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(54) **NONWOVEN CELLULOSE FIBER FABRIC WITH INCREASED OIL ABSORBING CAPABILITY**

(57) It is described a nonwoven cellulose fiber fabric (102) directly manufactured from a lyocell spinning solution (104). The fabric (102) comprises a network of substantially endless fibers (108), wherein the fabric (102) exhibits an oil absorbing capability of at least 1900 mass

percent. It is further described a method and a device for manufacturing such a fabric (102), a product or composite comprising such a fabric, and various use applications for such a fabric (102).

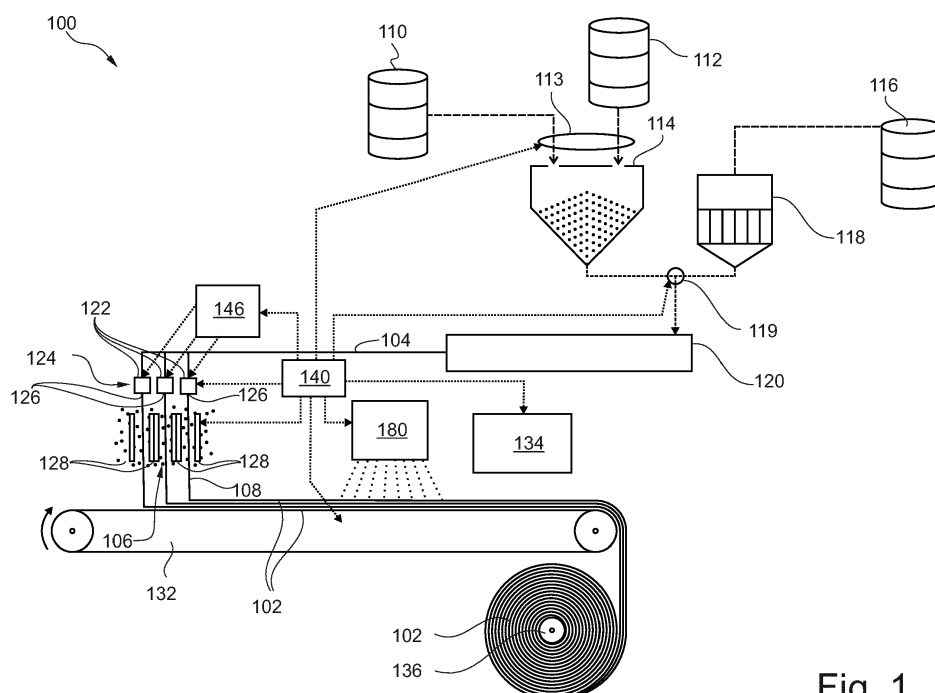


Fig. 1

Description

Field of invention

[0001] The invention relates to a nonwoven cellulose fiber fabric, a method of manufacturing a nonwoven cellulose fiber fabric, a device for manufacturing a nonwoven cellulose fiber fabric, a product or composite and a method of use for such a fabric.

Background of the invention

[0002] Lyocell technology relates to the direct dissolution of cellulose wood pulp or other cellulose-based feedstock in a polar solvent (for example n-methyl morpholine n-oxide, which may also be denoted as "amine oxide" or "AO") to produce a viscous highly shear-thinning solution which can be transformed into a range of useful cellulose-based materials. Commercially, the technology is used to produce a family of cellulose staple fibers (commercially available from Lenzing AG, Lenzing, Austria under the trademark TENCEL®) which are widely used in the textile industry. Other cellulose products from lyocell technology have also been used.

[0003] Cellulose staple fibers have long been used as a component for conversion to nonwoven webs. However, adaption of lyocell technology to produce nonwoven webs directly would access properties and performance not possible for current cellulose web products. This could be considered as the cellulosic version of the melt-blow and spunbond technologies widely used in the synthetic fiber industry, although it is not possible to directly adapt synthetic polymer technology to lyocell due to important technical differences.

[0004] Much research has been carried out to develop technology to directly form cellulose webs from lyocell solutions (*inter alia*, WO 98/26122, WO 99/47733, WO 98/07911, US 6,197,230, WO 99/64649, WO 05/106085, EP 1 358 369, EP 2 013 390). Further art is disclosed in WO 07/124521 A1 and WO 07/124522 A1.

[0005] It is commonly known that cellulose material is rather hydrophilic than oleophilic. In many applications this is an appreciated property of cellulose containing products. However, there are also many (potential) applications for which an oleophilic respectively a pronounced oil absorbing capability would be welcome. This might improve the usability of cellulose material for products for known applications and might make cellulose products applicable for new, so far unknown applications.

Summary of the Invention

[0006] There may be a need for improving the oil absorbing capability of cellulose material and in particular nonwoven cellulose fiber fabrics.

[0007] This need may be met by the subject matter according to the independent claims. Advantageous embodiments of the present invention are described by the

dependent claims.

[0008] According to a first aspect of the invention there is provided a nonwoven cellulose fiber fabric, which is in particular directly manufactured from a lyocell spinning solution. The provided fabric comprises a network of substantially endless fibers. The fabric exhibits an oil absorbing capability of at least 1900 mass percent.

[0009] The described fabric is based on the idea that the nonwoven fiber fabric or fiber web can be considered as to represent a structure comprising a plurality of cavities or voids formed in between various neighboring fibers. In the original non soaked state of the fabric these voids are filled with air. When the fabric absorbs oil, the voids get filled with (liquid, semifluid or pasty) oil or grease particles having a size which at least approximately fits to the size of the respective void.

[0010] In this exemplary physical picture the plurality of voids within the fabric can be seen as to represent a plurality of capillary cages within which the oil can be received. In this respect it is pointed out that when being loaded / unloaded with a fluid a capillary cage has the effect of a capillary hysteresis. This means that compared to the steady state of a liquid loaded cage for entering the liquid into the cage there is needed a higher pressure (in case the contact angle is larger than 90°) or a higher capillary suction force (in case the contact angle is smaller than 90°). Regarding the stability of oil absorption it is essential how stable the liquid oil particles rest within their voids. Specifically, the more stable the oil particles are accommodated within the voids the larger is the oil absorbing capability. The stability of the "accommodation" depends on the capillary conditions, in particular (a) on the size of the voids respectively the cavities and (b) on the contact angle which in accordance with basic physical principle depends on the surface properties of the involved materials. Further, it should be clear that the extent of the oil absorbing capability depends on the density of (appropriately sized) voids within the fabric.

[0011] It has been discovered that a parameter for adapting the size of the capillary cages is the so called titer value, which is indicative for the diameter of the fibers. In case of a varying titer value within the fiber network respectively the fabric, a large number of capillary cages having different sizes can be offered for an absorption of different sized oil particles. Descriptively speaking, certain adjustments in the fiber manufacturing process may translate into a variation of the diameter distribution of the fibers in the fabric as a whole.

[0012] Already at this point it is mentioned that not only the size but also the geometry of the voids is a parameter for the affinity of oil particles to be absorbed within the respective cavity. Further details in this respect are presented below with regard to a merging factor, which is also a very important parameter for the oil absorption capability.

[0013] For determining oil absorbing capability (or liquid absorptive capacity) of a fabric, an analysis concerning evaluation of oil and fatty liquids absorption based on

Edana standard NWSP 010.4.R0(15) can be carried out using engine oil. For the analysis, a fabric sample of a size of 10 cm x 10 cm is used. The weight of the sample is determined, and the sample is diagonally connected to a ruler by means of strings. The sample is then dropped into a container filled with oil. The time required for wetting the fabric with oil is measured. Subsequently, the fabric is immersed in the oil for 120 seconds. The fabric is then lifted out of the oil by raising the ruler. Thereafter, oil is allowed to drip off from the fabric for 30 seconds. The weight of the oil wetted fabric is determined, and the oil absorbing capability is calculated by subtracting the original weight of the fabric sample from the oil wetted sample weight and calculating the mass% of the so received up-taken oil weight in relation to the dry weight of the fabric sample.

[0014] In connection with experimental studies with emulsions, i.e. a mixture of oily and aqueous components, the suction speed respectively a wicking speed of the aqueous components into the capillary voids yields an entraining respectively a dragging of the oily components together with the aqueous components. Therefore, for applications with such emulsions this dragging effect may also be taken into account. Specifically, not only the capillary effects between the described fabric structure and the oil respectively the oily components but also the capillary effects between the described network structure of the fabric and the aqueous components should be taken into account when selecting an appropriate design for the network structure of the fabric. Descriptively speaking, the aqueous components may push or drag the oily components through an oleophobic barrier between the described fabric and the oil particles and yield an improved oil absorption capability. Due to this liquid handling properties this effect may be in particular of advantage for face masks which can have a comparatively low base weight.

[0015] Experimental studies have further revealed that the described fabric exhibits a high degree of regularity respectively orderliness in its spatial structure. This property makes it easier to adapt the size and/or the shape of the voids by an appropriate selection of process parameter values. Without being bound to a specific physical theory, the physical reason for a high degree of regularity or even crystallinity of the described fabric can be seen in the pronounced polarity of the lyocell fibers which is based on three hydroxyl groups for each monomer unit. Since glucose molecules arrange themselves in chains comprising several hundreds of such molecules practically without any contamination by means of other similar glucose molecules when manufacturing the described fabric the mentioned high degree of regularity is obtained. The hydroxyl groups form an ordered network of hydrogen bridges which may allow to understand the following properties of the described fabric: (a) High degree of crystallinity, (b) extremely high hydrophilic behavior, (b) high water retaining capability, (c) thermosetting properties (no melting point) (s) coagulation capability

from an aqueous N-methyl-morpholine (NMMO) solvent, and (e) moisture dependent inherent antistatic properties.

[0016] It is pointed out that by controlling the process parameters of the lyocell spinning solution manufacturing procedure in an appropriate manner the described oil absorbing capability may already be achieved without any additional (further) treatment of the fabric, in particular without applying and/or using any additional chemical substances. This may provide the advantage that a final product comprising the described fabric will automatically be free from any remainders of such chemical substances.

[0017] In the context of this application, the term "non-woven cellulose fiber fabric" (which may also be denoted as nonwoven cellulose filament fabric) may particularly denote a fabric or web composed of a plurality of substantially endless fibers. The term "substantially endless fibers" has in particular the meaning of filament fibers having a significantly longer length than conventional staple fibers. In an alternative formulation, the term "substantially endless fibers" may in particular have the meaning of a web formed of filament fibers having a significantly smaller amount of fiber ends per volume than conventional staple fibers. In particular, endless fibers of a fabric according to an exemplary embodiment of the invention may have an amount of fiber ends per volume of less than 10,000 ends/cm³, in particular less than 5,000 ends/cm³. For instance, when staple fibers are used as a substitute for cotton, they may have a length of 38 mm (corresponding to a typical natural length of cotton fibers). In contrast to this, substantially endless fibers of the non-woven cellulose fiber fabric may have a length of at least 200 mm, in particular at least 1000 mm. However, a person skilled in the art will be aware of the fact that even endless cellulose fibers may have interruptions, which may be formed by processes during and/or after fiber formation. As a consequence, a nonwoven cellulose fiber fabric made of substantially endless cellulose fibers has a significantly lower number of fibers per mass compared to nonwoven fabric made from staple fibers of the same denier. A nonwoven cellulose fiber fabric may be manufactured by spinning a plurality of fibers and by attenuating and stretching the latter towards a preferably moving fiber support unit. Thereby, a three-dimensional network or web of cellulose fibers is formed, constituting the non-woven cellulose fiber fabric. The fabric may be made of cellulose as main or only constituent.

[0018] In the context of this application, the term "lyocell spinning solution" may particularly denote a solvent (for example a polar solution of a material such as N-methyl-morpholine, NMMO, "amine oxide" or "AO") in which cellulose (for instance wood pulp or other cellulose-based feedstock) is dissolved. The lyocell spinning solution is a solution rather than a melt. Cellulose filaments may be generated from the lyocell spinning solution by reducing the concentration of the solvent, for instance by contacting said filaments with water. The proc-

ess of initial generation of cellulose fibers from a lyocell spinning solution can be described as coagulation.

[0019] In the context of this application, the term "gas flow" may particularly denote a flow of gas such as air substantially parallel to the moving direction of the cellulose fiber or its preform (i.e. lyocell spinning solution) while and/or after the lyocell spinning solution leaves or has left the spinneret.

[0020] In the context of this application, the term "coagulation fluid" may particularly denote a non-solvent fluid (i.e. a gas and/or a liquid, optionally including solid particles) which has the capability of diluting the lyocell spinning solution and exchanging with the solvent to such an extent that the cellulose fibers are formed from the lyocell filaments. For instance, such a coagulation fluid may be water mist.

[0021] In the context of this application, the term "process parameters" may particularly denote all physical parameters and/or chemical parameters and/or device parameters of substances and/or device components used for manufacturing nonwoven cellulose fiber fabric which may have an impact on the properties of the fibers and/or the fabric, in particular on fiber diameter and/or fiber diameter distribution. Such process parameters may be adjustable automatically by a control unit and/or manually by a user to thereby tune or adjust the properties of the fibers of the nonwoven cellulose fiber fabric. Physical parameters which may have an impact on the properties of the fibers (in particular on their diameter or diameter distribution) may be temperature, pressure and/or density of the various media involved in the process (such as the lyocell spinning solution, the coagulation fluid, the gas flow, etc.). Chemical parameters may be concentration, amount, pH value of involved media (such as the lyocell spinning solution, the coagulation fluid, etc.). Device parameters may be size of and/or distances between orifices, distance between orifices and fiber support unit, speed of transportation of fiber support unit, the provision of one or more optional *in situ* post processing units, the gas flow, etc.

[0022] The term "fibers" may particularly denote elongated pieces of a material comprising cellulose, for instance roughly round or non-regularly formed in cross-section, optionally twisted with other fibers. Fibers may have an aspect ratio which is larger than 10, particularly larger than 100, more particularly larger than 1000. The aspect ratio is the ratio between the length of the fiber and a diameter of the fiber. Fibers may form networks by being interconnected by merging (so that an integral multi-fiber structure is formed) or by friction (so that the fibers remain separate but are weakly mechanically coupled by a friction force exerted when mutually moving the fibers being in physical contact with one another). Fibers may have a substantially cylindrical form which may however be straight, bent, kinked, or curved. Fibers may consist of a single homogenous material (i.e. cellulose). However, the fibers may also comprise one or more additives. Liquid materials such as water or oil may be ac-

cumulated between the fibers.

[0023] According to an embodiment of the invention the fabric comprises a mass per unit area which is smaller than 150 gram per square meter, in particular smaller than 100 gram per square meter, further in particular smaller than 50 gram per square meter and even more in particular smaller than 20 gram per square meter.

[0024] Improving the oil absorption capability for fabrics having a small mass per unit area, these fabrics may have the advantage that they can be used for a variety of applications, which require for instance a thin wipe.

[0025] It is mentioned that the term "mass per unit area" is often also denominated basis weight.

[0026] According to a further embodiment of the invention the network exhibits a merging factor of the fibers, which is in a range between 0,1% and 100%, in particular in a range between 0,5% and 10%.

[0027] For determining the merging factor (which may also be denoted as area merging factor) of a fabric, the following determination process may be carried out: A square sample of the fabric is optically analyzed. A circle, which has a diameter which has to stay fully inside the square sample, is drawn around each merging position (in particular merging point, merging pad and/or merging line) of fibers crossing at least one of the diagonals of the square sample. The size of the circle is determined so that the circle encompasses the merging area between the merged fibers. An arithmetic average of the values of the diameter of the determined circles is calculated. The merging factor is calculated as ratio between the averaged diameter value and the diagonal length of the square sample, and may be given in percent.

[0028] A merging factor of zero or 0% corresponds to a fabric without any merging points, i.e. completely separate fibers interacting with one another only by inter-fiber hydrogen bonding or friction. A merging factor of one or 100% describes a fabric which is constituted by completely integral fibers forming a continuous structure such as a film. By adjusting the merging factor, also the physical properties (in particular the mechanical stability) of the corresponding fabric may be adjusted.

[0029] By controlling the merging factor several properties of the resulting fabric can be adjusted. In the context with the oil absorbing capability in particular the cavities between the fibers respectively the filaments can be controlled. In combination with the fiber diameter variation, tailor made fabric structures especially for high oil or grease uptake can be achieved.

[0030] In an embodiment, the merging positions (of the merging points) are asymmetrically and/or anisotropically distributed throughout the fabric. This means that the merging factor, the density of merging points or any other parameter indicative of a degree of a local occurrence of merging between fibers may be different for different volume sections of the fabric. For instance, a fabric composed of two layers may be composed of one layer having a larger merging factor than another layer having a smaller merging factor. The merging factor of a respective lay-

er may be adjusted by an adjustment or a process control of the formation of this layer independently or differently of an adjustment or process control of the formation of the other layer.

[0031] According to a further embodiment of the invention at least some individual fibers are twisted with each other and/or at least one other fiber structure is twisted with another fiber structure. This may (further) improve the mechanical stability of the described fabric.

[0032] In the context of this document a "fiber structure" may be any fiber arrangement comprising at least two fibers. Thereby, the fibers may be individual fibers that touch each other at least partially. Alternatively or in combination, a fiber structure may also be a structure comprising at least two fibers which are integrally connected at at least one merging position.

[0033] According to a further embodiment of the invention the fabric exhibits an oil absorbing capability of at least 2100 mass percent, in particular of at least 2300 mass percent, and more in particular of at least 2500 mass percent.

[0034] It is mentioned that with appropriate process parameter values for manufacturing the described fabric, which due to its cellulose material intrinsically exhibits a very small oil absorbing capability, an oil absorbing ability can be achieved which is in the same order as the oil absorption capability of polyethylene terephthalate (PET), which from its nature is a highly oleophilic material. Further, the described oil absorbing capability is even larger than the oil absorbing capability of certain tested polypropylene (PP) fabrics.

[0035] According to a further embodiment of the invention different ones of the fibers are located at least partially in different distinguishable layers. In this context "distinguishable" may mean in particular that the fabric shows a visible separation or interface region in between the layers at least within an image captured e.g. by means of an electron microscope.

[0036] Descriptively speaking, the described fabric exhibits a multilayer structure with at least two network layers formed over each other. By controlling the process parameters in such a manner that the various different network layers have qualitatively and/or quantitatively different functionalities the physical and/or chemical properties of the entire fabric can be tailored in a specific manner to(wards) many specific applications. This may significantly widen the field of technical applicability of the described fabric.

[0037] An at least three layer fabric may be used for instance for a wipe, wherein an inner layer can be preferably soaked with a liquid, in particular an oily liquid, which during use is released in a controlled manner through at least one of the outer layers. Thereby, the different functional properties of the respective layers can be adjusted for instance by choosing an appropriate range of fiber diameters.

[0038] It is mentioned that there is no principal limitation with regard to the maximum number of stacked net-

work layers. Depending on the specific applications multilayer fabrics can be produced which consist of 2 to 4 or even more, e.g. 5 to 20, stacked network layers.

[0039] Compared to known multilayer fabrics the inter-layer merging positions or inter-layer merging points allow for a mutual attachment between the two layers without using any additional adhesion material, which by nature would include a certain penetration into the interior of at least one of the two network layers. Further, a mutual attachment does not rely on any penetration of fibers of one type into the layer being assigned to the other type of fibers. As a consequence, when tearing apart the two layers, which may be desired in certain applications, there will be only a minimum amount of fiber breaks and the former adhered surfaces of the layers will be substantially free of fringing. Further, a desired tearing apart will only cause minimum linting.

[0040] Due to the matter of fact that there is no need for additional adhesion material for a mutual attachment of the two layers the fabric can be realized in an environmentally compatible manner. Specifically, the described multilayer fabric can be used for a product being completely biodegradable. Further, an absence of any additional adhesion material such as a binder between neighboring layers may provide the advantage that liquid can spread through the respective layer interface without any hindrance.

[0041] According to a further embodiment of the invention the fabric comprises at least one of the following features:

- (a) fibers of different layers are integrally connected at at least one inter layer merging position between the layers;
- (b) different ones of the fibers being located at least partially in different layers differ concerning fiber diameter, in particular differ concerning an averaged fiber diameter;
- (c) fibers of different layers have the same fiber diameter, in particular have substantially the same averaged fiber diameter;
- (d) fibers networks of different layers provide different functionality, wherein the different functionality in particular comprises at least one of the group consisting of different wicking, different anisotropic behavior, different liquid absorbing capability, different cleanability, different optical properties, different roughness, different smoothness, and different mechanical properties.

[0042] Inter layer merging positions as described above under item (a) may be generated by serially aligning two (or more) jets with orifices through which lyocell spinning solution is extruded for coagulation and fiber formation. When such an arrangement is combined with a moving fiber support unit (such as a conveyor belt with a fiber accommodation surface), a first layer of fibers is formed on the fiber support unit by the first jet, and the

second jet forms a second layer of fibers on top of the first layer when the moving fiber support unit reaches the position of the second jet. The process parameters of this method may be adjusted so that merging points are formed between the first layer and the second layer.

[0043] In the context of the present application, the term "merging" may particularly denote an interconnection of different fibers at the respective merging point which results in the formation of one integrally connected fiber structure composed of the previously two separate fibers which previously related to the different layers. Interconnected fibers may strongly adhere to one another at a merging point. In particular, fibers of the second layer under formation being not yet fully cured or solidified by coagulation may for example still have exterior skin or surface regions which are still in the liquid lyocell solution phase and not yet in the fully cured solid state. When such pre-fiber structures come into contact with one another and fully cure into the solid fiber state thereafter, this may result in the formation of two merged fibers at an interface between different layers. The higher the number of merging points, the higher is the stability of the interconnection between the layers of the fabric. Thus, controlling merging allows to control rigidity of the connection between the layers of the fabric. Merging can be controlled, for example, by adjusting the degree of curing or coagulation before pre-fiber structures of a respective layer reach the fiber support plate on an underlying layer of fibers or pre-fiber structures. By merging fibers of different layers at an interface there between, undesired separation of the layers may be prevented. In the absence of merging points between the layers, peeling off one layer from the other layer of fibers may be made possible.

[0044] When different layers of the fabric are formed of fibers having different (average) diameters as described above under item (b), the mechanical properties of the different layers may be adjusted separately and differently. For example, one of the layers may be provided with a stiff character by using fibers having a relatively large diameter, whereas the other layer may be provided with a smooth or elastic character (for example by using fibers having a relatively low diameter). For instance, a wipe can be manufactured having a rougher surface for cleaning by mechanically removing dirt and having a smoother surface for wiping, i.e. being configured for absorbing water or the like from a surface to be cleaned.

[0045] If fibers of different layers have the same (average) diameter as described above under item (c), adjacent layers may have similar or identical physical properties. They may be interconnected strongly or weakly at merging points in between. The number of such merging points per interface area may define the coupling strength between adjacent layers. With a small coupling strength, the layers may be easily separated by a user. With a high coupling strength, the layers may remain permanently attached to one another.

[0046] According to a further embodiment of the invention the fiber networks in different layers have different merging factors. This may contribute to an increased mechanical stability of the described fabric.

5 **[0047]** Specifically, by controlling the merging factor along a height- or z-direction being perpendicular to the planes of the layers, a certain pre-tension can be achieved when the endless fibers touch down onto a fiber support unit collecting the fibers during the manufacturing process of the described fabric. Thereby, a height dependent distribution of different merging factors may allow to build up a "force absorbing spring system" which yields the high mechanical stability and effectively prevents a collapse of capillary cavities or voids formed within the described fabric upon the pressure of adhesion forces when oil particles are embedded within the fabric.

10 **[0048]** According to a further embodiment of the invention the fibers have a copper content of less than 5 ppm and/or have a nickel content of less than 2 ppm. The ppm values mentioned in this application all relate to mass (rather than to volume). Apart from this, the heavy metal contamination of the fibers or the fabric may be not more than 10 ppm for each individual heavy metal element. Due to the use of a lyocell spinning solution as a basis for the formation of the endless fiber-based fabric (in particular when involving a solvent such as N-methyl-morpholine, NMMO), the contamination of the fabric with heavy metals such as copper or nickel (which may cause allergic reactions of a user) may be kept extremely small.

15 **[0049]** According to a further aspect of the invention there is provided a method of manufacturing nonwoven cellulose fiber fabric, in particular a fabric as described above, directly from a lyocell spinning solution. The provided method comprises (a) extruding the lyocell spinning solution through an jet with orifices supported by a gas flow into a coagulation fluid atmosphere to thereby form substantially endless fibers; (b) collecting the fibers on a fiber support unit to thereby form the fabric; (c) adjusting process parameters of the manufacturing process so that the fabric exhibits an oil absorbing capability of at least 1900 mass percent.

20 **[0050]** The provided method is based on the idea that a plurality of cavities or voids can be formed in between various neighboring fibers. By selecting appropriate process parameters these voids can be dimensioned properly in size and/or shape. In an original non soaked state of the fabric these voids are filled with air. When the fabric absorbs oil, the voids get filled with (liquid, semi-fluid or pasty) oil or grease particles having a size which at least approximately fits to the size of the respective void.

25 **[0051]** In the context of this document a "jet with orifices" (which may for instance be denoted as an "arrangement of orifices") may be any structure comprising an arrangement of orifices which are linearly arranged.

30 **[0052]** According to an embodiment of the invention adjusting the process parameters comprises at least one of the following features:

(a) forming at least part of the merging position after the lyocell spinning solution has left the orifices and before the lyocell spinning solution has reached the fiber support unit by triggering an interaction between lyocell spinning solution extruded through different ones of the orifices;

(b) forming at least part of the merging positions after the lyocell spinning solution has reached the fiber support unit by triggering coagulation of at least part of the fibers when laying on the fiber support unit;

(c) serially arranging multiple jets with orifices along a movable fiber support unit, depositing a first layer of fibers on the fiber support unit, and depositing a second layer of fibers on the first layer before coagulation of at least part of the fibers at an interface between the layers has been completed.

[0053] Forming at least part of the merging positions after the lyocell spinning solution has left the orifices and before the lyocell spinning solution has reached the fiber support unit as described above under item (a) may be achieved for example by triggering an interaction between strands of lyocell spinning solution extruded through different ones of the orifices while being accelerated downwardly. For example, the gas flow may be adjusted in terms of velocity and direction so that different strands or filaments of the (not yet fully coagulated) spinning solution are forced to get into interaction with one another in a lateral direction before reaching the fiber support unit. It is also possible that the gas flow is operated to be close or in the regime of turbulent flow so as to promote a mutual interaction between the various preforms of the fibers. Therefore, the individual preforms of the fibers may be brought in contact with one another prior to coagulation, thereby forming merging positions.

[0054] Forming at least a part of the merging positions after the lyocell spinning solution has reached the fiber support unit as described above under item (b) may be achieved by intentionally delaying the process of coagulation. This delay may be adjusted by a corresponding operation of a coagulation unit, in particular by correspondingly adjusting the properties and the position of supply of the coagulation fluid. More specifically, the process of coagulation may be delayed until the spinning solution has reached the fiber support plate. In such an embodiment, the preforms of the fibers, still prior to coagulation, reach the fiber support unit and thereby get into contact with other preforms of the fiber, also still prior to coagulation. Spinning solution of different strands or preforms may thereby be forced to flow into contact with one another, and only thereafter coagulation may be triggered or completed. Thus, coagulation following initial contact between different preforms of fibers being still in the non-coagulated state is an efficient measure of forming merging positions.

[0055] Serially arranging multiple jets with orifices along a movable fiber support unit and the following steps as described above under item (c) may also contribute

that an appropriate oil absorbing capability is achieved. Thereby, for each layer to be formed, the process parameters of operating the corresponding jets with orifices may be adjusted so as to obtain a layer specific coagulation behavior. Layer specific coagulation behavior of the different layers may be adjusted so that (intra-layer) merging positions are formed within the respective layer and (inter-layer) merging positions are formed between adjacent layers. More specifically, process control may be adjusted so that merging positions are formed between two adjacent layers by promoting coagulation of both layers only after initial contact between spinning solution related to the different layers.

[0056] According to a further embodiment of the invention the method further comprises further processing the fibers and/or the fabric in situ after collection on the fiber support unit. This further processing comprises in particular at least one of the group consisting of hydro-entanglement, needle punching, impregnation, steam treatment with a pressurized steam, and calendering.

[0057] Such in situ processes may be those processes being carried out before the manufactured (in particular substantially endless) fabric is stored (for instance wound by a winder) for shipping to a product manufacture destination. For instance, such a further processing or post processing may involve hydroentanglement. Hydroentanglement may be denoted as a bonding process for wet or dry fibrous webs, the resulting bonded fabric being a nonwoven. Hydroentanglement may use fine, high pressure jets of water which penetrate the web, hit a fiber support unit (in particular a conveyor belt) and bounce back causing the fibers to entangle. A corresponding compression of the fabric may render the fabric more compact and mechanically more stable. Additionally or alternatively to hydroentanglement, steam treatment of the fibers with a pressurized steam may be carried out. Additionally or alternatively, such a further processing or post processing may involve a needling treatment of the manufactured fabric. A needle punching system may be used to bond the fibers of the fabric or web. Needle punched fabrics may be produced when barbed needles are pushed through the fibrous web forcing some fibers through the web, where they remain when the needles are withdrawn. If sufficient fibers are suitably displaced the web may be converted into a fabric by the consolidating effect of these fibers plugs. Yet another further processing or post processing treatment of the web or fabric is an impregnating treatment. Impregnating the network of endless fibers may involve the application of one or more chemicals (such as a softening agent, a hydrophobic agent, and antistatic agent, etc.) on the fabric. Still another further processing treatment of the fabric is calendering. Calendering may be denoted as a finishing process for treating the fabric and may employ a calender to smooth, coat, and/or compress the fabric.

[0058] According to a further aspect of the invention there is provided a device for manufacturing nonwoven cellulose fiber fabric directly from a lyocell spinning so-

lution and in particular for manufacturing a fabric as described above. The provided device comprises (a) an jet with orifices configured for extruding the lyocell spinning solution supported by a gas flow; (b) a coagulation unit configured for providing a coagulation fluid atmosphere for the extruded lyocell spinning solution to thereby form substantially endless fibers; (c) a fiber support unit configured for collecting the fibers to thereby form the fabric; and (d) a control unit configured for adjusting process parameters so that the fabric exhibits an oil absorbing capability of at least 1900 mass percent.

[0059] The described device is based on the idea that the control unit allows to carry out in a reliable manner the above described method for manufacturing the further above described nonwoven cellulose fiber fabric.

[0060] According to a further aspect of the invention there is provided a method of using a nonwoven cellulose fiber fabric as described above. The fabric is used for at least one of the group consisting of a dryer sheet, a facial mask, a hygiene product, a wipe, a filter, a medical application product, a geotextile, agrotexile, clothing, a product for building technology, an automotive product, a furnishing, an industrial product, a product related to leisure, beauty, sports or travel, and a product related to school or office.

[0061] When using the described fabric for a dryer sheet the oil absorbing capability may be used for depositing active components which are released during a drying procedure carried out within a laundry dryer. The process of releasing can be supported e.g. by means of the thermal shrinkage and a corresponding squeezing of cavities containing oil particles.

[0062] When using the described fabric for a facial mask special benefits can be taken from the large receiving capability for oils and/or emulsions, which are best suited for the human skin.

[0063] When using the described fabric for a cleaning wipe, e.g. a household wipe, benefits can be taken from the high oil uptake when removing oily residues in the kitchen without using any chemicals or surfactants.

[0064] The high oil uptake of the described fabric may be especially also beneficial for personal care wipes, e.g. for removing make up without any need of surfactants containing lotions.

[0065] According to a further aspect of the invention there is provided a product or composite comprising a nonwoven cellulose fiber fabric as described above.

[0066] A nonwoven cellulose fiber fabric according to an exemplary embodiment of the invention may also be combined (for instance *in situ* or in a subsequent process) with one or more other materials, to thereby form a composite according to an exemplary embodiment of the invention. Exemplary materials, which can be combined with the fabric for forming such a composite may be selected from a group of materials comprising, but not being limited to, the following materials or combinations thereof: fluff pulp, a fiber suspension, a wetlaid nonwoven, an airlaid nonwoven, a spunbond web, a meltblown web, a

carded spunlaced or needlepunched web or other sheet like structures made of various materials. In an embodiment, the connection between the different materials can be done by (but not limited to) one or a combination of the following processes: merging, hydroentanglement, needle punching, hydrogen bonding, thermobonding, gluing by a binder, laminating, and/or calendering.

[0067] Particular uses of the webs, either 100% cellulose fiber webs, or for example webs comprising or consisting of two or more fibers, or chemically modified fibers or fibers with incorporated materials such as anti-bacterial materials, ion exchange materials, active carbon, nano particles, lotions, medical agents or fire retardants, or bicomponent fibers may be as follows:

The nonwoven cellulose fiber fabric according to exemplary embodiments of the invention may be used for manufacturing wipes such as baby, kitchen, wet wipes, cosmetic, hygiene, medical, cleaning, polishing (car, furniture), dust, industrial, duster and mops wipes.

[0068] It is also possible that the nonwoven cellulose fiber fabric according to exemplary embodiments of the invention is used for manufacturing a filter. For instance, such a filter may be an air filter, a HVAC, air condition filter, flue gas filter, liquid filters, coffee filters, tea bags, coffee bags, food filters, water purification filter, blood filter, cigarette filter; cabin filters, oil filters, cartridge filter, vacuum filter, vacuum cleaner bag, dust filter, hydraulic filter, kitchen filter, fan filter, moisture exchange filters, pollen filter, HEVAC/HEPA/ULPA filters, beer filter, milk filter, liquid coolant filter and fruit juices filters.

[0069] In yet another embodiment, the nonwoven cellulose fiber fabric may be used for manufacturing absorbent hygiene products. Examples thereof are an acquisition layer, a coverstock, a distribution layer, an absorbent cover, sanitary pads, topsheets, backsheets, leg cuffs, flushable products, pads, nursing pads, disposal underwear, training pants, face masks, beauty facial masks, cosmetic removal pads, washcloths, diapers, and sheets for a laundry dryer releasing an active component (such as a textile softener).

[0070] In still another embodiment, the nonwoven cellulose fiber fabric may be used for manufacturing a medical application product. For instance, such medical application products may be disposable caps, gowns, masks and shoe cover, wound care products, sterile packaging products, coverstock products, dressing materials, one way clothing, dialyses products, nasal strips, adhesives for dental plates, disposal underwear, drapes, wraps and packs, sponges, dressings and wipes, bed linen, transdermal drug delivery, shrouds, underpads, procedure packs, heat packs, ostomy bag liners, fixation tapes and incubator mattresses.

[0071] In yet another embodiment, the nonwoven cellulose fiber fabric may be used for manufacturing geotextiles. This may involve the production of crop protec-

tion covers, capillary matting, water purification, irrigation control, asphalt overlay, soil stabilisation, drainage, sedimentation and erosion control, pond liners, impregnation based, drainage channel liners, ground stabilisation, pit linings, seed blankets, weed control fabrics, greenhouse shading, root bags and biodegradable plant pots. It is also possible to use the nonwoven cellulose fiber fabric for a plant foil (for instance providing a light protection and/or a mechanical protection for a plant, and/or providing the plant or soil with dung or seed).

[0072] In another embodiment, the nonwoven cellulose fiber fabric may be used for manufacturing clothing. For example, interlinings, clothing insulation and protection, handbag components, shoe components, belt liners, industrial headwear/foodwear, disposable workwear, clothing and shoe bags and thermal insulation may be manufactured on the basis of such fabric.

[0073] In still another embodiment, the nonwoven cellulose fiber fabric may be used for manufacturing products used for building technology. For instance, roofing and tile underlay, underslating, thermal and noise insulation, house wrap, facings for plaster board, pipe wrap, concrete moulding layers, foundations and ground stabilisation, vertical drainages, shingles, roofing felts, noise abatement, reinforcement, sealing material, and damping material (mechanical) may be manufactured using such fabric.

[0074] In still another embodiment, the nonwoven cellulose fiber fabric may be used for manufacturing an automotive product. Examples are a cabin filter, boot liners, parcel shelves, heat shields, shelf trim, moulded bonnet liners, boot floor covering, oil filter, headliners, rear parcel shelves, decorative fabrics, airbags, silencer pads, insulation materials, car covers, underpadding, car mats, tapes, backing and tufted carpets, seat covers, door trim, needled carpet, and auto carpet backing.

[0075] Still another field of application of fabric manufactured according to exemplary embodiments of the invention are furnishings, such as furniture, construction, insulator to arms and backs, cushion thickening, dust covers, linings, stitch reinforcements, edge trim materials, bedding constructions, quilt backing, spring wrap, mattress pad components, mattress covers, window curtains, wall coverings, carpet backings, lampshades, mattress components, spring insulators, sealings, pillow ticking, and mattress ticking.

[0076] In yet another embodiment, the nonwoven cellulose fiber fabric may be used for manufacturing industrial products. This may involve electronics, floppy disc liners, cable insulation, abrasives, insulation tapes, conveyor belts, noise absorbent layers, air conditioning, battery separators, acid systems, anti-slip matting stain removers, food wraps, adhesive tape, sausage casing, cheese casing, artificial leather, oil recovery booms and socks, and papermaking felts.

[0077] Nonwoven cellulose fiber fabric according to exemplary embodiments of the invention is also appropriate for manufacturing products related to leisure and travel.

Examples for such an application are sleeping bags, tents, luggage, handbags, shopping bags, airline headrests, CD-protection, pillowcases, and sandwich packaging.

[0078] Still another field of application of exemplary embodiment of the invention relates to school and office products. As examples, book covers, mailing envelopes, maps, signs and pennants, towels, and flags shall be mentioned.

[0079] It has to be noted that embodiments of the invention have been described with reference to different subject matters. In particular, some embodiments have been described with reference to apparatus type claims whereas other embodiments have been described with reference to method type claims. However, a person skilled in the art will gather from the above and the following description that, unless other notified, in addition to any combination of features belonging to one type of subject matter also any combination between features relating to different subject matters, in particular between features of the apparatus type claims and features of the method type claims is considered as to be disclosed with this document.

[0080] The aspects defined above and further aspects of the present invention are apparent from the examples of embodiment to be described hereinafter and are explained with reference to the examples of embodiment. The invention will be described in more detail hereinafter with reference to examples of embodiment but to which the invention is not limited.

Brief Description of the Drawing

[0081]

Figure 1 illustrates a device for manufacturing nonwoven cellulose fiber fabric which is directly formed from lyocell spinning solution being coagulated by a coagulation fluid according to an exemplary embodiment of the invention.

Figure 2 to Figure 4 show experimentally captured images of nonwoven cellulose fiber fabric according to an exemplary embodiment of the invention in which merging of individual fibers has been accomplished by a specific process control.

Figure 5 and Figure 6 show experimentally captured images of nonwoven cellulose fiber fabric according to an exemplary embodiment of the invention in which swelling of fibers has been accomplished, wherein Figure 5 shows the fiber fabric in a dry non-swollen state and Figure 6 shows the fiber fabric in a humid swollen state.

Figure 7 shows an experimentally captured image of nonwoven cellulose fiber fabric according to an exemplary embodiment of the invention in which for-

mation of two superposed layers of fibers has been accomplished by a specific process implementing two serial bars of nozzles.

Figure 8 shows an experimentally captured image of nonwoven cellulose fiber fabric according to an exemplary embodiment of the invention in which a merging factor of almost hundred percent has been adjusted by process control.

Figure 9 shows an experimentally captured image of nonwoven cellulose fiber fabric according to another exemplary embodiment of the invention in which a merging factor of almost zero percent has been adjusted by process control.

Figures 10 and 11 show two experimentally captured images of two nonwoven cellulose fiber fabrics which exhibit different oil absorbing capabilities due to different merging factors.

Figure 12 illustrates a part of a device for manufacturing nonwoven cellulose fiber fabric composed of two stacked layers of endless cellulose fiber webs according to an exemplary embodiment of the invention.

Figure 13 illustrates a nonwoven cellulose fiber fabric comprising three network layers.

Detailed Description of the Drawing

[0082] The illustration in the drawing is schematic. It is noted that in different figures, similar or identical elements or features are provided with the same reference signs. In order to avoid unnecessary repetitions elements or features which have already been elucidated with respect to a previously described embodiment are not elucidated again at a later position of the description.

[0083] Further, spatially relative terms, such as "front" and "back", "above" and "below", "left" and "right", et cetera are used to describe an element's relationship to another element(s) as illustrated in the figures. Thus, the spatially relative terms may apply to orientations in use which differ from the orientation depicted in the figures. Obviously all such spatially relative terms refer to the orientation shown in the figures only for ease of description and are not necessarily limiting as an apparatus according to an embodiment of the invention can assume orientations different than those illustrated in the figures when in use.

[0084] Figure 1 illustrates a device 100 according to an exemplary embodiment of the invention for manufacturing nonwoven cellulose fiber fabric 102 which is directly formed from lyocell spinning solution 104. The latter is at least partly coagulated by a coagulation fluid 106 to be converted into partly-formed cellulose fibers 108. By the device 100, a lyocell solution blowing process ac-

cording to an exemplary embodiment of the invention may be carried out. In the context of the present application, the term "lyocell solution-blowing process" may particularly encompass processes which can result in essentially endless filaments or fibers 108 of a discrete length or mixtures of endless filaments and fibers of discrete length being obtained. As further described below, nozzles each having an orifice 126 are provided through which cellulose solution or lyocell spinning solution 104 is ejected together with a gas stream or gas flow 146 for manufacturing the nonwoven cellulose fiber fabric 102 according to an exemplary embodiment of the invention.

[0085] As can be taken from Figure 1, wood pulp 110, other cellulose-based feedstock or the like may be supplied to a storage tank 114 via a metering unit 113. Water from a water container 112 is also supplied to the storage tank 114 via metering unit 113. Thus, the metering unit 113, under control of a control unit 140 described below in further detail, may define relative amounts of water and wood pulp 110 to be supplied to the storage tank 114. A solvent (such as N-methyl-morpholine, NMMO) accommodated in a solvent container 116 may be concentrated in a concentration unit 118 and may then be mixed with the mixture of water and wood pulp 110 or other cellulose-based feedstock with definable relative amounts in a mixing unit 119. Also the mixing unit 119 can be controlled by the control unit 140. Thereby, the water-wood pulp 110 medium is dissolved in the concentrated solvent in a dissolving unit 120 with adjustable relative amounts, thereby obtaining lyocell spinning solution 104. The aqueous lyocell spinning solution 104 can be a honey-viscous medium composed of (for instance 5 mass % to 15 mass %) cellulose comprising wood pulp 110 and (for instance 85 mass % to 95 mass %) solvent.

[0086] The lyocell spinning solution 104 is forwarded to a fiber formation unit 124 (which may be embodied as or which may comprise a number of spinning beams or jets 122). For instance, the number of orifices 126 of the jets 122 may be larger than 50, in particular larger than 100. In one embodiment, all orifices 126 of a fiber formation unit 124 (which may comprise a number of spinnerets of jets 122) of orifices 126 of the jets 122 may have the same size and/or shape. Alternatively, size and/or shape of different orifices 126 of one jet 122 and/or orifices 126 of different jets 122 (which may be arranged serially for forming a multilayer fabric) may be different. The orifices 126 may be arranged as one dimensional alignment of orifices 126.

[0087] When the lyocell spinning solution 104 passes through the orifices 126 of the jets 122, it is divided into a plurality of parallel strands of lyocell spinning solution 104. A vertically oriented gas flow, i.e. being oriented substantially parallel to spinning direction, forces the lyocell spinning solution 104 to transform into increasingly long and thin strands which can be adjusted by changing the process conditions under control of control unit 140. The gas flow may accelerate the lyocell spinning solution 104 along at least a part of its way from the orifices 126

to a fiber support unit 132.

[0088] While the lyocell spinning solution 104 moves through the jets 122 and further downward, the long and thin strands of the lyocell spinning solution 104 interact with non-solvent coagulation fluid 106. The coagulation fluid 106 is advantageously embodied as a vapor mist, for instance an aqueous mist. Process relevant properties of the coagulation fluid 106 are controlled by one or more coagulation units 128, providing the coagulation fluid 106 with adjustable properties. The coagulation units 128 are controlled, in turn, by control unit 140. Preferably, respective coagulation units 128 are provided between the individual nozzles or orifices 126 for individually adjusting properties of respective layers of fabric 102 being produced. Preferably, each jet 122 may have two assigned coagulation units 128, one from each side. The individual jets 122 can thus be provided with individual portions of lyocell spinning solution 104 which may also be adjusted to have different controllable properties of different layers of manufactured fabric 102.

[0089] When interacting with the coagulation fluid 106 (such as water), the solvent concentration of the lyocell spinning solution 104 is reduced, so that the cellulose of the former e.g. wood pulp 110 (or other feedstock) is at least partly coagulated as long and thin cellulose fibers 108 (which may still contain residual solvent and water).

[0090] During or after initial formation of the individual cellulose fibers 108 from the extruded lyocell spinning solution 104, the cellulose fibers 108 are deposited on fiber support unit 132, which is here embodied as a conveyor belt with a planar fiber accommodation surface. The cellulose fibers 108 form a nonwoven cellulose fiber fabric 102 (illustrated only schematically in Figure 1). The nonwoven cellulose fiber fabric 102 is composed of continuous and substantially endless filaments or fibers 108.

[0091] Although not shown in Figure 1, the solvent of the lyocell spinning solution 104 removed in coagulation by the coagulation unit 128 and in washing in a washing unit 180 can be at least partially recycled.

[0092] While being transported along the fiber support unit 132, the nonwoven cellulose fiber fabric 102 can be washed by washing unit 180 supplying wash liquor to remove residual solvent and may then be dried. It can be further processed by an optional but advantageous further processing unit 134. For instance, such a further processing may involve hydro-entanglement, needle punching, impregnation, steam treatment with a pressurized steam, calendaring, etc.

[0093] The fiber support unit 132 may also transport the nonwoven cellulose fiber fabric 102 to a winder 136 on which the nonwoven cellulose fiber fabric 102 may be collected as a substantially endless sheet. The nonwoven cellulose fiber fabric 102 may then be shipped as roll-good to an entity manufacturing products such as wipes or textiles based on the nonwoven cellulose fiber fabric 102.

[0094] As indicated in Figure 1, the described process may be controlled by control unit 140 (such as a proces-

sor, part of a processor, or a plurality of processors). The control unit 140 is configured for controlling operation of the various units shown in Figure 1, in particular one or more of the metering unit 113, the mixing unit 119, the fiber formation unit 124, the coagulation unit(s) 128, the further processing unit 134, the dissolution unit 120, the washing unit 118, etc. Thus, the control unit 140 (for instance by executing computer executable program code, and/or by executing control commands defined by a user) may precisely and flexibly define the process parameters according to which the nonwoven cellulose fiber fabric 102 is manufactured. Design parameters in this context are air flow along the orifices 126, properties of the coagulation fluid 106, drive speed of the fiber support unit 132, composition, temperature and/or pressure of the lyocell spinning solution 104, etc. Additional design parameters which may be adjusted for adjusting the properties of the nonwoven cellulose fiber fabric 102 are number and/or mutual distance and/or geometric arrangement of the orifices 126, chemical composition and degree of concentration of the lyocell spinning solution 104, etc. Thereby, the properties of the nonwoven cellulose fiber fabric 102 may be properly adjusted, as described below. Such adjustable properties (see below detailed description) may involve one or more of the following properties: diameter and/or diameter distribution of the fibers 108, amount and/or regions of merging between fibers 108, a purity level of the fibers 108, properties of a multilayer fabric 102, optical properties of the fabric 102, fluid retention and/or fluid release properties of the fabric 102, mechanical stability of the fabric 102, smoothness of a surface of the fabric 102, cross-sectional shape of the fibers 108, etc.

[0095] Although not shown, each spinning jet 122 may comprise a polymer solution inlet via which the lyocell spinning solution 104 is supplied to the jet 122. Via an air inlet, a gas flow 146 can be applied to the lyocell spinning solution 104. Starting from an interaction chamber in an interior of the jet 122 and delimited by a jet casing, the lyocell spinning solution 104 moves or is accelerated (by the gas flow 146 pulling the lyocell spinning solution 104 downwardly) downwardly through a respective orifice 126 and is laterally narrowed under the influence of the gas flow 146 so that continuously tapering cellulose filaments or cellulose fibers 108 are formed when the lyocell spinning solution 104 moves downwardly together with the gas flow 146 in the environment of the coagulation fluid 106.

[0096] Thus, processes involved in the manufacturing method described by reference to Figure 1 may include that the lyocell spinning solution 104, which may also be denoted as cellulose solution is shaped to form liquid strands or latent filaments, which are drawn by the gas flow 146 and significantly decreased in diameter and increased in length. Partial coagulation of latent filaments or fibers 108 (or preforms thereof) by coagulation fluid 106 prior to or during web formation on the fiber support unit 132 may also be involved. The filaments or fibers

108 are formed into web like fabric 102, washed, dried and may be further processed (see further processing unit 134), as required. The filaments or fibers 108 may for instance be collected, for example on a rotating drum or belt, whereby a web is formed.

[0097] As a result of the described manufacturing process and in particular the choice of solvent used, the fibers 108 have a copper content of less than 5 ppm and have a nickel content of less than 2 ppm. This advantageously improves purity of the fabric 102.

[0098] The lyocell solution blown web (i.e. the nonwoven cellulose fiber fabric 102) according to exemplary embodiments of the invention preferably exhibits one or more of the following properties:

(i) The dry weight of the web is from 5 to 300 g/m², preferably 10-80 g/m²

(ii) The thickness of the web according to the standard WSP120.6 respectively DIN29073 (in particular in the latest version as in force at the priority date of the present patent application) is from 0.05 to 10.0 mm, preferably 0.1 to 2.5 mm

(iii) The specific tenacity of the web in MD according to EN29073-3, respectively ISO9073-3 (in particular in the latest version as in force at the priority date of the present patent application) ranges from 0.1 to 3.0 Nm²/g, preferably from 0.4 to 2.3 Nm²/g

(iv) The average elongation of the web according to EN29073-3, respectively ISO9073-3 (in particular in the latest version as in force at the priority date of the present patent application) ranges from 0.5 to 100%, preferably from 4 to 50%.

(v) The MD/CD tenacity ratio of the web is from 1 to 12
(vi) The water retention of the web according to DIN 53814 (in particular in the latest version as in force at the priority date of the present patent application) is from 1 to 250%, preferably 30 to 150%

(vii) The water holding capacity of the web according to DIN 53923 (in particular in the latest version as in force at the priority date of the present patent application) ranges from 90 to 2000%, preferably 400 to 1100%.

(viii) Metal residue levels of copper content of less than 5 ppm and nickel content of less than 2 ppm according to the standards EN 15587-2 for the substrate decomposition and EN 17294-2 for the ICP-MS analysis.

[0099] Most preferably, the lyocell solution-blown web exhibits all of said properties (i) to (viii) mentioned above.

[0100] As described, the process to produce the nonwoven cellulose fiber fabric 102 preferably comprises:

(a) Extruding a solution comprising cellulose dissolved in NMMO (see reference numeral 104) through the orifices 126 of at least one jet 122, thereby forming filaments of lyocell spinning solution 104
(b) Stretching said filaments of lyocell spinning so-

lution 104 by a gaseous stream (see reference numeral 146)

(c) Contacting said filaments with a vapor mist (see reference numeral 106), preferably containing water, thereby at least partly precipitating said fibers 108. Consequently, the filaments or fibers 108 are at least partly precipitated before forming web or nonwoven cellulose fiber fabric 102.

(d) Collecting and precipitating said filaments or fibers 108 in order to form a web or nonwoven cellulose fiber fabric 102

(e) Removing solvent in wash line (see washing unit 180)

(f) Optionally bonding via hydro-entanglement, needle punching, etc. (see further processing unit 134)

(g) Drying and roll collection

[0101] Constituents of the nonwoven cellulose fiber fabric 102 may be bonded by merging, intermingling, hydrogen bonding, physical bonding such as hydroentanglement or needle punching, and/or chemical bonding.

[0102] In order to be further processed, the nonwoven cellulose fiber fabric 102 may be combined with one or more layers of the same and/or other materials, such as (not shown) layers of synthetic polymers, cellulosic fluff pulp, nonwoven webs of cellulose or synthetic polymer fibers, bicomponent fibers, webs of cellulose pulp, such as airlaid or wetlaid pulp, webs or fabrics of high tenacity fibers, hydrophobic materials, high performance fibers (such as temperature resistant materials or flame retardant materials), layers imparting changed mechanical properties to the final products (such as Polypropylene or Polyester layers), biodegradable materials (e.g. films, fibers or webs from Polylactic acid), and/or high bulk materials.

[0103] It is also possible to combine several distinguishable layers of nonwoven cellulose fiber fabric 102, see for instance Figure 7.

[0104] The nonwoven cellulose fiber fabric 102 may essentially consist of cellulose alone. Alternatively, the nonwoven cellulose fiber fabric 102 may comprise a mixture of cellulose and one or more other fiber materials. The nonwoven cellulose fiber fabric 102, furthermore, may comprise a bicomponent fiber material. The fiber material in the nonwoven cellulose fiber fabric 102 may at least partly comprise a modifying substance. The modifying substance may be selected from, for example, the group consisting of a polymeric resin, an inorganic resin, inorganic pigments, antibacterial products, nanoparticles, lotions, fire-retardant products, absorbency-improving additives, such as superabsorbent resins, ion-exchange resins, carbon compounds such as active carbon, graphite, carbon for electrical conductivity, X-ray contrast substances, luminescent pigments, and dye stuffs.

[0105] Concluding, the cellulose nonwoven web or nonwoven cellulose fiber fabric 102 manufactured directly from the lyocell spinning solution 104 allows access to

value added web performance which is not possible via staple fiber route. This includes the possibility to form uniform lightweight webs, to manufacture microfiber products, and to manufacture continuous filaments or fibers 108 forming a web. Moreover, compared to webs from staple fibers, several manufacturing procedures are no longer required. Moreover, nonwoven cellulose fiber fabric 102 according to exemplary embodiments of the invention is biodegradable and manufactured from sustainably sourced raw material (i.e. wood pulp 110 or the like). Furthermore, it has advantages in terms of purity and absorbency. Beyond this, it has an adjustable mechanical strength, stiffness and softness. Furthermore, nonwoven cellulose fiber fabric 102 according to exemplary embodiments of the invention may be manufactured with low weight per area (for instance 10 to 30 g/m²). Very fine filaments down to a diameter of not more than 5 μm, in particular not more than 3 μm, can be manufactured with this technology. Furthermore, nonwoven cellulose fiber fabric 102 according to an exemplary embodiment of the invention may be formed with a wide range of web aesthetics, for instance in a flat crispy film-like way, in a paper-like way, or in a soft flexible textile-like way. By adapting the process parameters of the described process, it is furthermore possible to precisely adjust stiffness and mechanical rigidity or flexibility and softness of the nonwoven cellulose fiber fabric 102. This can be adjusted for instance by adjusting a number of merging positions, the number of layers, or by after-treatment (such as needle punch, hydro-entanglement and/or calendaring). It is in particular possible to manufacture the nonwoven cellulose fiber fabric 102 with a relatively low basis weight of down to 10 g/m² or lower, to obtain filaments or fibers 108 with a very small diameter (for instance of down to 3 to 5 μm, or less), etc.

[0106] Figure 2, Figure 3 and Figure 4 show experimentally captured images of nonwoven cellulose fiber fabric 102 according to an exemplary embodiment of the invention in which merging of individual fibers 108 has been accomplished by a corresponding process control. The oval markers in Figure 2 to Figure 4 show such merging regions where multiple fibers 108 are integrally connected to one another. At such merging points, two or more fibers 108 may be interconnected to form an integral structure.

[0107] Figure 5 and Figure 6 show experimentally captured images of nonwoven cellulose fiber fabric 102 according to an exemplary embodiment of the invention in which swelling of fibers 108 has been accomplished, wherein Figure 5 shows the fiber fabric 102 in a dry non-swollen state and Figure 6 shows the fiber fabric 102 in a humid swollen state. The pore diameters can be measured in both states of Figure 5 and Figure 6 and can be compared to one another. When calculating an average value of 30 measurements, a decrease of the pore size by swelling of the fibers 108 in an aqueous medium up to 47% of their initial diameter could be determined.

[0108] Figure 7 shows an experimentally captured im-

age of nonwoven cellulose fiber fabric 102 according to an exemplary embodiment of the invention in which formation of two superposed layers 200, 202 of fibers 108 has been accomplished by a corresponding process design, i.e. a serial arrangement of multiple spinnerets. The two separate, but connected layers 200, 202 are indicated by a horizontal line in Figure 7. For instance, an n-layer fabric 102 ($n \geq 2$) can be manufactured by serially arranging n spinnerets or jets 122 along the machine direction.

[0109] Specific exemplary embodiments of the invention will be described in the following in more detail:

Figure 8 shows an experimentally captured image of nonwoven cellulose fiber fabric 102 according to an exemplary embodiment of the invention. In the illustrated embodiment, a merging factor of almost hundred percent (more precisely: about 98%) has been adjusted by process control. As a result of the extremely high merging factor, the fabric 102 shown in Figure 8 is a substantially continuous sheet having a similar consistency as a film. Such a fabric 102 has a flat film like behavior. As can be taken from Figure 8, the process parameters may be adjusted for adjusting merging so as to trigger formation of such an amount of merging positions 204 that a substantially continuous film-shaped fabric 102 is obtained.

[0110] The upper left image of Figure 8 shows the fabric with a first scale which is illustrated in the left insert showing a bar indicating a length of 500 μm. The lower right image of Figure 8 shows the fabric with a second scale being significantly larger than the first scale. The corresponding bar in the right insert is indicative for a length of 20 μm.

[0111] Figure 9 shows an experimentally captured image of nonwoven cellulose fiber fabric 102 according to another exemplary embodiment of the invention. In the illustrated embodiment, a merging factor of almost zero (more precisely: below 2%) has been adjusted by process control. Such a fabric 102 has a soft flexible textile like behavior. As a result of the very small merging factor, the fabric 102 shown in Figure 9 is a network of fibers 108 being only weakly linked via few merging positions 204. Over the majority of the fabric 100 however, the fibers 108 are only friction-coupled and entangled with one another rather than being coupled by merging. The result is a relatively flexible fabric 102 being nevertheless suitably held together by the merging positions 204, entanglement, friction and inter-fiber hydrogen bonding.

[0112] The upper left image of Figure 9 shows the fabric with a first scale which is the same as the scale of the upper left image of Figure 8. The lower right image of Figure 9 shows the fabric with a second scale being larger than the first scale. The corresponding bar in the right insert is indicative for a length of 20 μm.

[0113] A fabric with such a small merging factor exhibits a plurality voids or gaps being provided in between

neighboring fibers. With regard to the capability of absorbing oil it may be crucial whether these voids or gaps have a proper size for accommodating oil particles. In any way, the oil absorbing capability of the fabric 102 shown in Figure 9 should definitely be significantly larger than oil absorbing capability of the fabric 102 shown in Figure 8.

[0114] Figures 10 and 11 show experimentally captured images of two nonwoven cellulose fiber fabrics which exhibit different merging factors. The merging factor of the fabric 102 of Figure 10 is smaller than the merging factor of the fabric 102 of Figure 11. Hence, when considering the capability of absorbing oil as a function of the merging factor it should be clear that in between a minimum merging factor and a maximum merging factor there should be an optimal value for the merging factor when a maximum capability of absorbing oil is desired.

[0115] Figure 12 illustrates a part of a device 100 for manufacturing nonwoven cellulose fiber fabric 102 composed of two stacked layers 200, 202 of endless cellulose fibers 108 according to an exemplary embodiment of the invention. A difference between the device 100 shown in Figure 12 and the device 100 shown in Figure 1 is that the device 100 according to Figure 12 comprises two serially aligned jets 122 with orifices 126 and respectively assigned coagulation units 128, as described above. In the embodiment described here, two coagulation units 128 are assigned to each one of the jets 122. In Figure 12, one coagulation unit 128 is located on the left side of the path of the lyocell spinning solution 104 extending between the jet 122 and the fiber support unit 132 and the other coagulation unit 128 is located on the respective right side of this path. In view of the movable fiber accommodation surface of the conveyor belt-type fiber support unit 132, the upstream jet 122 on the left-hand side of Figure 12 produces layer 200. Layer 202 is produced by the downstream jet 122 (see right hand side of Figure 12) and is attached to an upper main surface of the previously formed layer 202 so that a double layer 200, 202 of fabric 102 is obtained.

[0116] According to Figure 12, the control unit 140 (controlling the jets 122 and all the coagulation units 128) is configured for adjusting process parameters so that the fibers 108 of the different layers 200, 202 differ concerning fiber diameter by more than 50% in relation to a smallest diameter. Adjusting the fiber diameters of the fibers 108 of the layers 200, 202 by the control unit 140 may comprise adjusting an amount of coagulation fluid 106 interacting with the lyocell spinning solution 104. Additionally, the embodiment of Figure 12 adjusts the process parameters for adjusting fiber diameter by serially arranging multiple jets 122 with orifices 126 (optionally with different properties) along the movable fiber support unit 132. For instance, such different properties may be different orifice 126 diameters, different speed of gas flow 146, different amounts of gas flow 146, and/or different gas flow 146 pressure. Although not shown in Figure 12, it is possible to further process the fibers 108 after col-

lection on the fiber support unit 132 e.g. by hydro-entanglement, needle punching, impregnation, steam treatment with a pressurized steam, and/or calendering.

[0117] Still referring to the embodiment illustrated in Figure 12, one or more further nozzle bars or jets 122 may be provided and may be arranged serially along a transport direction of the fiber support unit 132. The multiple jets 122 may be arranged so that a further layer 202 of fibers 108 may be deposited on top of the previously formed layer 200, preferably before the coagulation or curing process of the fibers 108 of the layer 200 and/or of the layer 202 is fully completed, which may trigger merging. When properly adjusting the process parameters, this may have advantageous effects in terms of the properties of a multilayer fabric 102.

[0118] Without wishing to be bound to a specific theory, it is presently believed that the second layer 202 can be considered as a reinforcement of the first layer 200, increasing the total homogeneity of the resulting multilayer fabric 102. This increase of the mechanical stability can be further improved by fiber diameter variation (in particular *inter*-fiber diameter variation and/or *intra*-fiber longitudinal diameter variation of the individual fibers 108). When exerting deeper (in particular punctual) pressure (for instance provided by air or water), the cross-sectional shape of a fiber 108 can be further intentionally distorted, which may advantageously result in a further increased mechanical stability.

[0119] On the other hand, intended merging between fibers 108 of the fabric 102 according to Figure 12 can be triggered so as to further increase the mechanical stability of the fabric 102. In this context, merging may be a supported contact point adhesion of contacting filaments of fibers 108, in particular prior to the completion of a coagulation process of one or both of the fibers 108 being merged. For instance, merging may be promoted by increasing a contact pressure by a fluid flow (for instance a flow of air or water). By taking this measure, the strength of the coagulation on the one hand between filaments or fibers 108 of one of the layers 200, 202 and/or on the other hand between the layers 200, 202 may be increased.

[0120] The device 100 according to Figure 12, which is configured for the manufacture of multilayer fabric 102, implements a high number of process parameters which can be used for designing shape and/or diameter or diameter distribution of the fibers 108 as well as of fiber layers 200, 202. This is the result of the serial arrangement of multiple jets 122, each of which being operable with individually adjustable process parameters.

[0121] With device 100 according to Figure 12, it is in particular possible to manufacture a fabric 102 composed of at least two layers 200, 202 (preferably more than two layers). The fibers 108 of the different layers 200, 202 may have different values of diameter and may be formed in one continuous process. By taking this measure, a highly efficient production of the nonwoven cellulose fiber fabric 102 can be ensured, which in particular allows to

transfer the obtained multilayer fabric 102 in one transport procedure to a destination for further processing.

[0122] By the defined layer separation of a multilayer fabric 102, it is also possible to later separate the multilayer fabric 102 into the different individual layers 200, 202 or into different multilayer sections. According to exemplary embodiments of the invention, both *intra-layer* adhesion of the fibers 108 of one layer 200, 202 as well as *inter-layer* adhesion of the fibers 108 between adjacent layers 200, 202 (for instance by merging and/or by friction generating contact) may be properly and individually adjusted. A corresponding separate control for each layer 200, 202 individually may be in particular obtained when the process parameters are adjusted so that coagulation or curing of the fibers 108 of one layer 202 is already completed when the other layer 200 of fibers 108 is placed on top thereof.

[0123] Figure 13 illustrates a nonwoven cellulose fiber fabric 102 comprising three network layers. A first (lower) fiber network layer is denominated with reference numeral 200. A second (middle) fiber network layer, which is formed on top of the first fiber network layer 200, is denominated with reference numeral 202. A further (upper) fiber network layer, which is formed on top of the second fiber network layer 202, is denominated with reference numeral 202'. As has already been mentioned above, the fabric 102 may comprise more than three stacked fiber network layers.

[0124] As can be further seen from Figure 11, the three fiber network layers 200, 202, 202' have different thicknesses. The first fiber network layer 200 has a first thickness t1. The second fiber network layer 202 has a second thickness t2. The further fiber network layer 202' has a third thickness t3.

[0125] It should be noted that the term "comprising" does not exclude other elements or steps and the use of articles "a" or "an" does not exclude a plurality. Also elements described in association with different embodiments may be combined. It should also be noted that reference signs in the claims should not be construed as limiting the scope of the claims.

List of reference signs:

[0126]

100	device for manufacturing nonwoven cellulose fiber fabric
102	nonwoven cellulose fiber fabric / web like fabric
104	lyocell spinning solution
106	coagulation fluid
108	fibers
110	wood pulp
112	water container
113	metering unit
114	storage tank
116	solvent container

118	washing unit
119	mixing unit
120	dissolving unit
122	jet
5 124	fiber formation unit
126	orifices
128	coagulation unit
132	(conveyor belt-type) fiber support unit
134	further processing unit
10 136	roll
140	control unit
146	gas flow
200	merged layer / first network layer
202	merged layer / second network layer
15 202'	merged layer / further network layer
204	merging position
t1, t2, t3	layer thicknesses

20 Claims

1. A nonwoven cellulose fiber fabric (102), in particular directly manufactured from a lyocell spinning solution (104), the fabric (102) comprising
 - 25 a network of substantially endless fibers (108), wherein
 - 30 the fabric (102) exhibits an oil absorbing capability of at least 1900 mass percent.
2. The fabric (102) as set forth in the preceding claim, wherein
 - 35 the fabric (102) comprises a mass per unit area which is smaller than 150 gram per square meter, in particular smaller than 100 gram per square meter, further in particular smaller than 50 gram per square meter and even more in particular smaller than 20 gram per square meter.
3. The fabric (102) as set forth in any one of the preceding claims, wherein
 - 40 the network exhibits a merging factor of the fibers (108), which is in a range between 0,1% and 100%, in particular in a range between 0,5% and 10%.
4. The fabric (102) as set forth in any one of the preceding claims, wherein
 - 45 at least some individual fibers are twisted with each other and/or
 - 50 at least one other fiber structure is twisted with another fiber structure.
5. The fabric (102) as set forth in any one of the preceding claims, wherein
 - 55 the fabric (102) exhibits an oil absorbing capability of at least 2100 mass percent, in particular of at least 2300 mass percent, and more in particular of at least

2500 mass percent.

6. The fabric (102) as set forth in any one of the preceding claims, wherein different ones of the fibers (108) are located at least partially in different distinguishable layers (200, 202). 5
7. The fabric (102) as set forth in the preceding claim, comprising at least one of the following features: 10
 - fibers (108) of different layers (200, 202) are integrally connected at at least one inter layer merging position (204) between the layers (200, 202);
 - different ones of the fibers (108) being located at least partially in different layers (200, 202) differ concerning fiber diameter, in particular differ concerning an averaged fiber diameter;
 - fibers (108) of different layers (200, 202) have the same fiber diameter, in particular have substantially the same averaged fiber diameter;
 - fibers (108) networks of different layers (200, 202) provide different functionality, wherein the different functionality in particular comprises at least one of the group consisting of different wicking, different anisotropic behavior, different liquid absorbing capability, different cleanability, different optical properties, different roughness, different smoothness, and different mechanical properties. 20 25 30
8. The fabric (102) as set forth in any one of the two preceding claims 6 and 7, wherein the fiber networks in different layers have different merging factors. 35
9. The fabric (102) as set forth in any one of the preceding claims, wherein the fibers (108) have a copper content of less than 5 ppm and/or have a nickel content of less than 2 ppm. 40
10. A method of manufacturing nonwoven cellulose fiber fabric (102), in particular a fabric (102) as set forth in any one of the preceding claims, directly from a lyocell spinning solution (104), the method comprising 45
 - extruding the lyocell spinning solution (104) through a jet (122) with orifices (126) supported by a gas flow (146) into a coagulation fluid (106) atmosphere to thereby form substantially endless fibers (108);
 - collecting the fibers (108) on a fiber support unit (132) to thereby form the fabric (102);
 - adjusting process parameters of the manufacturing process so that the fabric (102) exhibits an oil absorbing capability of at least 1900 mass percent. 50 55

11. The method as set forth in the preceding claim, wherein adjusting the process parameters comprises at least one of the following features:

forming at least part of the merging position (204) after the lyocell spinning solution (104) has left the orifices (126) and before the lyocell spinning solution (104) has reached the fiber support unit (132) by triggering an interaction between lyocell spinning solution (104) extruded through different ones of the orifices (126); forming at least a part of the merging positions (204) after the lyocell spinning solution (104) has reached the fiber support unit (132) by triggering coagulation of at least part of the fibers (108) when laying on the fiber support unit (132); serially arranging multiple jets (122) with orifices (126) along a movable fiber support unit (132), depositing a first layer (202) of fibers (108) on the fiber support unit (132), and depositing a second layer (200) of fibers (108) on the first layer (202) before coagulation of at least part of the fibers (108) at an interface between the layers (200, 202) has been completed.

12. The method as set forth in any one of the preceding claims 10 and 11, further comprising further processing the fibers (108) and/or the fabric (102) in situ after collection on the fiber support unit (132), in particular by at least one of the group consisting of hydro-entanglement, needle punching, impregnation, steam treatment with a pressurized steam, and calendering. 35

13. A device (100) for manufacturing nonwoven cellulose fiber fabric (102) directly from a lyocell spinning solution (104), in particular for manufacturing a fabric as set forth in any one of the preceding claims 1 to 9, the device (100) comprising

a jet (122) with orifices (126) configured for extruding the lyocell spinning solution (104) supported by a gas flow (146); a coagulation unit (128) configured for providing a coagulation fluid (106) atmosphere for the extruded lyocell spinning solution (104) to thereby form substantially endless fibers (108); a fiber support unit (132) configured for collecting the fibers (108) to thereby form the fabric (102); and a control unit (140) configured for adjusting process parameters so that the fabric (102) exhibits an oil absorbing capability of at least 1900 mass percent.

14. A method of using a nonwoven cellulose fiber fabric (102) according to any of claims 1 to 9 for at least

one of the group consisting of a dryer sheet, a facial mask, a hygiene product, a wipe, a filter, a medical application product, a geotextile, agrotextile, clothing, a product for building technology, an automotive product, a furnishing, an industrial product, a product related to leisure, beauty, sports or travel, and a product related to school or office. 5

15. A product or composite comprising a nonwoven cellulose fiber fabric as set forth in any one of the preceding claims 1 to 9. 10

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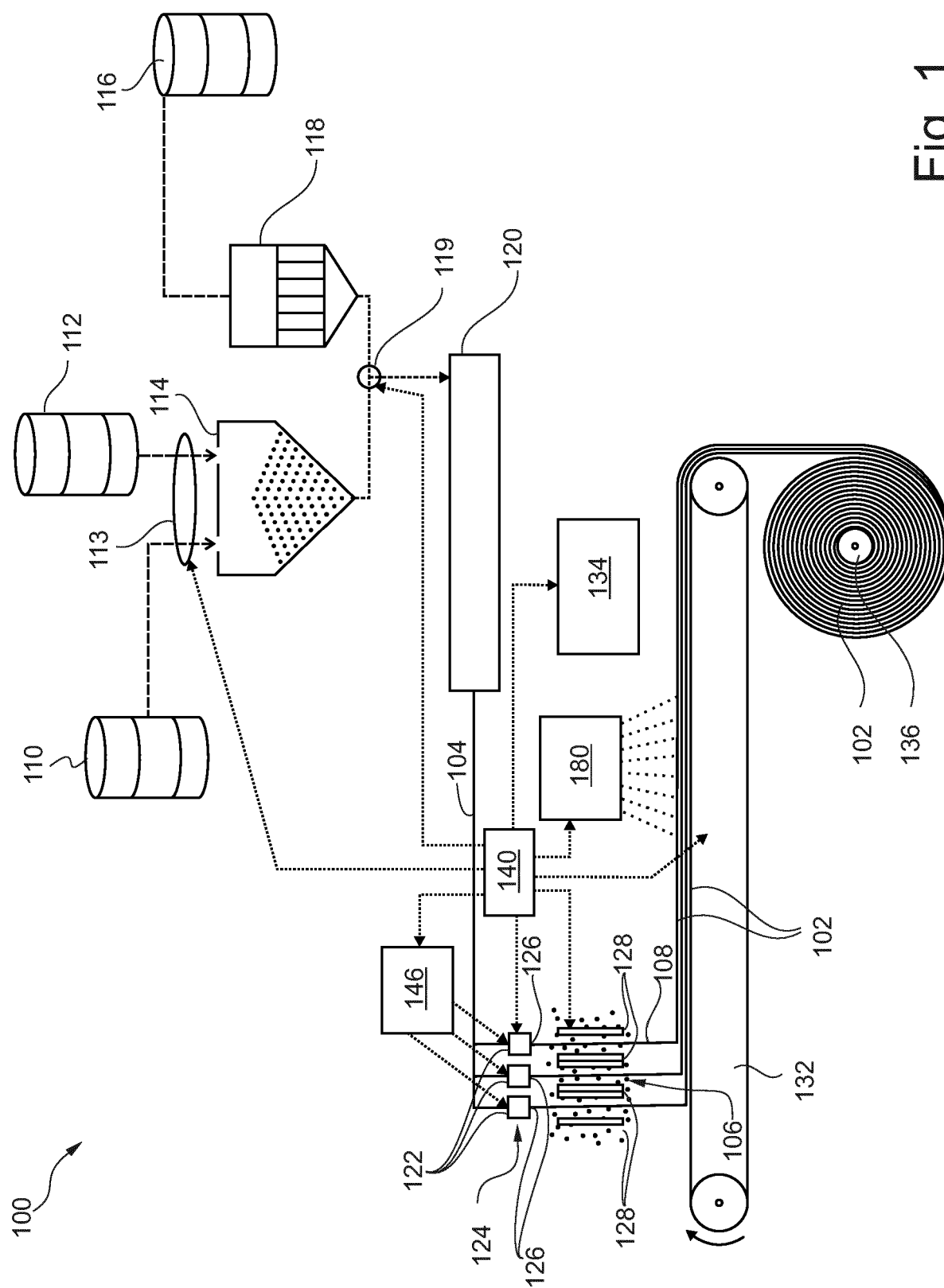


Fig. 1

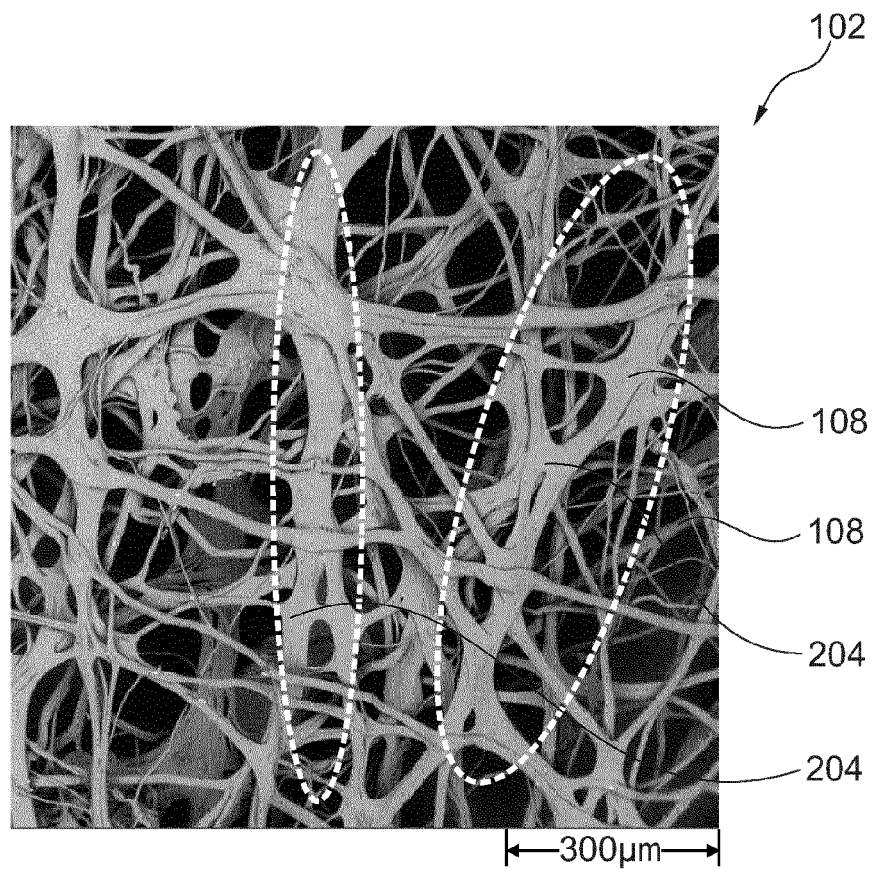


Fig. 2

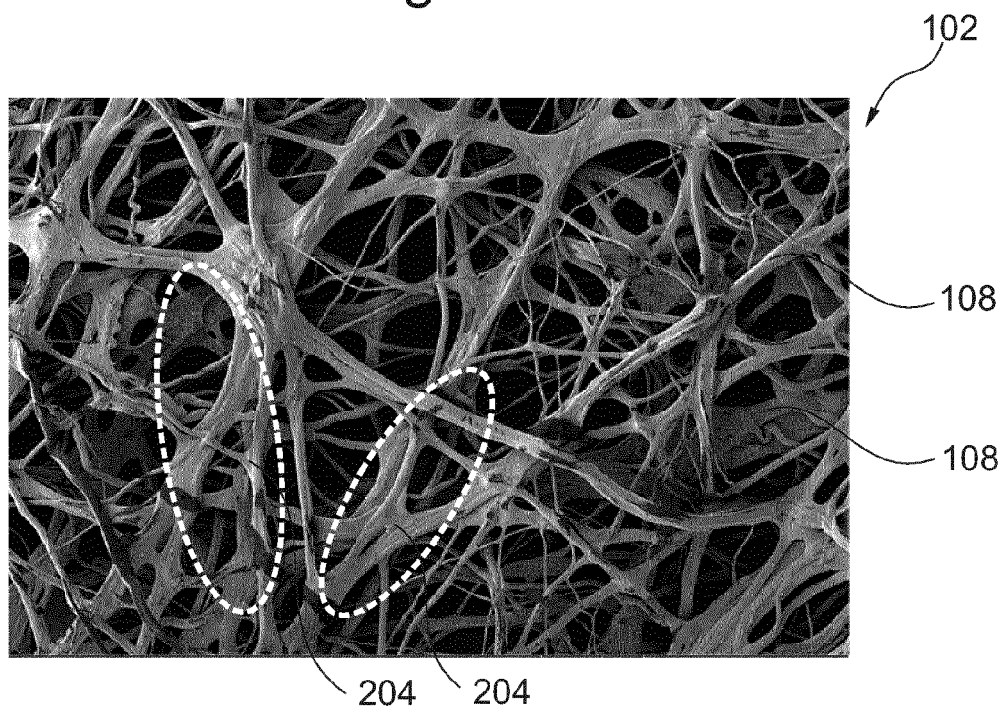


Fig. 3

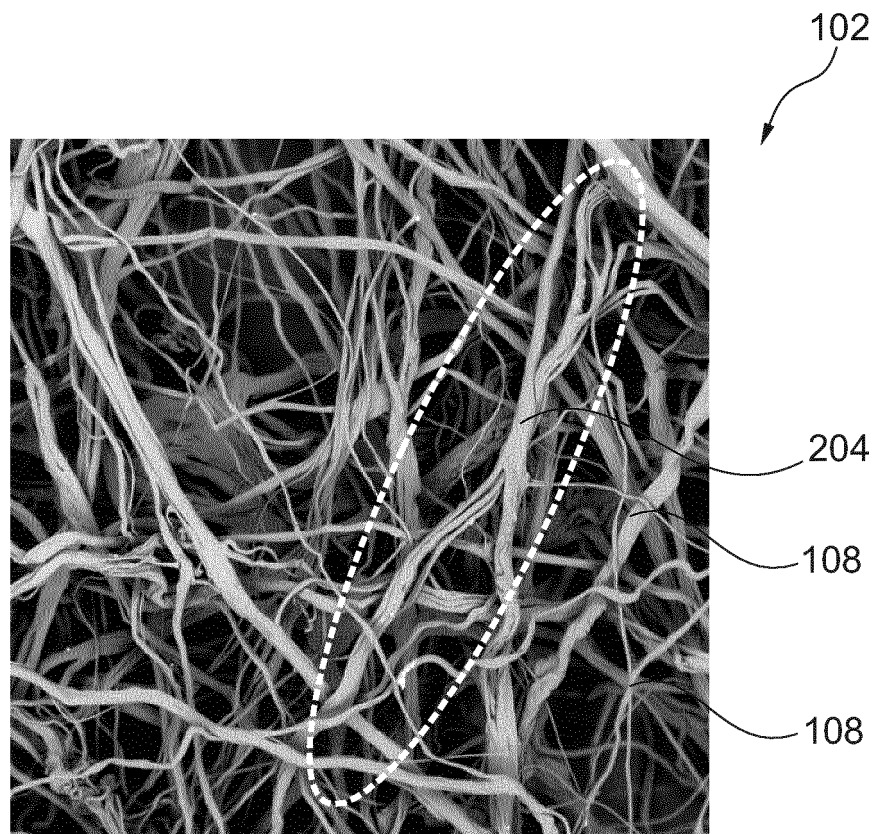


Fig. 4

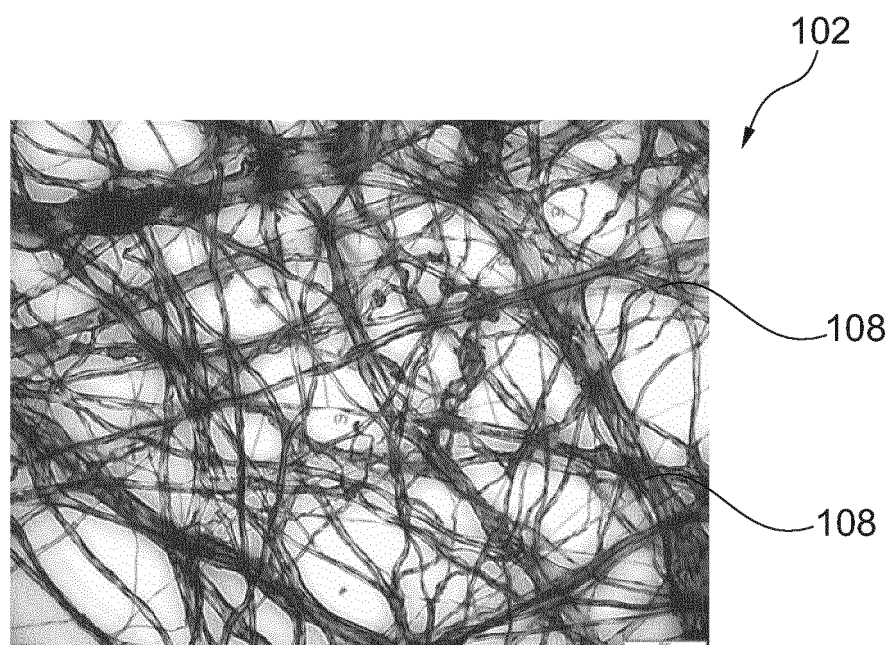


Fig. 5

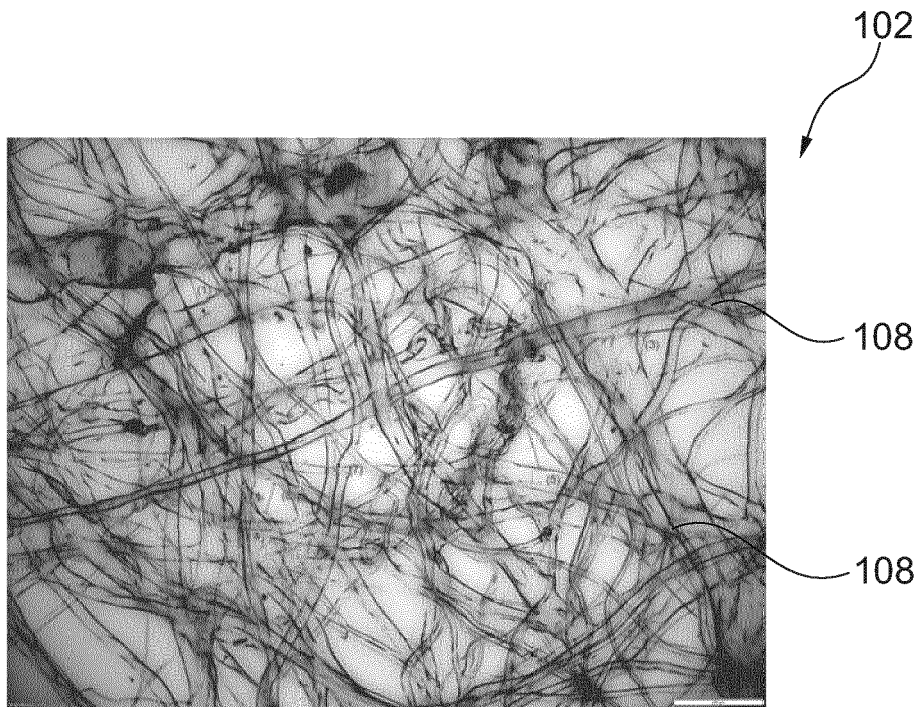


Fig. 6

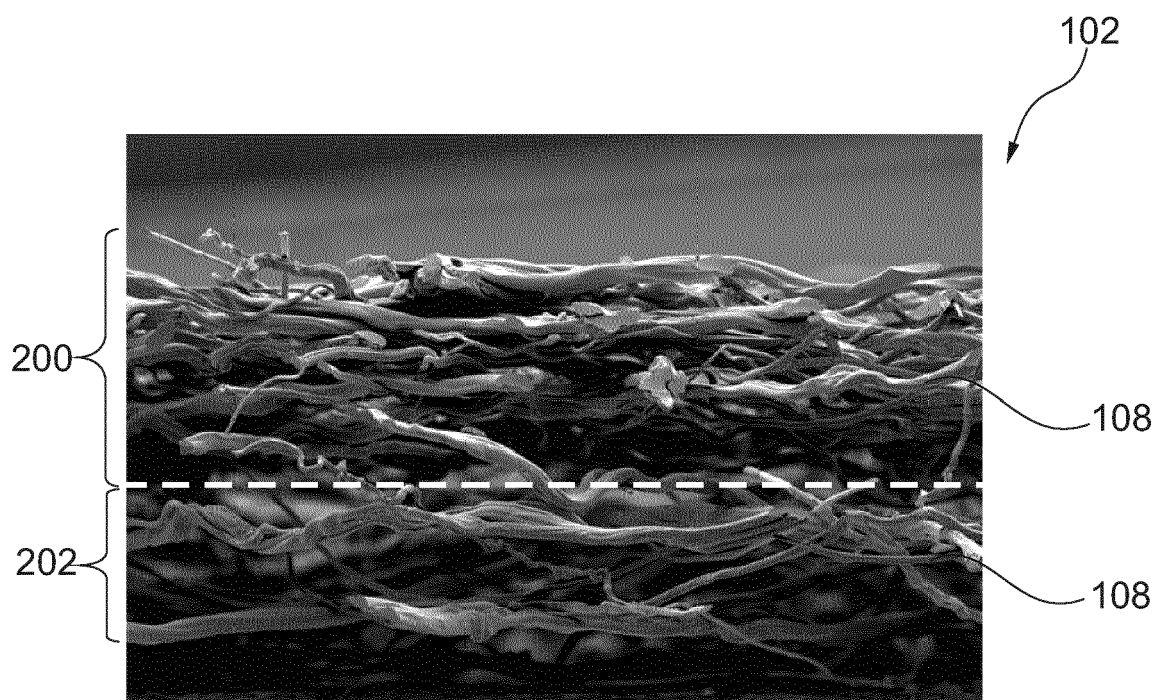


Fig. 7

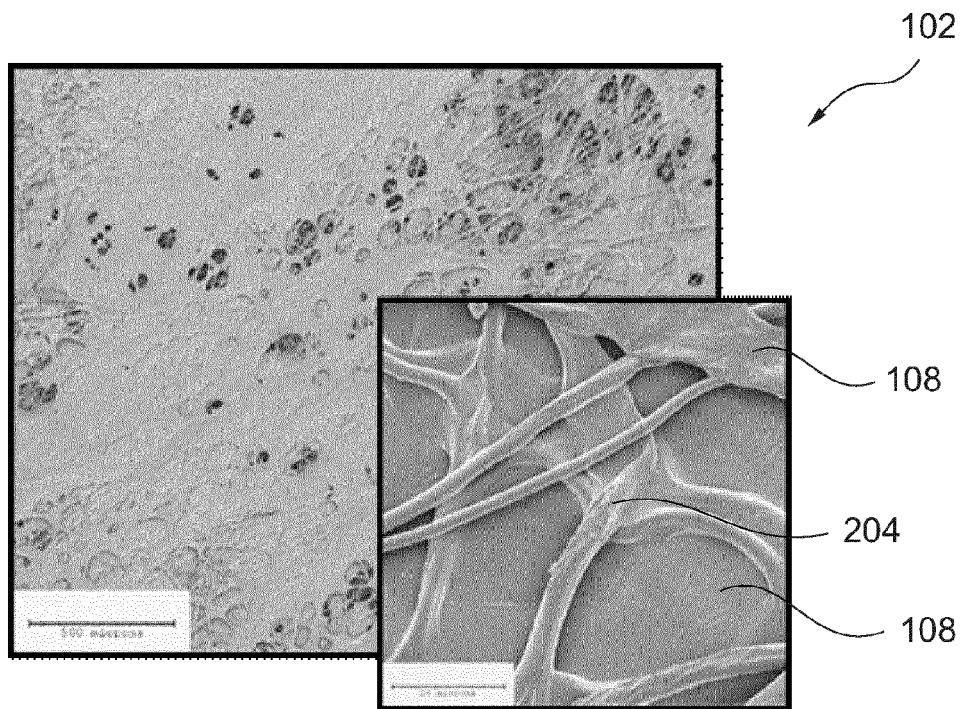


Fig. 8

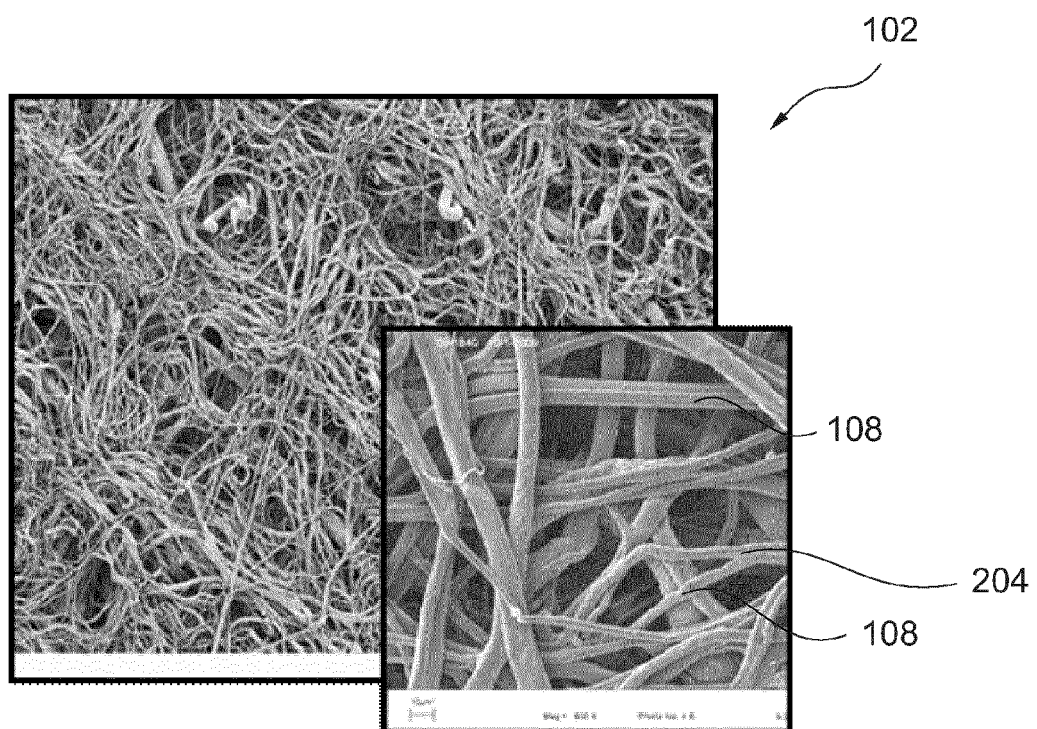


Fig. 9

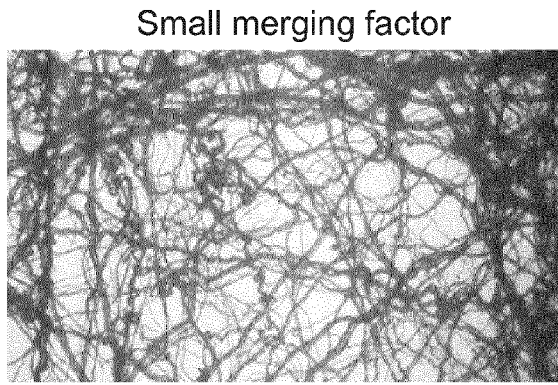


Fig. 10

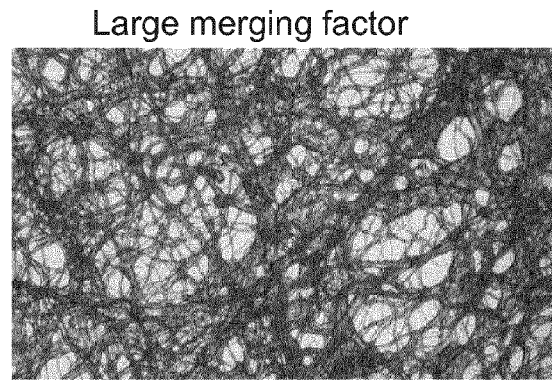


Fig. 11

Fig. 12

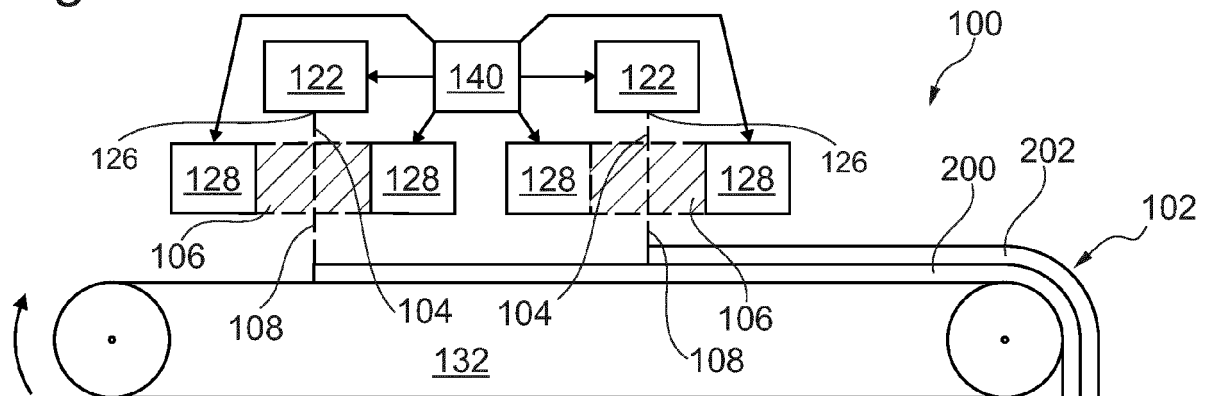
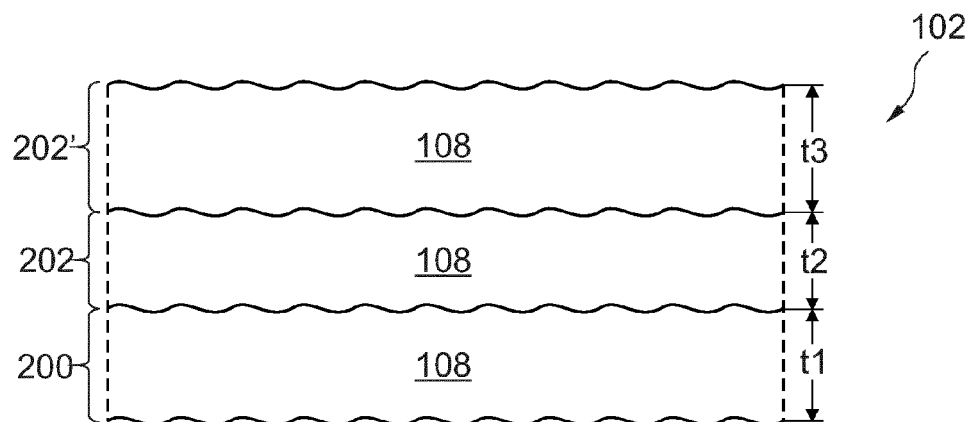


Fig. 13





EUROPEAN SEARCH REPORT

Application Number
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EPO FORM 1503 03.02 (P04C01)

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	US 2009/324926 A1 (LUO MENGKUI [US]) 31 December 2009 (2009-12-31) * paragraphs [0003], [0015] - [0016], [0021] *	1-15	INV. D04H3/013 D04H3/016
X	US 2010/162542 A1 (LUO MENGKUI [US] ET AL) 1 July 2010 (2010-07-01) * paragraphs [0020] - [0031] *	1-15	
X	WO 2016/052527 A1 (KURARAY KURAFLEX CO LTD [JP]; MANDOM CORP [JP]) 7 April 2016 (2016-04-07) * abstract *	1-15	
X	JP 2006 291437 A (MITSUBISHI PAPER MILLS LTD) 26 October 2006 (2006-10-26) * abstract *	1-15	
			TECHNICAL FIELDS SEARCHED (IPC)
			D04H
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 13 September 2017	Examiner Mangin, Sophie
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ON EUROPEAN PATENT APPLICATION NO.**

EP 17 16 4491

5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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13-09-2017

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009324926 A1	31-12-2009	NONE	
US 2010162542 A1	01-07-2010	NONE	
WO 2016052527 A1	07-04-2016	CN 106714641 A	24-05-2017
		JP WO2016052527 A1	31-08-2017
		KR 20170045309 A	26-04-2017
		TW 201632675 A	16-09-2016
		WO 2016052527 A1	07-04-2016
JP 2006291437 A	26-10-2006	JP 4976675 B2	18-07-2012
		JP 2006291437 A	26-10-2006

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 9826122 A [0004]
- WO 9947733 A [0004]
- WO 9807911 A [0004]
- US 6197230 B [0004]
- WO 9964649 A [0004]
- WO 05106085 A [0004]
- EP 1358369 A [0004]
- EP 2013390 A [0004]
- WO 07124521 A1 [0004]
- WO 07124522 A1 [0004]