



(11) **EP 3 594 396 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
15.01.2020 Bulletin 2020/03

(51) Int Cl.:
D06C 23/04 (2006.01)

(21) Application number: **18182690.0**

(22) Date of filing: **10.07.2018**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(71) Applicant: **Karlsruher Institut für Technologie**
76131 Karlsruhe (DE)

(72) Inventors:
• **Striegel, Andreas**
63820 Elsenfeld (DE)
• **Schneider, Marc**
76356 Weingarten (DE)
• **Worgull, Matthias**
76297 Stutensee (DE)

(74) Representative: **Müller-Boré & Partner**
Patentanwälte PartG mbB
Friedenheimer Brücke 21
80639 München (DE)

(54) **PROCESS FOR PRODUCING MICRO- AND NANO-STRUCTURED FIBER-BASED SUBSTRATES**

(57) The present disclosure relates to a process for preparing fiber-based surfaces, such as nonwoven surfaces, that exhibit enhanced properties, as e.g. hydrophobic properties, without the addition of a chemical treatment.

EP 3 594 396 A1

Description

BACKGROUND

5 **[0001]** The present disclosure relates to a process for preparing fiber-based surfaces, such as nonwoven surfaces, that exhibit enhanced properties, as e.g. hydrophobic properties, without the addition of a chemical treatment.

[0002] A hydrophobic surface exhibits a sessile water contact angle of from about 90° to about 120°. If, additionally, the surface exhibits a water droplet roll-off (sliding) angle of less than 10°, the surface is deemed to be "self-cleaning." Most man-made materials such as fabrics, nonwovens, cellulose tissues, polymer films, etc., do not have surfaces with such properties. Currently, there are several methods to modify a non-hydrophobic surface to achieve hydrophobicity. One method is to graft hydrophobic polymer(s) (using a monomer, comonomers, etc.) onto every exposed surface of a non-hydrophobic material. Such a method makes the material hydrophobic throughout the thickness of the material, which might not be desired in most cases. It is also not cost effective, cannot be used for a continuous production, and can lead to undesirable environment issues.

15 **[0003]** Another method of achieving enhanced properties, such as enhanced hydrophobicity, includes the application of a chemical treatment to the surface. Various fluorinated and non-fluorinated formulations, both water- and solvent-based, have been attempted for achieving hydrophobicity. Over the past several decades, many approaches to these hydrophobic surfaces have been developed that commonly require harsh organic solvents, complex processing methods, and/or environmentally undesirable fluorinated chemistry. In addition, many of the demonstrated methods are not relevant in practice on large scales in commercial application, not only for their negative consequences to the environment, but also the inability to economically prepare large-area fluid repellent surfaces at sufficiently low-cost. Imparting liquid repellency via large-area approaches, such as spray-casting or size press coating, have been shown to be viable for low-cost and substrate-independent fluid management.

25 **[0004]** A standard approach is to coat a specially-formulated liquid dispersion onto a surface. Upon subsequent drying, a nano-structured hydrophobic film forms. To use such an approach, the deposited film must exhibit a chemical and physical morphology characteristic of hydrophobic surfaces. First, the formulation requires at least one low-surface energy (i.e., hydrophobic) component, and second, the treated surface has to have a rough surface texture, preferably extending over several length-scales characteristic of micro- and/or nano-roughness.

30 **[0005]** Low-cost, large-area hydrophobicity-inducing methods are of great value to many applications requiring a passive means for attaining efficient liquid repellency. While many applications are envisioned, only few are realizable due to either the high-cost or low-durability of such treatments. Recently, spray deposition of polymer-particle dispersions has been demonstrated as a means for producing low-cost, large-area, durable, hydrophobic composite coatings/films; however, the dispersions used for spray deposition of hydrophobic coatings generally contain harsh or volatile solvents. Solvents are required for wet processing of e.g. polymers, as well as for dispersing hydrophobic nanoparticles, thus inhibiting scalability due to the increased cost in chemical handling and safety concerns. This problem can be overcome by replacing solvents with water, but this situation is paradoxical: producing a highly water-repellent coating from an aqueous dispersion.

35 **[0006]** Also, such coatings usually contain fluoropolymers. A low-surface energy fluoropolymer (e.g., fluoroacrylic copolymers, poly(tetrafluoroethylene), etc.) is typically incorporated into the formulation to achieve liquid repellency. However, concerns over their bio-persistence have provided an impetus for eliminating these chemicals. The problems with the byproducts of fluoropolymer degradation, e.g. long-chain perfluorinated acids (PFAs) that have a documented ability to bioaccumulate, as well as the potential adverse effects PFA in maternal concentrations can have on human offspring, have led to a shift in the manufacture and usage of fluoropolymers. One common PFA of particular concern is perfluorooctanoic acid (PFOA). In 2006, the EPA (United States Environmental Protection Agency) introduced its PFOA (perfluorooctanoic acid) Stewardship Program and invited eight major fluoropolymer and telomer manufacturers to commit to eliminating precursor chemicals that can break down into PFOA; in one case, DuPont has since introduced so-called short-chain chemistry, whereby the length of perfluorinated chains within polymers are kept below a threshold to avoid degradation into PFOA. In other applications, usage of fluoropolymers in products that come in sustained contact with the human body or in disposable items intended for landfilling after consumption must be minimized.

50 SUMMARY

[0007] Using a mechanical instead of a chemical process eliminates the need for fluorinated compounds, organic solvents, and other potentially harmful and/or expensive chemicals. This novel, environmentally-friendly process is herein characterized as having potential in numerous fluid management applications by virtue of its simplicity, efficiency, and versatility. For a multitude of safety, health, economic, and environmental issues, it is important that the process be independent of any liquid treatments.

BRIEF DESCRIPTION OF THE FIGURES

[0008] 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 schematically illustrates the micro- and nano-embossing process of the present disclosure;

Figure 2 graphically illustrates the relationship between contact angle to surface roughness and pattern coverage on a material provided using the process of Fig. 1;

Figure 3 is a photographic scanning electron microscope (SEM) illustration of a nonwoven substrate produced using a silicone backing material in the process of Fig. 1;

Figure 4 is a photographic SEM illustration of a nonwoven substrate produced using a felt backing material and six cycles of embossing in the process of Fig. 1; and

Figure 5 is a photographic SEM illustration of a control nonwoven substrate without the embossing process of Fig. 1.

[0009] 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

[0010] All percentages are by weight of the total solid composition unless specifically stated otherwise. All ratios are weight ratios unless specifically stated otherwise.

[0011] The term "superhydrophobic" refers to the property of a surface to repel water very effectively. This property is quantified by a water contact angle exceeding 150°.

[0012] 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°.

[0013] The term "hydrophilic," as used herein, refers to surfaces with water contact angles well below 90°.

[0014] The term "self-cleaning," as used herein, refers to the property to repel water with the water roll-off angle on a tilting surface being below 10°.

[0015] The term "fiber-based" substrate refers to any substrate that is fully or partially made of fibers (i.e. the substrate includes or is composed of fibers and in one embodiment consists of fibers). Corresponding substrates are known in the art and examples thereof represent nonwovens, wovens, knitted fabrics, or rowings. Preferably, the fiber-based substrate is a nonwoven substrate. The fibers of the fiber-based substrate are not particularly limited and can e.g. be polymer fibers or fibers made of composite materials, such as multicomponent fibers and nanocomposite fibers. The fibers of the fiber-based substrate are preferably polymer fibers.

[0016] 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 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, osy must be multiplied by 33.91.

[0017] 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 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.

[0018] 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.

5 [0019] 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 such fibers. 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 state is different from the other 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 purposefully 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, 10 50/50, 25/75 or any other desired ratios.

15 [0020] As used herein, the term "substantially continuous fibers" is intended to mean fibers 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.

20 [0021] 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 made of the above-mentioned materials for the fibers of the fiber-based substrate and can e.g. 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. 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, 25 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.

30 [0022] 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.

35 [0023] As used herein, the term "disposable absorbent products" refers to diapers, training pants, absorbent under-pants, adult incontinence products, sanitary wipes, and feminine hygiene products, such as sanitary napkins, pads, liners, and tampons, and other similar products. Disposable absorbent products includes absorbent medical products, which include products such as medical bandages, tampons intended for medical, dental, surgical, and/or nasal use, surgical drapes and garments, coverings in medical settings, and the like.

40 [0024] Prior art formulations used to prepare a substrate to demonstrate hydrophobicity can require harmful fluorinated polymers in conjunction with solvents that include harmful volatile organic compounds (VOCs). The present disclosure solves these problems for these applications by eliminating the need for any chemical treatments of the substrate to minimize the use of harmful VOCs, a common, non-trivial problem with coatings aiming to achieve hydrophobicity upon deposition.

45 [0025] The present disclosure describes a pattern impressed on the fibers of a fiber-based substrate, preferably a nonwoven substrate, using a thermomechanical process for the formation of a surface having enhanced properties, such as an enhanced hydrophobic surface. The fiber-based substrate has a micro- or nano-structure imprinted into the fibers after the initial forming of the substrate. The micro- or nano-structure has a feature size that is smaller than the fiber diameter, such that the structures can be resolved on individual fibers on the surface of the substrate. The pattern is imprinted into the fiber surface while largely retaining the porosity, thickness, and softness (lack of rigidity) of the fiber-based, preferably nonwoven, substrate. The micro-structures confer functional benefit such as elevated contact angle.

50 [0026] A hydrophobic surface of the present disclosure can be produced on a fiber-based substrate, preferably a nonwoven substrate, by employing a micro- or nano-embossing process that impresses a sub-fiber-width pattern on the fibers of that substrate.

55 [0027] For liquid-repellent functionality, specifically to water, the surface requires low surface energies and a suitable degree of roughness to reduce the liquid-to-solid interfacial contact area, thus increasing the contact angle of water droplets used as a measure of surface wettability. The wettability of a smooth un-textured surface in an air environment is determined by the free surface energies of the liquid and solid being introduced; whether the surface is hydrophobic

or hydrophilic, the interaction with water is tunable via the surface roughness imparted by the imposition of micro- or nano-patterns. A high-degree of surface roughness modifies the intrinsic wettability of the surface into hydrophobicity, or having a contact angle to water of about 90° to about 120°.

5 [0028] In practice until recently, the fabrication of super-repellent composites requiring polymers with sufficiently low surface energies (i.e., for repelling water, $\gamma \ll 72$ mN/m) demanded the use of harsh solvents for wet-processing, thus hindering the development of entirely water-based systems. Fluorine-free and water-compatible polymer systems capable of delivering low surface energy have been the primary challenge for the development of truly environmentally-benign superhydrophobic coatings. A low surface energy, waterborne fluoropolymer dispersion (DuPont Capstone ST-100) was used in a water-based superhydrophobic spray, where the correlation between contact angle and hydrostatic resistance was studied, but again, the presence of fluorinated compounds in the composite still posed environmental concerns. At one point the EPA initiated a reduction in the manufacture of many dangerous fluoropolymer compounds; such compounds have a high risk of breaking down into perfluorooctanoic acids (PFOA) and can have an extremely adverse environmental impact. PFOA, a known cause of birth defects, can enter into ground water, polluting reservoirs and aquatic wild-life, eventually being ingested by humans where it can accumulate to hazardous levels. Although short-chain fluoropolymers made in response to the EPA initiative, such as DuPont's Capstone ST-100, are available and pose less environmental risk; eliminating the necessity of fluorine altogether for repellency has been a primary goal of this work. The methods described herein have the potential to create surfaces having enhanced properties, such as e.g. hydrophobic surfaces, without the use of fluorinated composites, organic solvents, or other chemicals. In that respect, the methods described herein are a more environmentally-conscious, so-called "green" alternative.

10 [0029] Choosing patterns having nano-scale dimensions allows for fine control over surface roughness and a greater reduction in the liquid-to-solid interfacial contact area; for hydrophobic, or low-surface energy surfaces, this translates into an increased resistance to fluid wetting by allowing the solid surface to retain pockets of vapor that limit liquid/solid contact.

15 [0030] The present disclosure relates to a surface of a substrate, or the substrate itself, exhibiting enhanced characteristics, such as hydrophobic characteristics, when a thermomechanical patterning process is applied. The enhanced characteristics, such as hydrophobicity, can be applied either over the entire surface or patterned throughout or on the substrate material. Further examples of potential benefits from surface structuring include modification of wetting and fluid handling properties, friction, adhesion, tactile properties, optical effects, and anti-microbial effects.

20 [0031] In a particular aspect, the fiber-based substrate, e.g. the nonwoven substrate, is made of a thermoplastic polymer (for example, polypropylene) and the pattern is imprinted by means of roll-to-roll embossing, such as continuous roll-to-roll micro-hot embossing, roll-to-roll thermal nanoimprint, roll-to-roll soft embossing and discontinuous micro/nano hot embossing, thermal nanoimprint, soft embossing. The fiber-based substrate itself is formed by processes well known to those skilled in the art. If a fiber-based substrate such as a nonwoven substrate includes melt-bonded points, these melt-bonded points can be formed prior to embossing, or the embossing pattern and the bond pattern can be incorporated into the same roll and process. The bond points are typically at least an order of magnitude larger than the much finer micro- and nano-embossed features.

25 [0032] In another aspect illustrated in Fig. 1, the present disclosure relates to a patterning apparatus 10, comprising a pattern roll 20 and a pressure roll 30 forming a nip 40, wherein the pattern roll 20 comprises protrusions or grooves having a diameter being smaller than a diameter of fibers included in a fiber-based substrate 15, preferably a nonwoven substrate, introduced into the nip 40 for roll-to-roll (micro-hot) embossing. The statements and definitions given with respect to the other aspects of the present disclosure, when not differing from the following statements and definitions, analogously apply to this aspect of the present disclosure.

30 [0033] According to the present disclosure, the pattern roll 20 comprises protrusions or grooves having a diameter being smaller than the diameter of the fibers included in the fiber-based substrate 15 as used in the present invention. The shape, diameter and further dimensions of the protrusions or grooves and the spaces between the protrusions or grooves are not particularly limited, with the exception that the protrusions or grooves have a diameter being smaller than the diameter of the fibers included in the substrate 15. For example, the protrusions or grooves each may have a diameter/length of the edge of 20 μm or less, more particularly from 5.0 nm to 20 μm . Moreover, the protrusions or grooves may have the shapes of e.g. pins, such as cylindrical pins, triangular pins, square pins, polygonal pins, cylinders, and star-shaped pins, pipe-like cross-sectional shapes (also circular, square etc.), all preferably 2.5D, cones, pyramids, 3D bell-shaped curves, free formed surfaces, statistical surfaces (sandblasted, self-assembled, random etc.), and combinations of the same. Moreover, the spaces between the protrusions or grooves each may be 20 μm or less, more particularly from 5.0 nm to 20 μm .

35 [0034] The material of the pattern roll 20 and the pressure roll 30 is not particularly limited. All the rolls known to a person skilled in the art can thus be used. For example, rolls made of polymers, cotton, felt, rubber, ceramics, compounds, composite materials, combinations of different materials, such as fiber-reinforced silicon materials or fiber-reinforced foamed materials or the like, or metal or combinations of said materials may be used. The rolls may be coated e.g. with a non-stick coating. Moreover, the rolls/structures may be covered with another material as the roll material. Accordingly,

the micro- or nano-pattern (i.e. the protrusions or grooves) of the pattern roll 20 may be included in the roll material itself or may be included in a material/tool, which is wrapped around the pattern roll 20. For example, in a corresponding process, a master micro- or nano-pattern may first be fabricated by processes well known by those skilled in the art, often from a polymeric material. Typically, a more durable tool may then be created from the fabricated master by well-known processes, including nickel electroplating. This durable tool can e.g. be a thin shim, a carbon tool, a tool made of a high performance polymer, such as e.g. PEEK, a tool made of composite materials, or a tool made of combinations of (such) materials that is wrapped around the pattern roll 20.

[0035] In a preferred embodiment, the pressure roll 30 is made of a material selected from an elastomeric material, such as silicon-based elastomers, non-silicon-based elastomers, foamed elastomers, and thermoplastic elastomers, and felt, preferably from a silicone rubber and felt, more preferably from a felt material. Micro-hot embossing was developed primarily for films. A common challenge with micro-hot embossing of fiber-based substrates, such as nonwoven substrates, is that the pressure and heat required to imprint a pattern into the fiber surface may also result in crushing the fiber structure, flattening the fibers, and/or fusing the fibers together. This can destroy the permeability, caliper, and softness of the material, in some cases even melting the substrate into a film. In case the pressure roll 30 is made of a soft/elastomeric material such side-effects may be reduced and even be overcome.

[0036] The felt material is not particularly limited and may e.g. be wool felt material. Preferably, the felt material is an uncarbonized wool felt material.

[0037] The apparatus may further comprise means for loosening the fibers of the fiber-based substrates 15, such as a nonwoven substrate, after it has been introduced into the nip 40. This may increase the loft and caliper and thus further reduce the above-mentioned side-effects. Loosening can be performed e.g. by using a ring rolling process or by any other suitable process known in the art. This loosening step reverses the potential negative effects of the embossing nip 40.

[0038] The pattern roll 20 and/or the pressure roll 30 may be heated and/or the fiber-based substrate may be preheated in an optional preheating unit 50 (see Figure 1) before being introduced into the nip 40. Suitable means for heating the rolls and/or suitable preheating units (e.g. radiative, conductive, convective) are known in the art. For example, the preheating unit 50 may be IR heaters. For example, the substrate 15 can be heated by both the preheating unit 50 and the roll(s) 20, 30, can be heated with the preheating unit 50 and cooled with the roll(s) 20, 30, or can be heated only with the roll(s) 20, 30. Furthermore, it is also possible to use several heating and cooling rolls. The temperature/energy being applied to the substrate 15 depends on the material of the fiber-based substrate 15 and the desired structure. For example, a polymeric fiber-based substrate 15 may be heated to a temperature close to the glass transition temperature, such as e.g. $T_G \pm 20^\circ\text{C}$, or the softening range of the polymeric material. The glass transition temperature may be determined e.g. via DSC (differential scanning calorimetry) and DMA (Dynamic mechanical analysis). Although the temperature/energy being applied to the substrate 15 depends on the material of the fiber-based substrate 15 and the desired structure the temperature applied to the fiber-based substrate 15, such as a nonwoven substrate, may e.g. be from 30 to 350°C, preferably from 60 to 150°C, more preferably from 80 to 120°C, and most preferably from 85 to 110°C.

[0039] The pressure roll 30 and the pattern roll 20 are brought together under pressure to form the nip 40. The substrate 15 is brought to the nip 40 where the micro- or nano-pattern on the pattern roll 20 is imprinted into the substrate 15 by means of pressure and heat. The pressure being applied to the substrate 15 is not particularly limited. For example, the pressure may be from 10 to 100000 N, preferably from 4000 to 50000 N, more preferably from 5000 to 20000 N, most preferably from 5000 to 10000 N, e.g. at 100 mm substrate width e.g. when using a felt pressure roll 30.

[0040] In other aspects, suitable processes include serial (not continuous) hot embossing, roll-to-plate hot embossing, and nano-imprint lithography, in which the pattern is formed in a UV-cured printed coating. In addition, other coatings can be applied to the substrate 15 prior to imprinting.

[0041] Further parts which may be comprised in the apparatus such as e.g. storage means (for the treated and untreated substrate), such as unwinder 60 and upwinder 70 units as depicted in Fig. 1, and conveyors are known in the art.

[0042] The fiber-based substrate 15 may undergo embossing as well as the optional preheating and loosening more than once. For this purpose, the substrate may be subjected to the same pattern and pressure rolls 20, 30, optional preheating unit 50, and optional loosening means or to further installations of the corresponding means, which may be the same or which may differ from the first installations. The loosening step twists and re-arranges the fibers of the fiber-based substrate, in some cases exposing new fibers to the surface. As a result, carrying out embossing and loosening more than once can produce an end product with fibers imprinted on both the top and sides of a fiber, and imprinted fibers can end up not only at the surface but also in front of or behind other imprinted fibers, and may create a more robustly-patterned material.

[0043] Preferably, the embossing step as well as the optional preheating and loosening is carried out at least once, more preferably at least twice, more preferably at least three times, more preferably at least four times.

[0044] The fiber-based substrate may also be embossed on both sides (opposite surfaces) of the substrate 15, e.g. simultaneously in one embossing step or when subjecting the substrate 15 to multiple embossing steps (including e.g. turning the substrate).

[0045] The fiber-based substrate 15, such as a nonwoven substrate, as used in the present invention is introduced

into the nip 40. In a preferred embodiment, the fibers of the substrate 15 include a polymer, preferably a thermoplastic polymer. More preferably, the thermoplastic polymer is selected from polypropylene and/or polyethylene. Preferably, the fibers of the substrate 15 have diameter of 50 μm or less, more particularly from 1.0 nm to 50 μm , 10 nm to 50 μm , 100 nm to 50 μm , 100 nm to 40 μm , 100 nm to 35 μm , 500 nm to 35 μm , and from 1.0 μm to 25 μm .

5 **[0046]** If the fiber-based substrate 15, such as a nonwoven substrate, includes melt-bonded points, these melt-bonded points can be formed prior to embossing, or the embossing pattern and the bond pattern can be incorporated into the same roll and process. The bond points are typically at least an order of magnitude (i.e. at least by the factor of 10) larger than the much finer micro- and nano-embossed features. Means for forming melt-bonded points are known in the art and can be included in the apparatus of the present invention. For example, such means include thermal calendaring

10 bonding, ultrasonic bonding, and pressure bonding.
[0047] The micro-structures embossed on the fiber-based substrate 15 confer functional benefits such as an elevated contact angle. For example, the contact angle of the treated substrate is increased by at least 5°, in particular by at least 10°, when compared to the untreated substrate. For example, the contact angle of the treated substrate 15 is at least 110°, in particular at least 128°.

15 **[0048]** In a preferred embodiment, the micro-embossed pattern on the fiber-based substrate 15, such as a nonwoven substrate, has a pattern roughness of more than 1.5, more preferably of more than 1.7, more preferably of more than 2.3, more preferably of more than 3.0. Pattern roughness is the roughness ratio of the embossed regions of the fiber surface. Roughness ratio is the ratio between the actual and projected solid surface area ($r=1$ for smooth surface, $r>1$ for rough surface). This is the roughness value used in the Wenzel and Cassie-Baxter wetting equations. Characterization

20 was done using a Keyence laser confocal microscope with a 50 or 100x objective lens, showing the embossed pattern in sufficient resolution. Three or four characteristic fiber regions containing pattern were selected. VK Analyzer software from Keyence was used to automatically identify the 3D surface area and 2D projected area of the selection. The ratio of these two values is the roughness ratio. The average of these selections was used for the pattern roughness value.

25 **[0049]** Preferably, the treated fiber-based substrate 15, such as a nonwoven substrate, has a substrate density of less than 0.12 g/cm³, more preferably less than 0.1 g/cm³, and even more preferably less than 0.09 g/cm³.

[0050] The pattern coverage may be selected as needed for the corresponding application of the substrate 15. Accordingly, low to high pattern coverage can be obtained with the present invention. In a preferred embodiment, the pattern coverage is at least 20%, more preferably at least 40%, more preferably at least 60%, and most preferably at least 70% based on the projected fiber surface area visible from above.

30 **[0051]** Pattern coverage was measured using digital image analysis. An optical microscope with a 20X objective lens was used to acquire images, with resolution sufficient to determine which areas of the visible fiber surface contained embossed patterns. Pattern coverage is defined as the number of pixels identified as containing pattern in an image divided by the total number of pixels identified as containing fiber in the same image. "Pattern" regions were identified using an edge detection method to identify only the high contrast areas of the image corresponding to embossed patterns.

35 "Fiber" regions were identified based on the brightness of the image.
[0052] In another aspect, the present invention relates to a patterning process comprising the step of (a) subjecting a fiber-based substrate 15, preferably a nonwoven substrate, to roll-to-roll (micro-hot) embossing by introducing the substrate into a nip 40 provided by a pattern roll 20 and a pressure roll 30, wherein the pattern roll 20 comprises protrusions or grooves having a diameter being smaller than the diameter of fibers included in the substrate 15. The statements and

40 definitions given with respect to the other aspects of the present invention, when not differing from the following statements and definitions, analogously apply to this aspect of the present invention. In a preferred embodiment, the patterning apparatus according to the present invention is used for carrying out the patterning process.
[0053] Preferably, the patterning process further comprises the step of (a0) preheating the substrate 15 before the step (a). As mentioned with respect to the apparatus, said preheating step can be carried out with a respective preheating unit 50. The substrate 15 may also or alternatively be heated or cooled by the pattern roll 20 and/or the pressure roll 30 or other additional rolls.

45 **[0054]** In a preferred embodiment, the patterning process further comprises the step of (b) loosening the fibers of the substrate 15 after the step (a). As mentioned with respect to the apparatus, said loosening step can be carried out with respective loosening means.

50 **[0055]** Furthermore, the step (a) as well as the optional steps (a0) and (b) may be carried out in the given order at least once, preferably at least twice, more preferably at least three times, more preferably at least four times.

[0056] In one embodiment, the patterning process further comprises the step of forming melt-bonded points before or during the step (a) in the fiber-based substrate 15, such as a nonwoven substrate.

55 **[0057]** Following the processes described herein, the micro- or nano-patterned fiber-based substrate 15 has increased surface roughness resulting in greater hydrophobicity. In other aspects, the micro- or nano-structure could impart additional benefits to the fiber-based substrate 15, including but not limited to changes in friction, adhesion, tactile properties, optical effects, and/or anti-microbial effects.

[0058] In some aspects of the present disclosure, the substrate 15 that is treated is a nonwoven web. Suitable substrates

of the present disclosure can include a nonwoven fabric and laminates of nonwoven fabrics. The substrate 15 can also be a tissue or towel, as described herein, provided the tissue or towel includes a thermoplastic synthetic component. Materials and processes suitable for forming such substrates 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 webs, 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 15 of the present disclosure is a nonwoven fabric.

[0059] 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.

[0060] 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 can be 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.

[0061] In another aspect, the substrate 15 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 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.

[0062] When utilized, 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.

[0063] The substrate 15 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.

[0064] Additionally, the substrate 15 can also be formed from a material that is imparted with texture on one or more surfaces. For instance, in some aspects, the substrate 15 can be formed from a dual-textured spunbond or meltblown material, such as described in U.S. Pat. No. 4,659,609 to Lamers, et al. and U.S. Patent No. 4,833,003 to Win, et al.

[0065] In one particular aspect of the present disclosure, the substrate 15 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 to Boulton. 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.

[0066] Of these nonwoven fabrics, hydroentangled nonwoven webs with staple fibers entangled with thermoplastic fibers is especially suited as the substrate 15. 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 staple 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 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.

[0067] 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.

[0068] The substrate 15 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 15 contains both thermoplastic fibers and non-thermoplastic fibers, the thermoplastic fibers make up from about 10% to about 90%, by weight of the substrate 15. In a particular aspect, the substrate 15 contains between about 10% and about 30%, by weight, thermoplastic fibers.

[0069] Generally, a fiber-based substrate 15, such as a nonwoven substrate, will have a basis weight (BW) in the range of about 10 gsm (grams per square meter) to about 200 gsm, depending on the product application. In other aspects, a fiber-based substrate 15, such as a nonwoven substrate, will have a basis weight in the range between about 33 gsm and about 200 gsm. The actual basis weight can be higher than 200 gsm, but for many applications, the basis weight will be in the 12 gsm to 150 gsm range.

[0070] The materials of the fibers making-up at least a portion of the substrate 15 can essentially be any polymer. Suitable 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); 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); poly(3-methyl-1-pentene); poly(4-methyl-1-pentene); and copolymers and blends thereof. 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, polybutylene terephthalate, polytetramethylene terephthalate, polycyclohexylene-1,4-dimethylene terephthalate, and isophthalate copolymers thereof, as well as blends thereof. These polymers can be used to prepare both substantially continuous fibers and staple fibers, in accordance with the present disclosure.

[0071] Nonwoven fabrics are used extensively in disposable absorbent products, in which the nonwoven is designed to interact with liquids. Tuning of nonwoven wetting properties allows novel benefits in a disposable absorbent product. For example, a liner with controlled zones of relative hydrophobicity and hydrophilicity allows greater control over the distribution of liquid into the absorbent core.

[0072] The present disclosure includes improved personal care products, particularly disposable absorbent articles. Personal care products of the present disclosure include, but are not limited to, feminine hygiene products like sanitary wipes and menses absorbing devices (e.g., sanitary napkins and tampons), infant and child care products such as disposable diapers, absorbent underpants, and training pants, wound dressings such as bandages, incontinent products, products for wiping and absorbing oils and/or organic solvents, and the like.

[0073] Disposable absorbent articles such as the feminine care absorbent product, for example, can include a liquid permeable topsheet, a substantially liquid impermeable backsheet joined to the topsheet, and an absorbent core positioned and held between the topsheet and the backsheet. The topsheet is operatively permeable to the liquids that are intended to be held or stored by the absorbent article, and the backsheet can be substantially impermeable or otherwise operatively impermeable to the intended liquids. The absorbent article can also include an additional layer(s). This additional layer(s) can be a liquid intake layer, liquid wicking layers, liquid distribution layers, transfer layers, barrier layers, and the like, as well as combinations thereof. Disposable absorbent articles and the components thereof can operate to provide a body-facing surface (top surface of the topsheet) and a garment-facing surface (back surface of

the backsheet). As used herein, the "body-facing" or "bodyside" surface refers to the surface of the topsheet that is disposed toward or placed adjacent to the body of the wearer during ordinary use. The "garment-side surface" refers to the backsheet where the back of the surface is disposed away from the wearer's body and adjacent to the garment of the wearer during ordinary use. Suitable absorbent articles are described in more detail in U.S. Patent No. 7,632,258.

5 **[0074]** The fluid permeable topsheet of the present disclosure can be left untreated or can be treated with a superhydrophobic composition that helps to keep fluids from sitting atop the surface that can leave an unpleasant and/or unclean feeling from stains, accumulated debris, or wetness on the surface. The disposable absorbent articles of the present disclosure are particularly adapted to receive fluids having viscoelastic properties, such as menses, mucous, blood products, and feces, among others to reduce stain area, reduce rewet, improve fluid intake, distribution, absorption properties, and decrease leakage.

10 **[0075]** It will be readily apparent to one skilled in the art based on the disclosure that the products and methods described herein can also be used in combination with numerous absorbent articles designed to absorb fluids other than menses such as runny BM, urine, and the like.

15 **[0076]** The absorbent articles of the present disclosure include a fluid permeable topsheet that is preferably a nonwoven, body-facing fibrous sheet material. The present disclosure provides an advantage over topsheets including a thermoplastic film because nonwovens are generally softer, cause less sweating and irritation from sweat, and avoid the plastic feel or rustling that is often associated with plastics and films.

EXAMPLES

20 **[0077]** 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.

Materials and Procedure

25 **[0078]** A 25gsm spunbond nonwoven substrate and a 17gsm spunbond nonwoven substrate with polypropylene fibers roughly 20 microns in diameter, were patterned via roll-to-roll micro-hot embossing with one of three metal tools. The first metal tool includes an array of pins one micron-wide with a pitch of about two microns, the second metal tool includes cylindrical holes 3 microns in diameter, and the third metal tool includes cylindrical holes 6 microns in diameter. All examples were run at a web speed of 2 m/min. The pins formed a pattern of indentations in the nonwoven fibers, and the cylindrical holes patterns formed hemispherical protrusions from the fibers. After embossing, the fabric was loosened by hand by pulling in several directions. Several runs were performed with different pressure roll materials and varying the number of cycles of embossing and loosening. See Table 1 for a description of the examples. Contact angle of purified water was measured using a KRÜSS Mobile Surface Analyzer with a 1 μ L droplet size. Water was purified to a resistance of 18.2M Ω -cm. A droplet is automatically dispensed onto the surface, an image of the droplet is acquired from the side, and Kruss Advance drop shape analysis software is used to measure the contact angle on the left and right sides of the droplet. The reported contact angle is an average of measurements from at least three droplets.

Table 1.

Code	BW (gsm)	Embossing pattern	Embossing steps	Temp (°C)	P (N)	Contact Angle (deg)	Density (g/cc)	Pattern roughness	Pattern Coverage
1 Control	25	--	0	--	--	122.7	0.067	1.06*	0.05*
2 Control	17	--	0	--	--	128.03	0.074	Not tested	Not tested
3	25	1 μm pins	3	91	5800	133.4	0.084	3.76	0.75
4	25	1 μm pins	4	91	6200	134.2	0.114	3.59	0.77
5	25	1 μm pins		92	3600	131.0	0.077	3.37	0.26
6	25	1 μm pins	1	89	4200	129.4	0.075	Not tested	Not tested
7	25	1 μm pins	1	89	8000	131.2	0.100	Not tested	Not tested
8	17	3 μm holes	1	93	9000	123.9	0.143	1.48	0.57
9	17	3 μm holes	3	93	9000	129.0	0.110	1.76	0.71
10	17	6 μm holes	1	93	9000	124.2	0.127	3.03	0.36
11	17	6 μm holes	4	93	9000	129.7	0.116	1.38	0.48

Results and Discussion

[0079] It was discovered that an increased contact angle occurs when three conditions are met from the embossing process. First, fibers are embossed with a pattern that confers a high pattern roughness. Second, the pattern covers a large fraction of the exposed sheet surface, leaving little un-patterned fiber surface. Finally, after embossing the nonwoven sheet remains lofty, retaining a low density.

[0080] For example, increased contact angle samples had a density below 0.12 g/cc, a pattern roughness above 1.5, and a pattern coverage above 20%. For examples with a density less than 0.12 g/cc, the contact angle (in degrees) was described by the expression $121.5 + 6.7 \times (\% \text{Pattern Coverage}) + 2.0 \times (\text{Pattern Roughness})$, with an R2 of 0.9 and a p-value of 0.03. Caliper was measured using a micrometer with 50-mm diameter platen and a pressure of 0.05psi. Density was calculated from caliper and nominal basis weight, and bulk inverse of density.

[0081] Surface roughness was defined as the 3D surface area / 2D projected area. Surfaces were characterized using Keyence laser confocal microscope, using a 50x or 100x objective lens sufficient to show the embossed patterns in detail. Three or four fiber regions containing patterns were selected and the 3D surface area, 2D projected area, and the ratio of the two were calculated by the VK Analyzer software from Keyence. Values in the table are average values.

[0082] Pattern coverage was identified using image analysis. Coverage = # of pixels identified as containing "pattern" / # of pixels identified as containing "fiber." Images of the patterned side of embossed nonwovens were acquired from a Keyence laser confocal/optical microscope with a 20x objective lens. Images had sufficient detail to clearly identify patterned versus un-patterned regions of the fibers. Images were acquired from the normal direction relative to the surface. Roughly, the top three fiber layers are clear in the images, while fibers at increasing depth are less clearly captured.

[0083] "Pattern" regions were identified using a "convolve" edge detection method in ImageJ, an open source detection software program developed by NIH (version 1.50b), to identify high contrast areas of the image. "Fiber" regions were identified using an intensity threshold combined with the "pattern" high contrast areas (to make sure all "pattern" pixels were also counted as "fiber" pixels).

[0084] It was determined that the soft, rubbery ELASTOSIL silicone (Wacker Chemie; Elastosil M4601 A+B; Part A : Part B; 9:1) surface did not prevent the crushing of the web (see Fig. 3). Conversely, the felt (uncarbonized wool felt, 4 mm material thickness, 0.375 g/cm³) pressure roll coating was effective in preventing the crushing of the web (see Fig. 4). Contact angle increased with each embossing cycle (other than the first) to a maximum of 134.2 degrees (see Fig. 2) based on measurable material attributes. After embossing/loosening cycles, the fiber maintained an open structure without fusing fibers or significantly stiffening the sheet.

[0085] Dynamic contact angles were measured for all substrates on glass slides to better understand the role of pattern size and the number of embossing cycles. For any hydrophobic surface, the sessile contact angle is generally considered limited for understanding how mobile droplets are expected to be when introduced to the surface.

Claims

1. A process for preparing surfaces that exhibit enhanced properties without the addition of a chemical treatment, comprising the step of

(a) subjecting a fiber-based substrate to roll-to-roll embossing by introducing the substrate into a nip provided by a pattern roll and a pressure roll, wherein the pattern roll comprises protrusions or grooves having a diameter being smaller than the diameter of fibers included in the substrate.

2. The process according to claim 1, wherein the fiber-based substrate is a nonwoven substrate.

3. The process according to claim 1 or 2, further comprising the step of (a0) preheating the substrate before the step (a).

4. The process according to any one of claims 1 to 3, further comprising the step of (b) loosening the fibers of the substrate after the step (a).

5. The process according to any one of claims 1 to 4, wherein the steps are conducted in the given order at least two times.

6. The process according to any one of claims 1 to 5, further comprising the step of forming melt-bonded points before or during step (a).

EP 3 594 396 A1

7. The process according to any one of claims 1 to 6, wherein the pressure roll is covered with or made of a felt material.
8. The process according to any one of claims 1 to 7, wherein the pattern and/or pressure roll is/are heated for heating the substrate during embossing.
- 5 9. The process according to any one of claims 1 to 8, wherein a temperature of from 30 to 350 °C is applied to the substrate.
- 10 10. The process according to any one of claims 1 to 9, wherein a pressure of from 10 to 100000 N is applied to the substrate.
11. The process according to any one of claims 1 to 10, wherein the diameter of the protrusions or grooves are each 20 μm or less.
- 15 12. The process according to any one of claims 1 to 11, wherein the fibers comprise a polymer, particularly wherein the polymer is selected from polypropylene and/or polyethylene.
13. The process according to any one of claims 1 to 12, wherein the micro-embossed pattern on the substrate has a pattern roughness of more than 1.5.
- 20 14. The process according to any one of claims 1 to 13, wherein the treated substrate has a substrate density of less than 0.12 g/cm³.
- 25 15. A patterning apparatus for the process according to any one of claims 1 to 14, comprising a pattern roll and a pressure roll forming a nip, wherein the pattern roll comprises protrusions or grooves having a diameter being smaller than a diameter of fibers included in a fiber-based substrate to be introduced into the nip for roll-to-roll embossing.
- 30
- 35
- 40
- 45
- 50
- 55

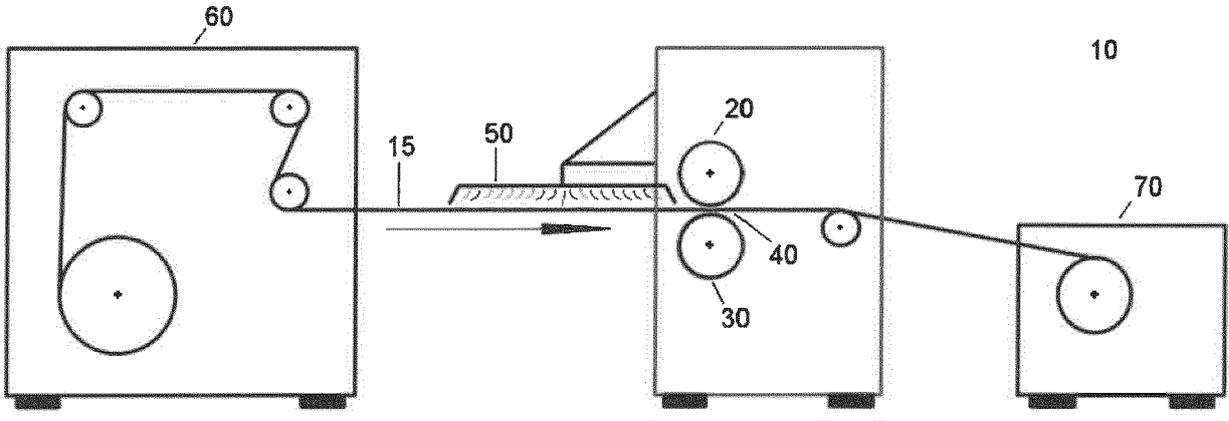


FIG. 1

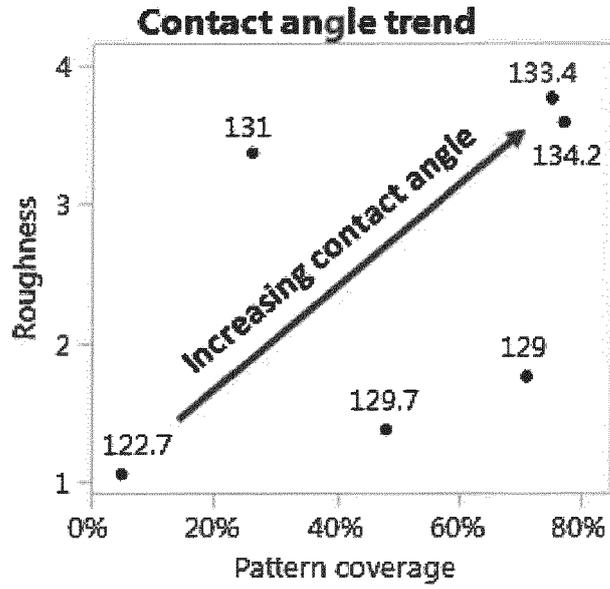


FIG. 2

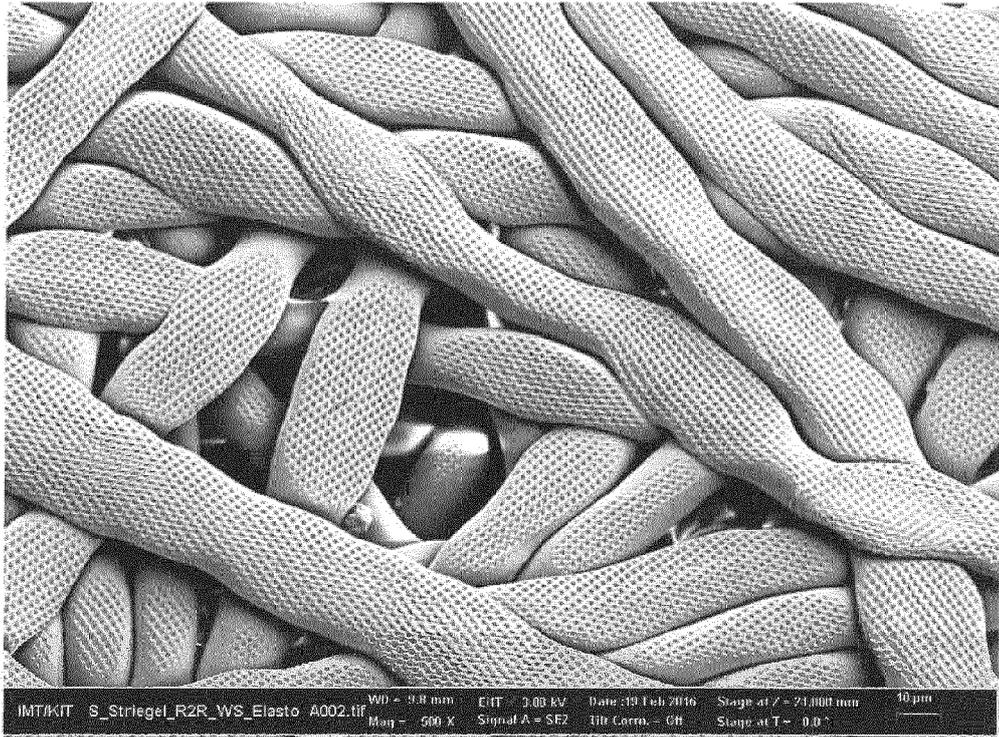


FIG. 3

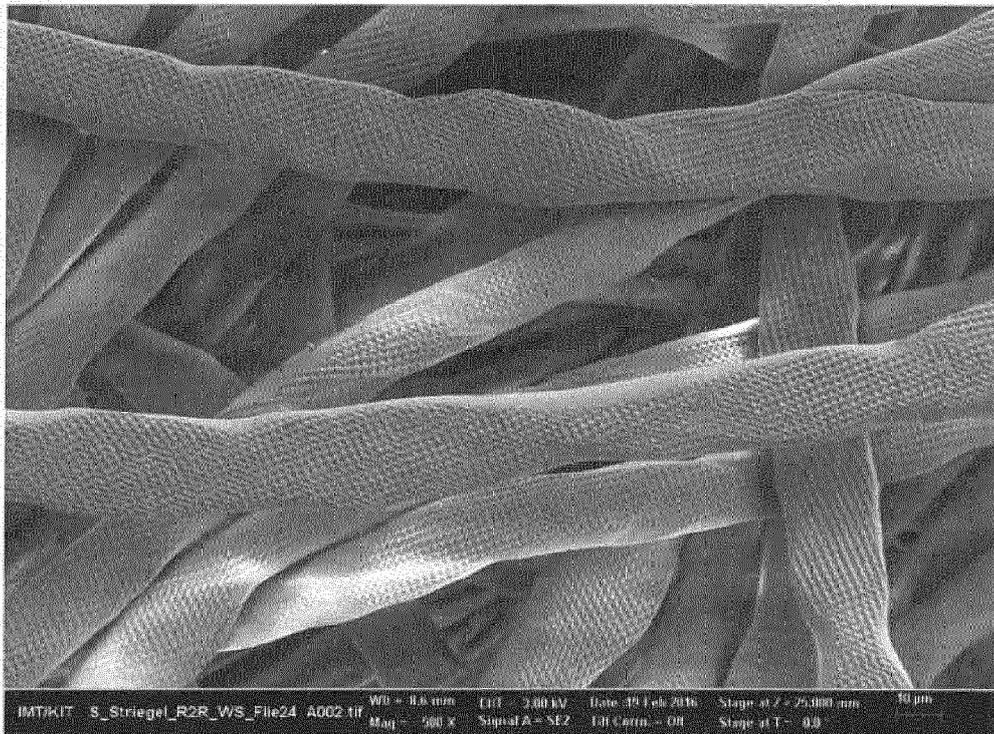


FIG. 4

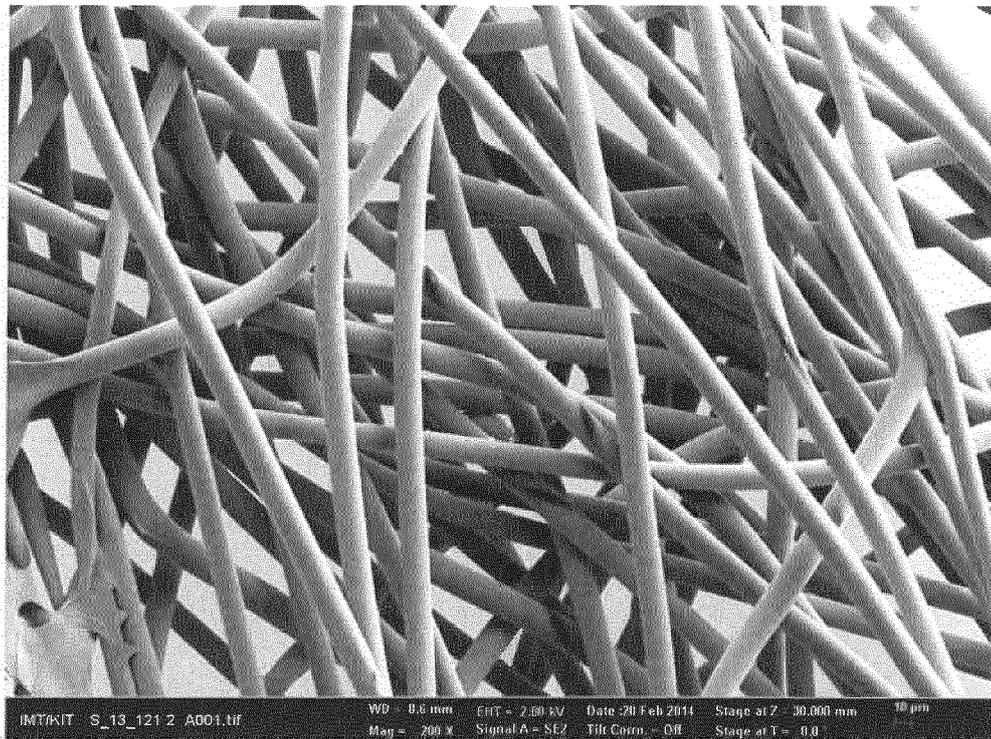


FIG. 5



EUROPEAN SEARCH REPORT

Application Number
EP 18 18 2690

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	JP 2014 025305 A (NITTOC CONSTRUCTION) 6 February 2014 (2014-02-06) * paragraphs 23,43 - page 2 *	1,7-10, 15	INV. D06C23/04
X	KR 2017 0061550 A (HAN CHEOR UN [KR]) 5 June 2017 (2017-06-05) * paragraphs [0018], [0049]; figures 1,2 *	15	
Y	US 2011/287203 A1 (VICTOR JARED J [CA] ET AL) 24 November 2011 (2011-11-24) * paragraphs [0001], [0007]; claim 1; figure 1 *	1,2, 11-13	
X	US 2011/221094 A1 (GROSS SARAH BETH [US] ET AL) 15 September 2011 (2011-09-15) * paragraphs [0033], [0067], [0068]; figure 3 *	15 1,2, 11-13	
T	EP 3 235 946 A1 (SEIREN CO LTD [JP]) 25 October 2017 (2017-10-25)	1	
X	GB 1 523 727 A (UNITEX LTD) 6 September 1978 (1978-09-06) * page 1, line 33 - line 38; figure 1 * * page 1, line 67 - line 71 *	15 1	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (IPC) D06C B29C A61F
Place of search Munich		Date of completion of the search 7 January 2019	Examiner Uhlig, Robert
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.02 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 18 18 2690

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-01-2019

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2014025305 A	06-02-2014	NONE	

KR 20170061550 A	05-06-2017	NONE	

US 2011287203 A1	24-11-2011	CA 2800381 A1	01-12-2011
		EP 2576171 A1	10-04-2013
		US 2011287203 A1	24-11-2011
		US 2013256944 A1	03-10-2013
		WO 2011147757 A1	01-12-2011

US 2011221094 A1	15-09-2011	NONE	

EP 3235946 A1	25-10-2017	CN 107109784 A	29-08-2017
		EP 3235946 A1	25-10-2017
		JP 6145584 B2	14-06-2017
		JP WO2016098324 A1	15-06-2017
		US 2017342658 A1	30-11-2017
		WO 2016098324 A1	23-06-2016

GB 1523727 A	06-09-1978	BE 835431 A	01-03-1976
		GB 1523727 A	06-09-1978

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 4340563 A, Appel **[0017]**
- US 3692618 A, Dorschner **[0017]**
- US 3802817 A, Matsuki **[0017]**
- US 3338992 A **[0017]**
- US 3341394 A, Kinney **[0017]**
- US 3502763 A, Hartman **[0017]**
- US 3542615 A, Dobo **[0017]**
- US 5382400 A, Pike **[0017] [0019]**
- US 6200669 B, Marmon **[0017] [0062]**
- US 5759926 A, Pike **[0017]**
- US 5108820 A, Kaneko **[0019]**
- US 5336552 A, Strack **[0019]**
- US 3855046 A, Hansen **[0059]**
- US 5620779 A, Levy **[0059]**
- US 5962112 A, Haynes **[0059]**
- US 6093665 A, Sayovitz **[0059]**
- US 428267 A, Romano **[0059]**
- US 390708 A, Brown **[0059]**
- US 5284703 A, Everhart **[0060] [0063] [0065]**
- US 6103061 A, Anderson **[0060]**
- US 6197404 B, Varona **[0060]**
- US 5935883 A, Pike **[0062]**
- US 4100324 A, Anderson **[0063]**
- US 5350624 A, Georger **[0063]**
- US 4659609 A, Lamers **[0064]**
- US 4833003 A, Win **[0064]**
- US 3494821 A, Evans **[0065]**
- US 4144370 A, Boulton **[0065]**
- US 6315864 B, Anderson **[0065]**
- US 7632258 B **[0073]**