the multicomponent fiber. For example, splittable multicomponent fibers and methods for making such fibers are described in U.S. Patent No. 5,935,883 to Pike and U.S. Patent No. 6,200,669 to Marmon, et al.

The substrate of the present disclosure can also contain a coform material. The term "coform material" generally refers to composite materials including a mixture or stabilized matrix of thermoplastic fibers and a second non-thermoplastic material. As an example, coform materials can be made by a process in which at least one meltblown die head is arranged near a chute through which other materials are added to the web while it is forming. Such other materials can include, but are not limited to, fibrous organic materials such as woody or non-woody pulp such as cotton, rayon, recycled paper, pulp fluff and also superabsorbent particles, inorganic absorbent materials, treated polymeric staple fibers and the like. Some examples of such coform materials are disclosed in U.S. Patent No. 4,100,324 to Anderson, et al.; U.S. Patent No. 5,284,703 to Everhart, et al.; and U.S. Patent No. 5,350,624 to Georger, et al.

Additionally, the substrate can also be formed from a material that is imparted with texture one or more surfaces. For instances, in some aspects, the substrate can be formed from a dual-textured spunbond or meltblown material, such as described in U.S. Patent No. 4,659,609 to Lamers, et al. and U.S. Patent No. 4,833,003 to Win, et al.

In one particular aspect of the present disclosure, the substrate is formed from a hydroentangled nonwoven fabric. Hydroentangling processes and hydroentangled composite webs containing various combinations of different fibers are known in the art. A typical hydroentangling process utilizes high pressure jet streams of water to entangle fibers and/or filaments to form a highly entangled consolidated fibrous structure, e.g., a nonwoven fabric. Hydroentangled nonwoven fabrics of staple length fibers and continuous filaments are disclosed, for example, in U.S. Patent No. 3,494,821 to Evans and U.S. Patent No. 4,144,370. Hydroentangled composite nonwoven fabrics of a continuous filament nonwoven web and a pulp layer are disclosed, for example, in U.S. Patent No. 5,284,703 to Everhart, et al. and U.S. Patent No. 6,315,864 to Anderson, et al.

Of these nonwoven fabrics, hydroentangled nonwoven webs with staple fibers entangled with thermoplastic fibers is especially suited as the substrate. In one particular example of a hydroentangled nonwoven web, the staple fibers are hydraulically entangled with substantially continuous thermoplastic

fibers. The staple can be cellulosic staple fiber, non-cellulosic stable fibers or a mixture thereof. Suitable non-cellulosic staple fibers includes thermoplastic staple fibers, such as polyolefin staple fibers, polyester staple fibers, nylon staple fibers, polyvinyl acetate staple fibers, and the like or mixtures thereof. Suitable cellulosic staple fibers include for example, pulp, thermomechanical pulp, synthetic cellulosic fibers, modified cellulosic fibers, and the like. Cellulosic fibers can be obtained from secondary or recycled sources. Some examples of suitable cellulosic fiber sources include virgin wood fibers, such as thermomechanical, bleached and unbleached softwood and hardwood pulps. Secondary or recycled cellulosic fibers can be obtained from office waste, newsprint, brown paper stock, paperboard scrap, etc., can also be used. Further, vegetable fibers, such as abaca, flax, milkweed, cotton, modified cotton, cotton linters, can also be used as the cellulosic fibers. In addition, synthetic cellulosic fibers such as, for example, rayon and viscose rayon can be used. Modified cellulosic fibers are generally are composed of derivatives of cellulose formed by substitution of appropriate radicals (e.g., carboxyl, alkyl, acetate, nitrate, etc.) for hydroxyl groups along the carbon chain.

One particularly suitable hydroentangled nonwoven web is a nonwoven web composite of polypropylene spunbond fibers, which are substantially continuous fibers, having pulp fibers hydraulically entangled with the spunbond fibers. Another particularly suitable hydroentangled nonwoven web is a nonwoven web composite of polypropylene spunbond fibers having a mixture of cellulosic and non-cellulosic staple fibers hydraulically entangled with the spunbond fibers.

The substrate of the present disclosure can be prepared solely from thermoplastic fibers or can contain both thermoplastic fibers and non-thermoplastic fibers. Generally, when the substrate contains both thermoplastic fibers and non-thermoplastic fibers, the thermoplastic fibers make up from about 10% to about 90%, by weight of the substrate. In a particular aspect, the substrate contains between about 10% and about 30%, by weight, thermoplastic fibers.

Generally, a nonwoven substrate will have a basis weight in the range of about 17 gsm (grams per square meter) to about 200 gsm, more typically, between about 33 gsm to about 200 gsm. The actual basis weight can be higher than 200 gsm, but for many applications, the basis weight will be in the 33 gsm to 150 gsm range.

The thermoplastic materials or fibers making-up at least a portion of the substrate can essentially be any thermoplastic polymer. Suitable thermoplastic polymers include polyolefins, polyesters, polyamides, polyurethanes, polyvinylchloride, polytetrafluoroethylene, polystyrene, polyethylene terephthalate, biodegradable polymers such as polylactic acid and copolymers and blends thereof. Suitable polyolefins include polyethylene, e.g., high density polyethylene, medium density polyethylene,

low density polyethylene and linear low density polyethylene; polypropylene, e.g., isotactic polypropylene, syndiotactic polypropylene, blends of isotactic polypropylene and atactic polypropylene, and blends thereof; polybutylene, e.g., poly(1-butene) and poly(2-butene); polypentene, e.g., poly(1-pentene) and poly(2-pentene); poly(3-methyl-1-pentene); poly(4-methyl 1-pentene); and copolymers and blends thereof.

5 Suitable copolymers include random and block copolymers prepared from two or more different unsaturated olefin monomers, such as ethylene/propylene and ethylene/butylene copolymers. Suitable polyamides include nylon 6, nylon 6/6, nylon 4/6, nylon 11, nylon 12, nylon 6/10, nylon 6/12, nylon 12/12, copolymers of caprolactam and alkylene oxide diamine, and the like, as well as blends and copolymers thereof. Suitable polyesters include polyethylene terephthalate, polytrimethylene terephthalate,
10 polybutylene terephthalate, polytetramethylene terephthalate, polycyclohexylene-1,4-dimethylene terephthalate, and isophthalate copolymers thereof, as well as blends thereof. These thermoplastic polymers can be used to prepare both substantially continuous fibers and staple fibers, in accordance with the present disclosure.

In another aspect, the substrate can be a tissue product. The tissue product can be of a
15 homogenous or multi-layered construction, and tissue products made therefrom can be of a single-ply or multi-ply construction. The tissue product desirably has a basis weight of about 10 g/m² to about 65 g/m², and density of about 0.6 g/cc or less. More desirably, the basis weight will be about 40 g/m² or less and the density will be about 0.3 g/cc or less. Most desirably, the density will be about 0.04 g/cc to about 0.2 g/cc. Unless otherwise specified, all amounts and weights relative to the paper are on a dry basis. Tensile
20 strengths in the machine direction can be in the range of from about 100 to about 5,000 grams per inch of width. Tensile strengths in the cross-machine direction are from about 50 grams to about 2,500 grams per inch of width. Absorbency is typically from about 5 grams of water per gram of fiber to about 9 grams of water per gram of fiber.

Conventionally pressed tissue products and methods for making such products are well known in
25 the art. Tissue products are typically made by depositing a papermaking furnish on a foraminous forming wire, often referred to in the art as a Fourdrinier wire. Once the furnish is deposited on the forming wire, it is referred to as a web. The web is dewatered by pressing the web and drying at elevated temperature. The particular techniques and typical equipment for making webs according to the process just described are well known to those skilled in the art. In a typical process, a low consistency pulp furnish is provided
30 from a pressurized headbox, which has an opening for delivering a thin deposit of pulp furnish onto the Fourdrinier wire to form a wet web. The web is then typically dewatered to a fiber consistency of from about 7% to about 25% (total web weight basis) by vacuum dewatering and further dried by pressing

operations wherein the web is subjected to pressure developed by opposing mechanical members, for example, cylindrical rolls. The dewatered web is then further pressed and dried by a steam drum apparatus known in the art as a Yankee dryer. Pressure can be developed at the Yankee dryer by mechanical means such as an opposing cylindrical drum pressing against the web. Multiple Yankee dryer drums can be employed, whereby additional pressing is optionally incurred between the drums. The formed sheets are considered to be compacted because the entire web is subjected to substantial mechanical compressional forces while the fibers are moist and are then dried while in a compressed state.

One particular aspect of the present disclosure utilizes an uncreped through-air-drying technique to form the tissue product. Through-air-drying can increase the bulk and softness of the web. Examples of such a technique are disclosed in U.S. Patent No. 5,048,589 to Cook, et al.; U.S. Patent No. 5,399,412 to Sudall, et al.; U.S. Patent No. 5,510,001 to Hermans, et al.; U.S. Patent No. 5,591,309 to Ruqowski, et al.; U.S. Patent No. 6,017,417 to Wendt, et al., and U.S. Patent No. 6,432,270 to Liu, et al. Uncreped through-air-drying generally involves the steps of: (1) forming a furnish of cellulosic fibers, water, and optionally, other additives; (2) depositing the furnish on a traveling foraminous belt, thereby forming a fibrous web on top of the traveling foraminous belt; (3) subjecting the fibrous web to through-air-drying to remove the water from the fibrous web; and (4) removing the dried fibrous web from the traveling foraminous belt.

Manufacture

Conventional scalable methods, such as spraying, can be used to apply a hydrophobic coating on a surface. In one aspect, a hydrophilic nano-structured filler (Nanomer® PGV nanoclay from Sigma Aldrich), which is a bentonite clay without organic modification, is used. As a hydrophobic component, a 20 wt. % dispersion of a fluorinated acrylic co-polymer (PMC) in water is used, as obtained from DuPont (trade name is CAPSTONE STC-100). The hydrophilic nanoclay is added to water and is sonicated until a stable suspension is produced. Sonication can be done by utilizing a probe sonicator at room temperature (Sonics®, 750 W, High Intensity Ultrasonic Processor, 13 mm diameter tip at 30 % amplitude). At these settings, it can take from about 15 to about 30 min for a stable 15.5g nanoclay-water suspension to form. The concentration of the nanoclay in water is kept below 2 wt. % of total suspension to prevent the formation of a gel, which renders the dispersion too viscous to spray. After placing the stable clay-water suspension under mechanical mixing at room temperature, the aqueous PMC dispersion is added drop-wise to the suspension to produce the final dispersion for spray. In such aspect, the concentrations of each component in the final dispersion for producing a superhydrophobic coating will be as follows: 95.5

wt.% water, 2.8% PMC, 1.7% nanoclay or 97.5 wt.% water, 1.25% PMC, 1.25% nanoclay. Coatings can be applied by spray onto cellulosic substrates at a distance of about 15 to about 25cm using an airbrush atomizer (Paasche VL siphon feed, 0.55 mm spray nozzle) either by hand or by mounting the device onto an industrial fluid dispensing robot (EFD, Ultra TT Series). EFD nozzles with air assist can also be utilized as this achieves extremely fine mists during spray application. The smallest nozzle diameter suggested for the EFD dispensing system is about 0.35mm. The air fans assist in shaping the spray cone into an oval shape, which is useful for producing a continuous uniform coating on a linearly moving substrate. For the airbrush, operation relies on pressurized air passing through the nozzle in order to siphon-feed the particle dispersion and also to facilitate fluid atomization at the nozzle exit. The pressure drop applied across the sprayer can vary from about 2.1 to about 3.4 bar, depending on conditions.

Some technical difficulties are typically encountered when spraying water-based dispersions: The first major problem is insufficient evaporation of the fluid during atomization and a high degree of wetting of the dispersion onto the coated substrate, both resulting in non-uniform coatings due to contact line pinning and the so called "coffee-stain effect" when the water eventually evaporates. The second major challenge is the relatively large surface tension of water when compared with other solvents used for spray coating. Water, due to its high surface tension, tends to form non-uniform films in spray applications, thus requiring great care to ensure that a uniform coating is attained. It was observed that the best approach for applying the aqueous dispersions of the present disclosure was to produce extremely fine droplets during atomization, and to apply only very thin coatings, so as not to saturate the substrate and re-orient hydrogen bonding within the substrate that, after drying, would cause cellulosic substrates (e.g. paper towel) to become stiff.

In another aspect, the coatings are spray cast first on a substrate, such as standard paperboard or other cellulosic substrate; multiple spray passes are used to achieve different coating thicknesses. The sprayed films are then subjected to drying in an oven at about 80°C for about 30 min to remove all excess water. The size of the substrate can be approximately, but not limited to about 7.5cm × 9cm. Once dried, the coatings are characterized for wettability (i.e., hydrophobic vs. hydrophilic). The substrates can be weighed on a microbalance (Sartorius® LE26P) before and after coating and drying in order to determine the minimum level of coating required to induce hydrophobicity. This "minimum coating" does not strictly mean that the sample will resist penetration by liquids, but rather that a water droplet will bead on the surface and roll off unimpeded. Liquid repellency of substrates before and after coating can be characterized by a hydrostatic pressure setup that determines liquid penetration pressures (in cm of liquid).

Performance characterization

Contact angle values can be obtained by a backlit optical image setup utilizing a CCD camera. For dynamic contact angle hysteresis measurements (which designate the self-cleaning property), the CCD camera can be replaced by a high-speed camera, such as Redlake™ Motion Pro, in order to accurately capture advancing and receding contact angle values. The lower the difference between advancing and receding contact angles (i.e. contact angle hysteresis), the more self-cleaning the surface is. Liquid penetration pressure can be determined by increasing the hydrostatic column pressure until liquid penetrates the sample in accordance with ASTM F903–10. Liquid penetration can be recorded by an optical image setup utilizing a CCD camera.

10

MOCON Water Vapor Transmission Rate Test:

A suitable technique for determining the water vapor transmission rate (WVTR) value of a material is the test procedure standardized by INDA (Association of the Nonwoven Fabrics Industry), number IST-70.4-99, entitled "Standard Test Method For Water Vapor Transmission Rate Through Nonwoven And Plastic Film Using A Guard Film And Vapor Pressure Sensor," which is incorporated by reference herein. The INDA procedure provides for the determination of WVTR, the permeance of the film to water vapor and, for homogeneous materials, water vapor permeability coefficient.

15

The INDA test method is well known and will not be set forth in detail herein. However, the test procedure is summarized as follows. A dry chamber is separated from a wet chamber of known temperature and humidity by a permanent guard film and the sample material to be tested. The purpose of the guard film is to define a definite air gap and to quiet or still the air in the air gap while the air gap is characterized. The dry chamber, guard film, and the wet chamber make up a diffusion cell in which the test film is sealed. The sample holder is known as the PERMATRAN-W® model 100K manufactured by Modern Controls, Inc. (MOCON) (Minneapolis, MN), USA. A first test is made of the WVTR of the guard film and air gap between an evaporator assembly that generates 100 percent relative humidity. Water vapor diffuses through the air gap and the guard film and then mixes with a dry gas flow that is proportional to water vapor concentration. The electrical signal is routed to a computer for processing. The computer calculates the transmission rate of the air gap and guard film and stores the value for further use.

20

25

The transmission rate of the guard film and air gap is stored in the computer as CalC. The sample material is then sealed in the test cell. Again, water vapor diffuses through the air gap to the guard film and the test material and then mixes with a dry gas flow that sweeps the test material. Also, again, this

30

mixture is carried to the vapor sensor. The computer then calculates the transmission rate of the combination of the air gap, the guard film, and the test material.

This information is then used to calculate the transmission rate at which moisture is transmitted through the test material according to the equation:

$$5 \quad TR^{-1}_{\text{test material}} = TR^{-1}_{\text{test material, guardfilm, airgap}} - TR^{-1}_{\text{guardfilm, airgap}}$$

The calculation of the WVTR uses the formula:

$$WVTR = F \rho_{\text{sat}}(T) RH / A p_{\text{sat}}(T) (1 - RH)$$

where:

F=the flow of water vapor in cc/min,

10 $\rho_{\text{sat}}(T)$ =the density of water in saturated air at temperature T,

RH=the relative humidity at specified locations in the cell,

A=the cross sectional area of the cell, and

$p_{\text{sat}}(T)$ =the saturation vapor pressure of water vapor at temperature T.

15

EXAMPLES

The following are provided for exemplary purposes to facilitate understanding of the disclosure and should not be construed to limit the disclosure to the examples.

Hydrophobic chemistries having similar contact angles (using 5 microliters of DI water) in the range of 125-140 degrees and similar roll-off angles (the angle to which the material needs to be tilted for the drop to roll off the material) in the range of 40 to 50 degrees were spray applied to one side of an otherwise untreated HYDROKNIT brand towel at similar add-on levels (1gsm and 5gsm) (see Figs. 1 and 2). The materials were assessed for barrier properties using the standard K-C hydrohead test with water. The hydrohead refers to the amount of hydrostatic pressure that a sample can support before water breaks through the sample. The standard test is done in the lab on an instrument such as the TEXTTEST FX 3000 HYDROTESTER III. One side of the sample is placed face down onto a surface of water and clamped into place. The sample size for the tests described herein was 100 cm². A button is pressed to start the test. Water is forced upward from below, pressing against the sample. The pressure is increased at a constant rate (1 mbar/sec) until the water breaks through the substrate in 3 distinct places. In some cases the material can "flood," meaning the water comes in from all sides at once and clearly the seal is broken. If this happens, the test is also stopped. Once the operator notices water breaking through the

substrate in 3 distinct places, the operator presses the "stop" button and the pressure in mbar is read off of the instrument.

Additional information related to hydrohead testing can be found at www.youtube.com/watch?v=HwQA4tg99ds and at www.ipstesting.com/AATCC127/tabid/196/Default.aspx.

5 Results illustrated in Fig. 3 show that, although the hydrophobicity properties are similar, the treatments did not yield the same hydrohead result. The Unidyne TGKC03, a fluorinated methylacrylate co-polymer treatment commercially available from Daikin Industries, Ltd., did not provide any barrier to fluid (zero hydrohead that is the same as control HYDROKNIT brand towel). Developmental formulations (UIC III and UIC V) were assessed and shown to provide improved barrier performance as measured by hydrohead. These treatments were 1) DuPont Capstone STC-100, a fluorinated co-polymer, in water and 10 2) DuPont Capstone STC-100, a fluorinated co-polymer, plus hydrophilic bentonite nanoclay from Sigma-Aldrich. A HYDROKNIT brand towel, originally a hydrophilic substrate with no hydrohead, gains a significant amount of hydrohead or barrier property once coated with a film-forming polymer (Capstone ST-100.) This is not seen with Daikin TG KC03 (bars absent). These showed hydrohead ranging from 15 approximately 5 mbar to 17 mbar, as illustrated in Fig. 3.

Micrograph images of the treated HYDROKNIT brand towel (see Fig. 4) as well as SMS (see Fig. 5) treated with the chemistries showed the Capstone STC-100 polymer forms a film between the nonwoven fibers thus creating film-like areas in the material that enhance barrier properties. Additionally, the film-forming treatment provides air permeability results that would not be possible with a film having the 20 same barrier properties. The SEM images of the UIC III and Daikin TG KC03 coatings show differences at the chemistry-substrate interface. The SEM images are better quality of the SMS substrate but it is believed that the film forming property also occurs on the HYDROKNIT brand towel. Fig. 6 shows TABCW (through air dried bonded carded web) fibers with UIC III hydrophobic treatment. This SEM micrograph is a more zoomed in image than those of Figs. 4 and 5. Fig. 6 demonstrates the film-forming nature of the 25 treatment. The film spread between the fibers is evident in Fig. 6.

Diaper outer cover material, typically has its breathability measured in Mocons. For this work, however, a more sensitive and aggressive air permeability test used an Air Permeability Tester FX-3300. The instrument is calibrated before the test. The sample is clamped into place and air blows from the lower test head to the upper test head. The area of the sample is 38 cm². An adjustment knob is turned 30 until the instrument indicates the sample is in range. The air permeability is read off of the digital display in CFM (cubic feet per minute). An example of such an air tester can be found at www.manufacturingsolutionscenter.org/air-permeability-us-standard.html.

The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm."

5 All documents cited in the Detailed Description are, in relevant part, incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present disclosure. To the extent that any meaning or definition of a term in this written document conflicts with any meaning or definition of the term in a document incorporated by reference, the meaning or definition assigned to the term in this written document shall govern.

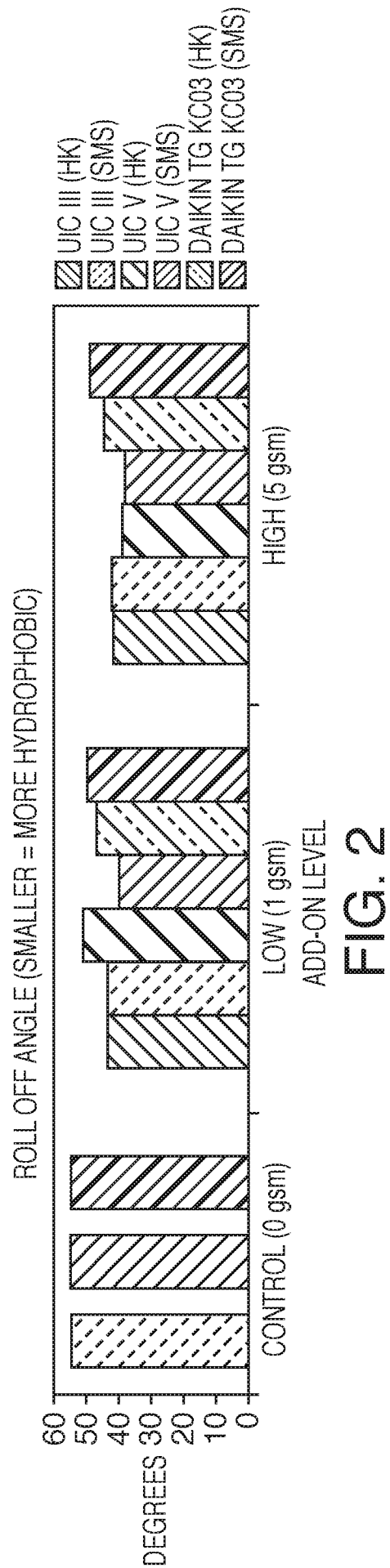
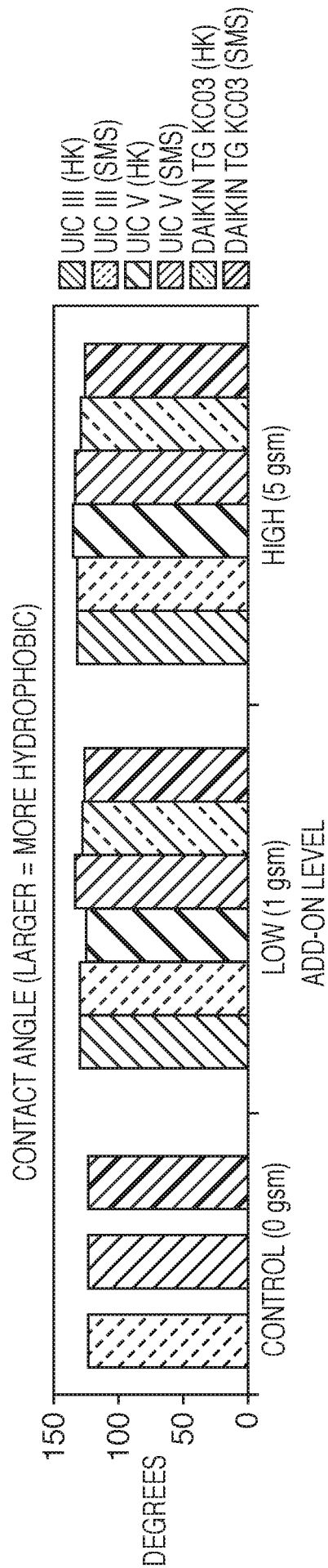
10 While particular aspects of the present disclosure have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the disclosure. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this disclosure.

What is claimed is:

1. A liquid-impermeable barrier material comprising:
a hydrophilic nonwoven web having two surfaces, the nonwoven web including fibers; and
a hydrophobic composition disposed on a surface, wherein the barrier material is breathable.
2. The barrier material of claim 1, wherein the barrier material exhibits a positive hydrohead value.
3. The barrier material of claim 1, wherein the hydrophobic composition includes a hydrophobic component selected from the group consisting of fluorinated polymers, perfluorinated polymers, and mixtures thereof.
4. The barrier material of claim 1, wherein the barrier material includes a hydrophilic surface opposite the surface having the hydrophobic composition.
5. The barrier material of claim 1, wherein the nonwoven web includes tissue.
6. The barrier material of claim 1, wherein the nonwoven web includes cellulose.
7. The barrier material of claim 1, wherein the hydrophobic composition is a film-like structure between a portion of the fibers.
8. A barrier material having a hydrophobic surface, the barrier material comprising:
a hydrophilic nonwoven substrate treated with a composition including a hydrophobic component and water.

9. The barrier material of claim 8, wherein the barrier material includes a hydrophilic surface opposite the hydrophobic surface.
10. The barrier material of claim 8, wherein the hydrophobic component is selected from the group consisting of fluorinated polymers, perfluorinated polymers, and mixtures thereof.
11. The barrier material of claim 8, the composition further comprising nano-structured particles.
12. The barrier material of claim 11, wherein the nano-structured particles are selected from the group consisting of fumed silica, hydrophobic titania, zinc oxide, nanoclay, and mixtures thereof.
13. The barrier material of claim 8, the composition further comprising a surfactant, wherein the surfactant is selected from nonionic, cationic, and anionic surfactants.
14. The barrier material of claim 8, wherein the hydrophobic component is a water-dispersible hydrophobic polymer.
15. The barrier material of claim 14, wherein the water-dispersible hydrophobic polymer includes a comonomer selected from acrylic monomers, acrylic precursors, and the like.
16. The barrier material of claim 8, the composition further comprising a stabilizing agent selected from the group consisting of long chain fatty acids, long chain fatty acid salts, ethylene-acrylic acid, ethylene-methacrylic acid copolymers, sulfonic acid, acetic acid, and the like.

17. The barrier material of claim 8, the composition further comprising a filler selected from the group consisting of milled glass, calcium carbonate, aluminum trihydrate, talc, antimony trioxide, fly ash, clays, and the like.
18. The barrier material of claim 8, wherein the nonwoven substrate is a tissue product.



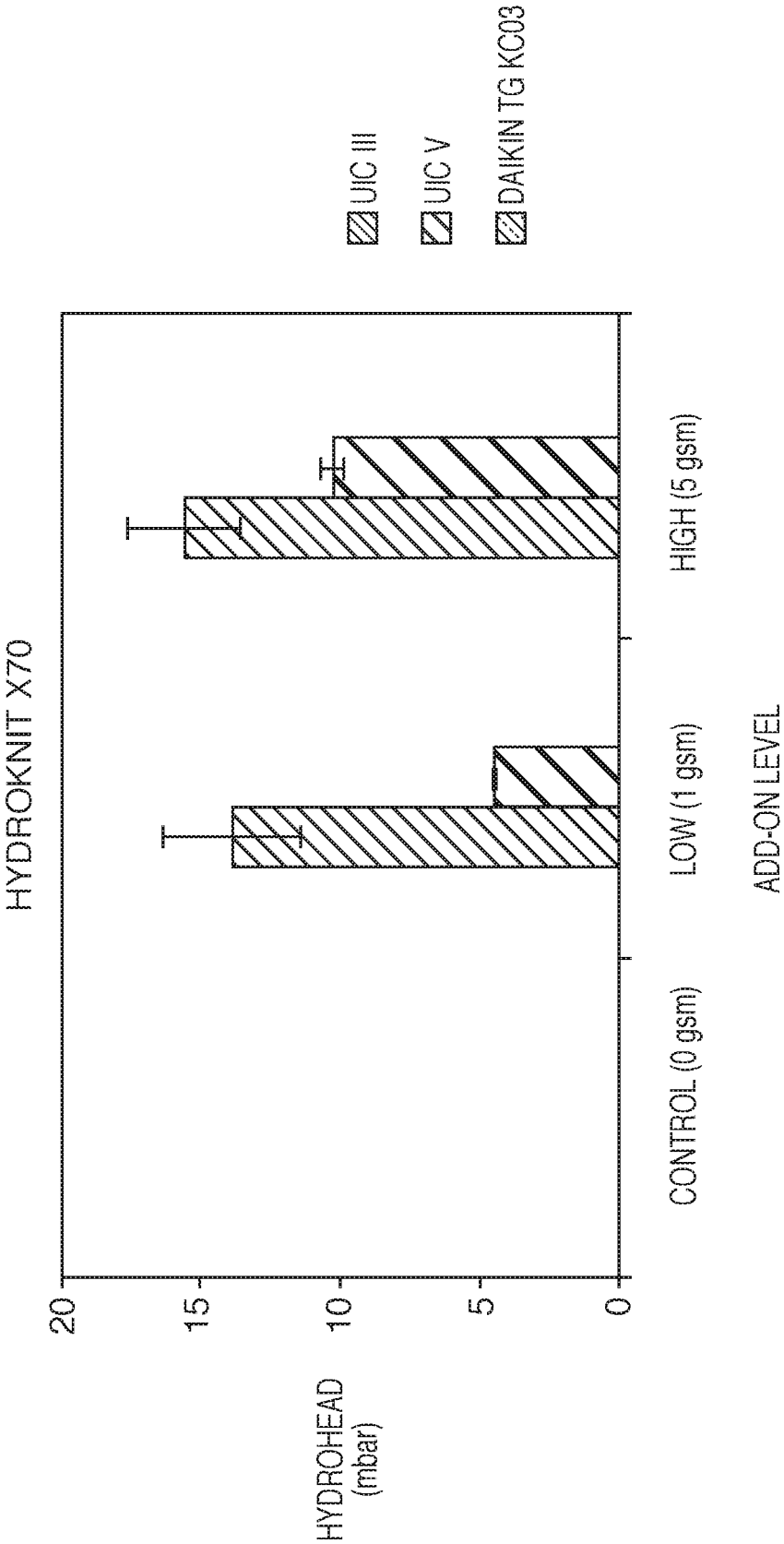


FIG. 3

3/5

SEM: HYDROKNIT X70 (HIGH, 5 gsm)

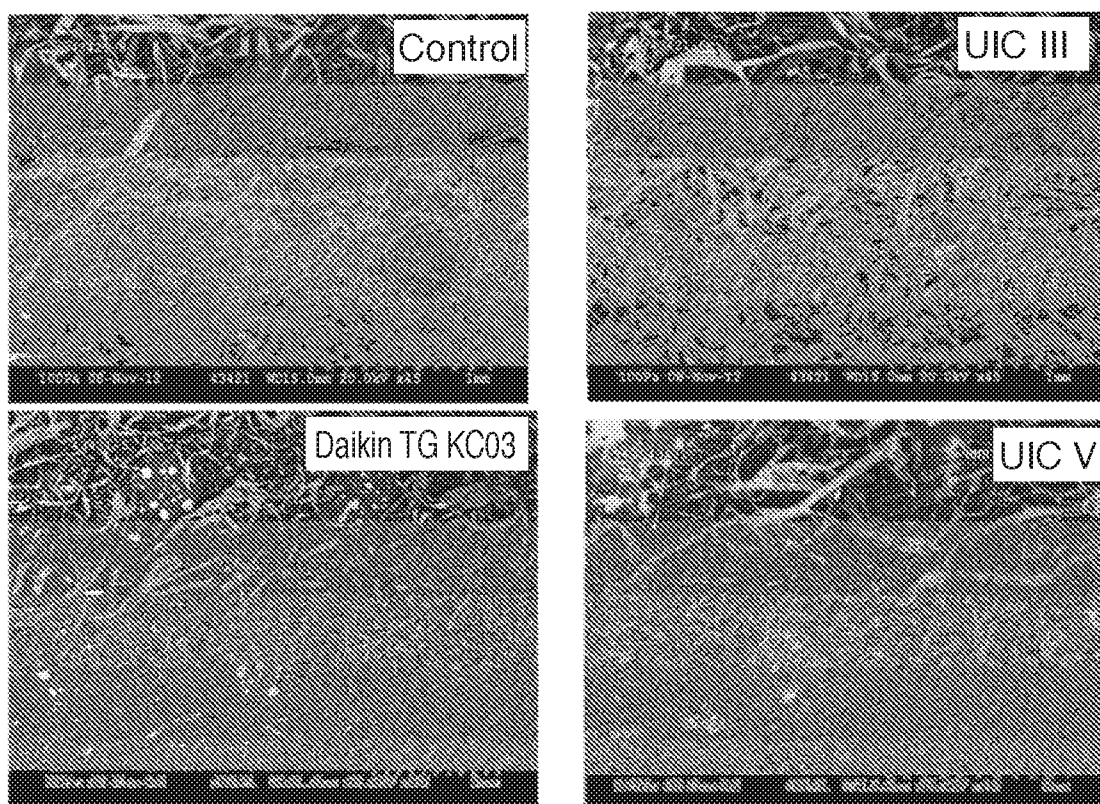


FIG. 4

4/5

SEM: SMS (HIGH, 5 gsm)

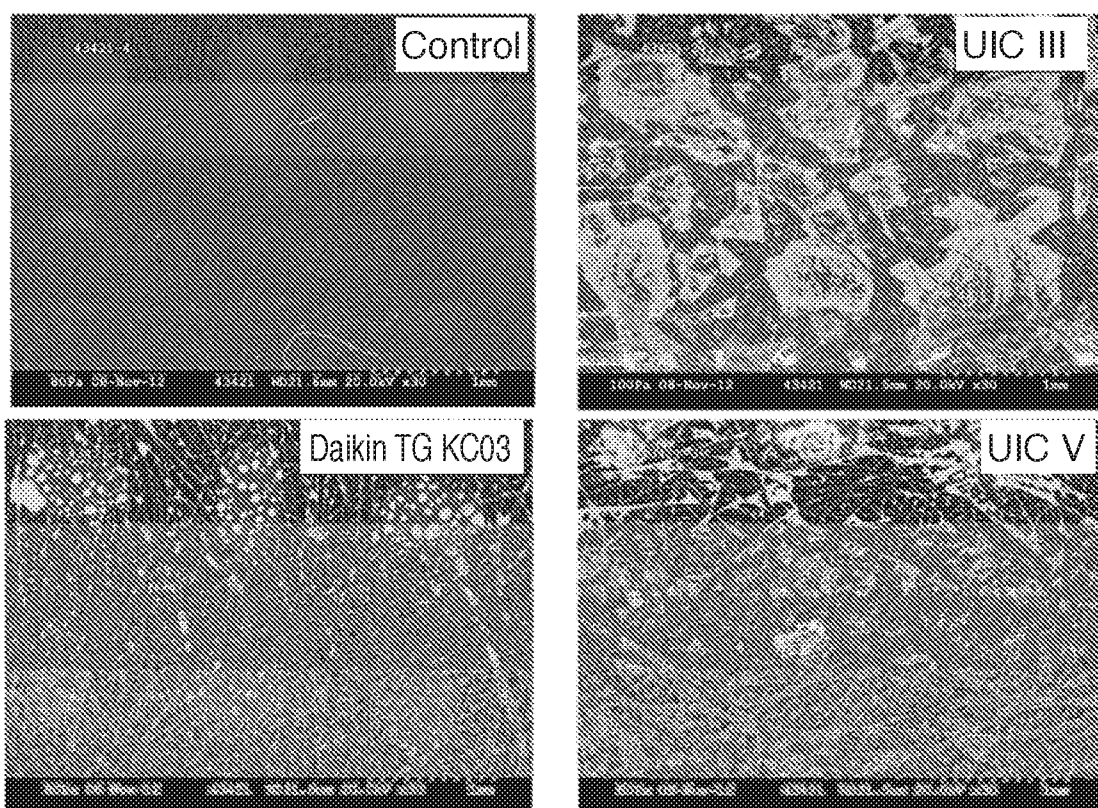


FIG. 5

5/5



FIG. 6

A. CLASSIFICATION OF SUBJECT MATTER**D06M 15/277(2006.01)i, D04H 13/00(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D06M 15/277; B32B 17/10; B05D 5/00; A61F 13/15; B32B 3/24; B32B 27/32; B32B 21/02; A61F 13/45; B32B 5/02; D21H 27/30; D04H 13/00

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: ,liquid-impermeable barrier, hydrophilic nonwoven web, hydrophobic composition, breathable, barrier, water**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010-0069864 A1 (BERLAND, CAROLYN et al.) 18 March 2010 See abstract; paragraphs [0059], [0071]; claims 1, 14-15.	1-2,4-7
Y		3
A		8-18
X	US 2013-0029551 A1 (QIN, JIAN et al.) 31 January 2013 See abstract; paragraphs [0005], [0051], [0060], [0068]-[0070], [0078], [0082]; claims 1-3, 7-10, 12-13, 16-17; table 1; figures 2, 6-9.	8-18
Y		3
A	US 2005-0274470 A1 (SHANNON, THOMAS GERARD et al.) 15 December 2005 See abstract; claim 1.	1-18
A	US 2005-0245159 A1 (CHMIELEWSKI, HARRY J. et al.) 03 November 2005 See abstract; paragraph [0037]; claims 1, 15-19, 23, 38.	1-18
A	US 2012-0225202 A1 (CHENG, DAH YU) 06 September 2012 See abstract; claim 1.	1-18



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

22 July 2015 (22.07.2015)

Date of mailing of the international search report

22 July 2015 (22.07.2015)

Name and mailing address of the ISA/KR

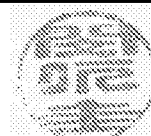
International Application Division
Korean Intellectual Property Office
189 Cheongsu-ro, Seo-gu, Daejeon Metropolitan City, 302-701,
Republic of Korea

Facsimile No. +82-42-472-7140

Authorized officer

MIN, In Gyou

Telephone No. +82-42-481-3326



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/IB2015/053124

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2010-0069864 A1	18/03/2010	CN 101557784 A CN 101557784 B EP 2091492 A1 EP 2091492 B1 WO 2008-071202 A1	14/10/2009 10/12/2014 26/08/2009 28/09/2011 19/06/2008
US 2013-0029551 A1	31/01/2013	AU 2012-288560 A1 CN 103687916 A EP 2736985 A2 EP 2736985 A4 KR 10-2014-0053127 A WO 2013-014546 A2 WO 2013-014546 A3	16/01/2014 26/03/2014 04/06/2014 22/04/2015 07/05/2014 31/01/2013 11/04/2013
US 2005-0274470 A1	15/12/2005	AU 2005-257803 A1 AU 2005-257803 B2 EP 1797241 A1 KR 10-2007-0019762 A US 7381299 B2 WO 2006-001901 A1	05/01/2006 24/12/2009 20/06/2007 15/02/2007 03/06/2008 05/01/2006
US 2005-0245159 A1	03/11/2005	None	
US 2012-0225202 A1	06/09/2012	CN 1835812 A CN 1835812 B EP 1644134 A2 EP 1644134 A4 JP 2007-526350 A JP 5101104 B2 US 2004-256310 A1 US 2007-102348 A1 WO 2004-112934 A2 WO 2004-112934 A3	20/09/2006 08/06/2011 12/04/2006 30/07/2008 13/09/2007 19/12/2012 23/12/2004 10/05/2007 29/12/2004 09/06/2005