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(71) Applicant: **Ahlstrom Corporation**
00100 Helsinki (FI)

(72) Inventors:
- **Cartier, Noël**
  38200 Jardin (FR)
- **Dufour, Menno**
  69007 Lyon (FR)
- **Mavrikos, Florence**
  26140 Andancette (FR)
- **Merlet, Samuel**
  38410 Vaulnaveys-le-Haut (FR)
- **Vincent, Audrey**
  69200 Venissieux (FR)

(74) Representative: **Genip Oy**
Heikinkatu 7
48100 Kotka (FI)

(54) Wet-laid nonwoven comprising nanofibrillar cellulose and a method of manufacturing such

(57) A wet-laid nonwoven comprising at least synthetic and/or natural fibers and nanofibrillar cellulose (NFC) in an amount of between 0.1 and 20% by dry weight compared with the dry weight of said nonwoven, the nonwoven being impregnated with the NFC for its entire thickness.

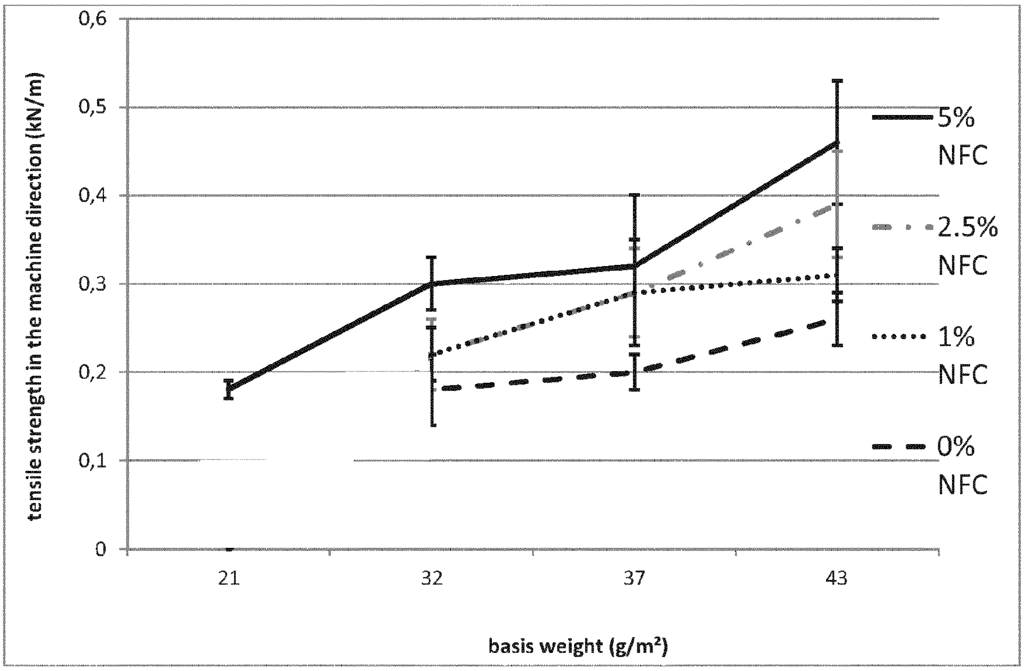

Fig. 1

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a wet-laid nonwoven comprising long fibers, and nanofibrillar cellulose, and a method of manufacturing such by using a wet-laying technology. The fibers of the nonwoven may be synthetic fibers including both mineral, ceramic and polymer fibers, optionally together with natural fibers. By wet-laying is here understood both liquid-laying and foam-laying, i.e. laying fibers suspended in liquid or foam on a foraminous surface.

[0002] The fields of use for the present invention relate in particular to healthcare, medical, surgical, personal care (wipes, napkins, hair-removal/depilatory strips, etc.), textiles (clothing), geotextiles, construction materials (plaster boards, acoustic panels, flooring materials), composite products (glass mat, natural fibers + PP/PLA fibers) decoration (wallpaper, indoor banners), automotive, filtration, agriculture, furniture, leisure, protective packaging, domestic use (for instance table tops, coffee pods and like beverage products).

PRIOR ART

[0003] A nonwoven substrate is characterized by entangling individual fibers to form a coherent web or batt. In other words, a nonwoven is a fabric-like material made of long synthetic fibers, bonded together by chemical, mechanical, heat or solvent treatment. The term is used predominantly in the textile manufacturing industry to denote fabrics, such as felt, which are neither woven nor knitted. Nonwoven materials typically lack strength. Generally, it comprises synthetic and optionally natural fibers. These fibers may be oriented randomly or more regularly depending on the technique used to make the nonwoven.

[0004] In the manufacture of nonwoven, including also glass fiber substrates, the following processes, among others, are commonly used:

- carding;
- air laying;
- meltblown (spun laid); and
- wet-laying (or paper route) including both liquid-laying and foam-laying technologies.

[0005] The cohesion of the nonwoven may be produced during its manufacture or also in a subsequent step. This consolidation may be conducted mechanically (needle punching), thermally, or chemically (incorporating a chemical binder) for example.

[0006] Nonwovens are distinguished from paper-type fibrous substrates in that they comprise long fibers whereas fibers constituting paper are shorter. By definition, paper is a web-like product formed of short natural fibers having a length of less than 4 mm. Naturally, paper comprises various fillers, sizing agents, retention agents etc, but the only fibrous constituent is short natural fiber.

[0007] Nevertheless, the prior art also comprises nonwovens containing, in addition to synthetic fibers, short cellulose fibers. These are generally made by the wet-laid process.

[0008] Regardless, generally, bearing in mind the presence of long synthetic fibers having preferably fiber diameters exceeding 0.8 μm, a nonwoven does not comprise as many hydrogen bonds, which give paper a certain strength.

[0009] Consequently, the mechanical properties of nonwovens depend not only on the nature and quantity of fibers used, but also how they are made. In this context, a hydroentangling or needle punching step or a binding agent being present may improve the cohesion of the nonwoven at equal basis weight.

[0010] The Applicant has developed a new nonwoven whose strength properties are improved compared to nonwovens of the prior art, and without increasing its weight or the ratio between its weight per unit of surface area and its thickness.

DESCRIPTION OF THE INVENTION

[0011] The Applicant has discovered that incorporating a low quantity of nanofibrillar cellulose (NFC) in the nonwoven according to the invention improves the mechanical properties compared with nonwovens of the prior art with the same weight and thickness.

[0012] More specifically, the present invention relates to a wet-laid nonwoven comprising natural and/or synthetic fibers. It further comprises nanofibrillar cellulose in an amount of between 0.1 and 20% by dry weight compared with the dry weight of said nonwoven.

[0013] Generally, the nonwoven according to the invention has a tensile strength (ISO standard 1924-2) in the machine direction that is, when divided by basis weight, greater than 5 Nm/g. It is advantageously between 5 and 12 Nm/g. Further, its tear resistance (ISO standard 1974 - 1990 E) in the machine direction is, when divided by basis weight, generally greater than 5 mNm^2/g. It is advantageously between 5 and 15 mNm^2/g.

[0014] According to a further specific embodiment, the wet-laid nonwoven may comprise up to 99% natural fibers, preferably between 0 and 89% natural fibers, or advantageously between 39.9 and 89%, and more advantageously between 59.9 and 80%, by dry weight compared with the dry weight of said nonwoven.

[0015] Further, the wet-laid nonwoven comprises between 0 and 90% synthetic fibers, preferably between 10 and 60%, more advantageously between 19.9 and 60%, even more advantageously between 19.9 and 40%, by dry weight compared with the dry weight of said nonwoven.

[0016] In an advantageous manner, the nonwoven comprises between 0.1 and 20% nanofibrillar cellulose, more advantageously between 1 and 5%, by dry weight compared with the dry weight of said nonwoven.

[0017] It advantageously comprises between 0.1 and 20% nanofibrillar cellulose when the nonwoven comprises up to 90% synthetic fibers, which does not mean that the nonwoven is necessarily devoid of natural fibers.

[0018] The nonwoven identified in the invention is advantageously constituted of x% natural fibers, y% synthetic fibers, and z% NFC. All the intermediate percentages resulting from at least two upper and/or lower values of the ranges indicated above are also within the scope of the invention, such that $x + y + z = 100$.

[0019] In other words, these percentages explicitly disclose a wet-laid nonwoven comprising 80% natural fibers, 5% NFC and 15% synthetic fibers, by dry weight compared with the dry weight of said nonwoven. In the same manner, the nonwoven comprising 30% natural fibers, 60% synthetic fibers and 10% NFC is explicitly disclosed.

[0020] A further feature of the nonwoven of the present invention is that it comprises long fibers in an amount of at least 15% by dry weight of the nonwoven, i.e. fibers having a length of at least 5 mm, preferably more than 7 mm, more preferably more than 10 mm. Advantageously the nonwoven of the invention comprises long fibers in an amount of at least 18%, more advantageously at least 25% by dry weight of the nonwoven. The long fibers may be synthetic fibers, natural fibers or a combination of both.

[0021] "Wet-laid nonwoven" is understood to mean a nonwoven obtained from an aqueous suspension of synthetic fibers, optionally together with natural fibers, and nanofibrillar cellulose. This suspension may also comprise at least one surfactant. It may then be in the form of a foam, whereby the nonwoven is obtained from a foam-laid suspension of synthetic fibers.

[0022] As already stated, a nonwoven comprises entangled fibers arranged randomly or more regularly. The fibers may be held together by using a binder, an adhesive, heat or pressure, or by needle punching for example.

[0023] In the scope of the present invention, the synthetic fibers have a relatively high length/diameter ratio, for example of the order of 600/1. It may be comprised between 100 and 1000. The length of the synthetic fibers is advantageously comprised between 0.1 cm and 4 cm, advantageously between 0.3 and 3 cm. Their diameter or thickness may be comprised between 2 and 40 micrometers, advantageously between 10 and 20 [micrometers]. Further, synthetic fibers having different lengths and diameters may be used in the same nonwoven.

[0024] Synthetic fibers, a term also encompassing mineral fibers, may in particular be chosen here from the group comprising:

- semi-synthetic fibers derived from cellulose, for example viscose, rayon, or lyocell, cellulose acetate;
- glass carbon, basalt, silicon, ceramic and metallic fibers;
- synthetic polymer fibers; and
- their mixtures.

[0025] According to a preferred embodiment, the synthetic polymer fibers are chosen from the group comprising polyamide, polyaramide, polyethylene, polypropylene, polyester, polyvinyl chloride fibers, and their mixtures.

[0026] In addition to the above listed options for synthetic fibers, also so called synthetic pulp may be used in combination with the above mentioned synthetic fibers or in place thereof. The synthetic pulp is discussed in detail in US-B2-8,513,147. In brief it is made of unicomponent fibers that rapidly disperse or dissolve in water and may be produced by melt-blowing or melt-spinning. The fibers may be prepared from a single sulfopolyester or a blend of the sulfopolyester with a water-dispersible or water non-dispersible polymer. Thus, the fiber of the present invention, optionally, may include a water-dispersible polymer blended with the sulfopolyester. In addition, the fiber may optionally include a water non-dispersible polymer blended with the sulfopolyester, provided that the blend is an immiscible blend. The synthetic pulp may also be manufactured of multicomponent fibers comprising a water-dispersible sulfopolyester and one or more water non-dispersible polymers.

[0027] Natural fibers are advantageously chosen from the group comprising cellulose-based natural fibers, for example fibers from wood pulp, cotton, sisal, abaca, kenaf, jute fibers, bagasse fibers, hemp fibers, flax fibers and their mixtures. Depending on their origin, these natural fibers may be short (cellulose) or long (bagasse, hemp, flax).

[0028] According to a specific embodiment, the natural fibers, and more specifically the cellulose-based fibers, may be bleached fibers. Bleaching of fibers is understood to mean that the suspension of fibers, or pulp, has undergone a bleaching treatment according to techniques known to the person skilled in the art.

[0029] Further, according to another specific embodiment, the natural fibers, and more specifically the cellulose-based fibers, are advantageously refined to less than 21 °SR, even more advantageously between 10 and 20 °SR.

[0030] The refining corresponds to a dewatering index, expressed in Schopper-Riegler degrees (°SR). The more the pulp (suspension of natural fibers) is refined, the more water is retained. A paper whose pulp has been less refined has low resistance properties, such as for instance paper towel. Refining allows the fibers to branch.

[0031] Refining hydrates and fibrillates the cellulose fibers, thus increasing the specific surface area of the fibers, whereby the number of hydrogen bonds between fibers is increased. This increase improves the mechanical properties of the fibrous material.

[0032] Generally, in the paper industry, the fibers are refined to between 25 and 90 °SR, on average between 50 and 60 °SR.

[0033] Regarding nanofibrillar cellulose (NFC), this is a nanofiber whose diameter, or thickness, is advantageously comprised between 5 and 100 nanometers, more advantageously of the order of 20 nanometers. Further, the length of the nanofibrils is less than 1 micrometer. It is advantageously comprised between 0.1 and 1 micrometer, more advantageously between 400 and 500 nanometers.

[0034] Nanofibrillar cellulose may in particular be prepared by dissolving pulp from resinous wood, from long fibers (softwood cellulose pulp), or from a mixture of pine and spruce.

[0035] This dissolving of pulp may undergo the following treatment to produce nanofibrillar cellulose:

- first refining to 25 °SR;
- enzymatic treatment at 50°C in the presence of endoglucanase;
- second refining to 80 °SR; and
- several passes in a homogenizer.

[0036] The synthetic fibers come from synthetic materials, i.e. man-made materials. However, these synthetic materials may be biodegradable and/or compostable.

[0037] Biodegradable/compostable synthetic fibers may in particular be chosen from the group comprising PLA-type polyesters (polylactic acid), PHA/PHB (polyhydroxyalkanoate/polyhydroxybutyrate), and PCL (polycaprolactone) or similar; polyvinyl alcohol; cellulose acetate; and their mixtures.

[0038] Accordingly, depending on the nature of these constituents, the nonwoven identified in the invention may be biodegradable and/or compostable.

[0039] The synthetic fibers and/or the natural fibers and/or the nanofibrillar cellulose may come from respective recycling processes.

[0040] According to a specific embodiment, the nonwoven identified in the invention may also comprise additives such as pigments, inorganic fillers (titanium, calcium carbonate, kaolin, etc.) binders, strengthening agents, dispersants, and retention agents. These additives are preferably added by impregnating the nonwoven with a solution comprising at least one additive. They may also be added to the aqueous suspension of fibers.

[0041] The retention agent is advantageously a cationic polymer. The person skilled in the art will know how to choose the right compound. It is added into the aqueous suspension of fibers. It advantageously represents between 0.01% and 2% by dry weight of the suspension (100 g to 20 kg per ton of fibers/NFC).

[0042] The binding agent may in particular be chosen from the group comprising binders based upon polyacrylics, polystyrene acrylics, polyvinyl acetate, polyvinyl acrylate, polystyrene butadienes, polyethylene vinyl acetate, polyvinyl chloride, polyvinyl alcohol and its derivatives (polyvinyl ethylalcohol), polyethylene vinyl chloride, polyurethane, polyamides, polyolefins (polyethylene and polypropylene), polyesters, elastomers of natural origin, urea formaldehyde, melamine formaldehyde, phenol formaldehyde, polymers from starch, and their mixtures.

[0043] These additives represent advantageously between 5 and 95 parts by dry weight, per 100 parts by weight of the dry nonwoven, even more advantageously between 20 and 60 parts by dry weight.

[0044] Generally, the nonwoven that is identified in the invention may have a basis weight advantageously between 5 and 1000 g/m^2, more advantageously between 40 and 160 g/m^2.

[0045] The ratio between the thickness and the weight per unit of surface area (basis weight) of the nonwoven is commonly denoted as "bulk", which is advantageously between 2 and 6 cm^3/g, more advantageously of the order of 4.5 cm^3/g.

[0046] Generally, the thickness of the nonwoven increases with basis weight whereas the bulk advantageously remains constant.

[0047] According to a specific embodiment, the wet-laid nonwoven according to the invention may comprise one or more layers of compositions that are identical or different.

[0048] Advantageously, the wet-laid nonwoven according to the invention has air permeability (related to porosity) greater than 50 $L/m^2/s$, advantageously between 500 and 2000 $L/m^2/s$.

[0049] The present invention further relates to a manufacturing process for the wet-laid nonwoven described hereinbefore, according to which, on a fiber web machine, a wet-laid suspension of at least synthetic fibers is deposited onto a foraminous surface, wherein nanofibrillar cellulose is added before, during or after depositing the synthetic fibers on the foraminous surface such that the nonwoven is impregnated with NFC for its entire thickness.

[0050] The present invention further relates to a manufacturing process for the wet-laid nonwoven, wherein the resulting nonwoven is dried.

[0051] The present invention further relates to a manufacturing process for the wet-laid nonwoven, wherein the nonwoven is soaked with a solution comprising at least one additive and the resulting nonwoven is dried.

[0052] According to a specific embodiment, the suspension of synthetic fibers may also comprise at least one surfactant. Therefore this is a suspension that may be in the form of a foam. More specifically, this is a foam comprising fibers in suspension.

[0053] The NFC may be added in the form of a suspension in water or in foam:

- in the headbox to be mixed with the fiber suspension,
- before the headbox into at least one fiber suspension,
- during depositing the synthetic fibers on the foraminous surface, for instance by means of spraying on the fibrous suspension,
- after depositing the synthetic fibers on the foraminous surface, for instance by means of spraying on the nonwoven to be formed,
- optionally to be mixed with natural fibers prior to their deposition, or
- after the nonwoven is formed, for instance by spraying on the nonwoven such that the NFC penetrates into the thickness of the nonwoven, whereby the nonwoven is impregnated with NFC throughout its entire thickness.
- after the nonwoven is formed, for instance by means of an impregnation step, where both faces of the nonwoven are in contact with the NFC prior to treatment in a nip between two rolls (or one roll and a counter-surface), which make the NFC penetrate into the thickness of the nonwoven, whereby the nonwoven is impregnated with NFC throughout its entire thickness. This step is conducted before, during or after the optional impregnation of the nonwoven with a suspension comprising at least one binding agent. However, according to a specific embodiment, NFC may also be added during a step where the nonwoven is impregnated with a suspension comprising at least one binding agent.

[0054] The NFC suspension may also comprise at least one surfactant. It can therefore be in the form of a foam. Therefore suspension in water is also understood to mean a suspension in the form of a foam. More specifically, this is a foam comprising NFC in suspension.

[0055] NFC and synthetic fibers, optionally together with natural fibers, represent advantageously from 0.01 to 1% by dry weight compared with the dry weight of the suspension of synthetic fibers, optionally together with natural fibers, advantageously between 0.01 and 0.1 %.

[0056] The wet-laid nonwoven identified in the invention may in particular find application in the fields of healthcare, medical, surgical, personal care (wipes, hair-removal strips, etc.), textiles (clothing), geotextiles, construction materials, decoration (wallpaper), automotive, filtration, agriculture, furniture, leisure, and domestic use.

[0057] The invention and the benefits it brings will be clearer upon reading the following figures and examples, given to illustrate the invention and not to limit it in any way.

FIGURES

[0058]

Figure 1 represents the tensile strength of nonwovens according to the invention as a function of basis weight, compared to a nonwoven of the prior art example 1.

Figure 2 represents the tear resistance of nonwovens according to the invention as a function of basis weight, compared to a nonwoven of the prior art example 1.

Figure 3 represents the permeability of nonwovens according to the invention as a function of basis weight, compared to a nonwoven of the prior art example 1.

EXAMPLES OF EMBODIMENTS OF THE INVENTION

Example 1:

[0059] Thirteen wet-laid nonwovens were prepared from the compositions in table 1, according to the classic preparation techniques for a wet-laid nonwoven, in this case liquid-laying on a foraminous surface.

Table 1: Compositions of the 13 wet-laid nonwovens prepared.

Example	basis weight (g/m^2)	natural fibers(% by weight)	synthetic fibers (% by weight)	NFC (% by weight)	MD tensile strength index (Nm/g)	MD tear resistance index (mNm^2/g)
1 (PA)	43 37 32	cellulose[a] 81%	Polyester[b] 19%	0	6.15 5.21 5.17	7.98 6.91 6.41
2 (INV)	43 37 32	cellulose 81%	polyester 18%	1	6.97 7.4 6.45	8.82 7.89 7.36
3 (INV)	43 37 32	cellulose 79,5%	polyester 18%	2.5	8.76 7.16 6.27	9.68 9.31 7.73
4 (INV)	43 37 32 21	cellulose 78%	polyester 17%	5	10.37 8.34 8.47 7.75	14.72 10.81 10.59 9.43

(a) the natural fiber furnish is formed of 33.3% Celbi PP high dry FSC cellulose pulp, 34.6% Joutseno Pine 90 PEF cellulose pulp, and 32.1% Alabama River softwood cellulose pulp
(b) the synthetic fiber furnish is formed of Dacron fibers (10 mm 1.7 dtex) from polyester recycling
MD: in the machine direction
PA: Wet-laid nonwoven according to the prior art
INV: Wet-laid nonwoven according to the invention

[0060] The 13 nonwovens in examples 1 - 4 were made on a conventional machine for preparing wet-laid nonwovens. Its operation rate is 20 m/min.

[0061] For each of the 13 experiments (examples 1 - 4), 400 linear meters 50 cm wide of each were produced.

[0062] The nonwovens were made from a suspension comprising 0.7% by weight nanofibrillar cellulose, natural fibers and synthetic fibers, compared with the total weight of the suspension.

[0063] The cellulose fibers (in the form of a paper pulp sheet: 40 kg) are first added to the pulper for 10 min. The synthetic fibers (9 kg) and the 2% solids content NFC are then added; that is, for 1%, 2.5% and 5% respectively: 22.7 liters (i.e. 0.45 kg if it were dry), 56.8 liters (i.e. 1.13 kg if it were dry) and 113.5 liters (i.e. 2.27 kg if it were dry).

[0064] 243 mL of Kymene are then added (agent for wet strength), and 19 mL Hydroperm (dispersing agent).

[0065] The total volume of the suspension is made up to 6436 liters (i.e. about 0.7% by weight of fibers and nanofibrillar cellulose, i.e.: 7 g/L).

[0066] These nonwovens have been prepared according to the following steps:

- depositing a wet-laid suspension of synthetic and natural fibers and NFC on a forming wire so as to form a nonwoven;
- drying the resulting nonwoven.

[0067] The tensile strength, tear resistance, and air permeability properties were then measured.

Tensile strength (figure 1)

[0068] Generally, at equal basis weight, incorporating NFC improves the tensile strength. So the nonwoven of the prior art at 43 g/m^2 has similar properties to wet-laid nonwovens of the invention at 32 g/m^2 (example 1 vs. examples 2 - 4 at 32 g/m^2).

[0069] When 5% NFC is added, the tensile strength improvement is 70% on average for nonwovens from 32 to 43 g/m^2.
[0070] The nonwoven of the invention at 21 g/m^2 comprising 5% NFC (example 4) has similar tensile strength to that of the nonwoven at 32 g/m^2 of the prior art (example 1).

Tear resistance (figure 2)

[0071] The presence of NFC improves the tear resistance. For example, it is increased by 100% for a nonwoven at 43 g/m^2 comprising 5% NFC (example 1 vs. example 4).
[0072] Further, the nonwoven of the invention at 32 g/m^2 comprising 2.5% NFC has similar properties to that of a nonwoven of the prior art at 43 g/m^2 (example 1 vs. example 3).
[0073] The nonwoven of the invention at 21 g/m^2 comprising 5% NFC (example 4) has similar tear resistance to that of the nonwoven of the prior art at 32 g/m^2 (example 1).

Air permeability (figure 3)

[0074] The air permeability of nonwovens according to the invention comprising NFC is lower than that of nonwovens of the prior art. However, this decrease is less than 10% when the nonwoven comprises from 1 to 5% NFC and has basis weight between 32 and 43 g/m^2.
[0075] Regarding the wet-laid nonwoven comprising 5% NFC and having basis weight of 21 g/m^2, the porosity is clearly greater than that of the nonwoven of the prior art at 32 g/m^2.
[0076] Consequently, adding NFC is not contrary to maintaining an open nonwoven structure.

Conclusions

[0077] These examples show that adding NFC maintains the mechanical properties of a wet-laid nonwoven while reducing its basis weight, thereby reducing the necessary quantity of natural and synthetic fibers (of the order of 25% in this case).

Example 2:

[0078] Three wet-laid nonwovens were prepared from compositions in table 2, according to the classic preparation techniques for a wet-laid nonwoven i.e. in this case liquid-laying on a foraminous surface.

Table 2: compositions of three prepared wet-laid nonwovens

Example	basis weight (g/m^2)	natural fibers (% by weight)	synthetic fibers (% by weight)	NFC (% by weight)	tensile strength index (Nm/g)	tear resistance index (mNm^2/g)
1b (PA)	60.2	cellulose 0%	Polylactic acid[(c)] 100%	0	0 (not measurable)	0.21
2b (INV)	65.6	cellulose 0%	Polylactic acid[(c)] 91%	9	9.6	5.83
3b (INV)	71.7	cellulose 0%	Polylactic acid[(c)] 84%	16	13.24	10.72
[(c)] Polylactic acid fibers (PLA) (6 mm, 1.7 dtex) MD: in the machine direction PA: wet-laid nonwoven according to the prior art INV: wet-laid nonwoven according to the invention						

[0079] The three nonwovens in examples 1b to 3b were manufactured on a Frank sheet-former or similar device well known to the person skilled in the art. A retention agent (Percol 1830 by BASF) was used at 0.2% dry weight compared with fiber dry weight.
[0080] The following were used: for example 1 b, 2 g of PLA fibers; for example 2b, 2 g of PLA and 0.2 g NFC; and for example 3b, 2 g of PLA fibers and 0.4 g NFC. In all examples NFC and PLA fibers were mixed in water to form a suspension prior to feeding such on the Frank sheet-former.
[0081] The quantity of retention agent has been adjusted as a function of the quantity of fibers (PLA and NFC) used

to obtain a quantity equal to 0.2% of the nonwoven. The resulting sheet is dried on a glazing machine between two canvases for 5 minutes.

[0082] The tensile strength, tear resistance, and air permeability properties were then measured (See tables 2 and 3).

Table 3: air permeability of nonwovens 1 b, 2b and 3b

sample	1b (PA)	2b (INV)	3b (INV
Textest Porosity at 200 Pa (L/m^2/s)	Not measurable	1058	299

Tensile strength

[0083] Adding NFC to the mixture of synthetic fibers considerably increases the mechanical properties of the nonwoven and in particular the tensile strength. A nonwoven made only of synthetic fibers (here PLA) has no mechanical cohesion, since the synthetic fibers cannot generate bonds between themselves in the wet-laid nonwoven manufacturing process (the paper route). Therefore the tensile strength cannot be measured.

[0084] By adding 10% NFC compared to the quantity of synthetic fibers (example 1 b), it is possible to generate bonds between the synthetic fibers due to the NFC and to reach remarkable tensile strength index: 9.6 Nm/g for example 2b and 13.24 Nm/g for example 3b, respectively.

Tear resistance

[0085] Similarly to tensile strength, tear resistance was increased substantially. Nonwoven 1 b not containing NFC has a relatively low tear index value: 0.21 mNm^2/g. Incorporating 10% and 20% NFC in nonwovens 2b and 3b respectively increased the tear resistance index to values of 5.83 mNm^2/g and 10.72 mNm^2/g respectively, i.e. 2700% and 5100% increase respectively compared with the initial nonwoven.

Air permeability

[0086] The Textest air permeability measurement device could not measure air permeability on the nonwoven product with only PLA fibers (example 1a), as the nonwoven was destroyed when air passed through the sample. By contrast the nonwovens containing NFC were measureable and have values greater than 50 L/m^2/s and therefore in the range of a classic nonwoven, in particular for example 2b with a value of 1058 L/m^2/s.

Conclusions:

[0087] These examples show that adding NFC to a mixture of fibers constituted only of synthetic fibers generates cohesion between the synthetic fibers to allow a nonwoven web to be produced. Increasing the quantity of NFC also increases the mechanical properties of a wet-laid nonwoven. Therefore this means the quantity of synthetic fibers required can be reduced.

Example 3:

[0088] Three wet-laid nonwovens were prepared from compositions in table 4, according to the classic preparation techniques for a wet-laid nonwoven, i.e. in this case liquid-laying on a foraminous surface.

Table 4: compositions of three prepared wet-laid nonwovens

Example	basis weight (g/m^2)	natural fibers (% by weight)	Mineral Fibers (% by weight)	NFC (% by weight)	tensile strength index (Nm/g)	tear resistance index (mNm^2/g)
1c (PA)	73.9	cellulose 0%	Glass Fibers[(d)] 100%	0	0 (not measurable)	0.22
2c (INV)	78	cellulose 0%	Glass Fibers[(d)] 91%	9	5.13	7.49

(continued)

Example	basis weight (g/m^2)	natural fibers (% by weight)	Mineral Fibers (% by weight)	NFC (% by weight)	tensile strength index (Nm/g)	tear resistance index (mNm^2/g)
3c (INV)	83.3	cellulose 0%	Glass Fibers[(d)] 84%	16	13.33	16

[(d)] Glass Fibers (6 mm, 0.85 dtex)
MD: in the machine direction
PA: wet-laid nonwoven according to the prior art
INV: wet-laid nonwoven according to the invention

[0089] The three nonwovens in examples 1c to 3c were manufactured on a Frank sheet-former or similar device well known to the person skilled in the art. A retention agent (Percol 1830 by BASF) was used at 0.2% dry weight compared with fiber dry weight.

[0090] The following were used: for example 1c, 2 g of Glass Fibers; for example 2c, 2 g of Glass Fibers and 0.2 g NFC; and for example 3c, 2 g of Glass Fibers and 0.4 g NFC. In all examples NFC and Glass Fibers were mixed in water to form a suspension prior to feeding such on the Frank sheet-former.

[0091] The quantity of retention agent has been adjusted as a function of the quantity of fibers (Glass Fibers and NFC) used to obtain a quantity equal to 0.2% of the nonwoven. The resulting sheet is dried on a glazing machine between two canvases for 12 minutes at 100 °C.

[0092] The tensile strength, tear resistance, and air permeability properties were then measured (See tables 4 and 5).

Table 5: air permeability of nonwovens 1c, 2c and 3c

sample	1c (PA)	2c (INV)	3c (INV)
Textest Porosity at 200 Pa ($L/m^2/s$)	Not measurable	1203	137

Tensile strength

[0093] Adding NFC to the mixture of mineral fibers considerably increases the mechanical properties of the nonwoven and in particular the tensile strength. A nonwoven made only of mineral fibers (here Glass Fibers) has no mechanical cohesion, since the mineral fibers cannot generate bonds between themselves in the wet-laid nonwoven manufacturing process (the paper route). Therefore the tensile strength cannot be measured.

[0094] By adding 10% NFC compared to the quantity of mineral fibers (example 1c), it is possible to generate bonds between the mineral fibers due to the NFC and to reach remarkable tensile strength index: 5.13 Nm/g for example 2c and 13.33 Nm/g for example 3c, respectively.

Tear resistance

[0095] Similarly to tensile strength, tear resistance was increased substantially. Nonwoven 1c not containing NFC has a relatively low tear index value: 0.22 mNm^2/g. Incorporating 10% and 20% NFC in nonwovens 2c and 3c respectively increased the tear resistance index to values of 7.49 mNm^2/g and 16 mNm^2/g respectively, i.e. 3400% and 7200% increase respectively compared with the initial nonwoven.

Air permeability

[0096] The Textest air permeability measurement device could not measure air permeability on the nonwoven product with only Glass Fibers (example 1c), as the nonwoven was destroyed when air passed through the sample. By contrast the nonwovens containing NFC were measureable and have values greater than 50 $L/m^2/s$ and therefore in the range of a classic nonwoven, in particular for example 2c with a value of 1203 $L/m^2/s$.

Conclusions

[0097] These examples show that adding NFC to a mixture of fibers constituted only of mineral fibers generates cohesion between the synthetic fibers to allow a nonwoven web to be produced. Increasing the quantity of NFC also increases the mechanical properties of a wet-laid nonwoven. Therefore this means the quantity of minerals fibers required can be reduced.

[0098] The research leading to these results received financial support under the Seventh Framework Program of the European Community in accordance with grant agreement No. 228802.

Claims

1. A wet-laid nonwoven comprising long fibers in an amount of at least 15% by dry weight compared with the dry weight of said nonwoven, and nanofibrillar cellulose (NFC) in an amount of between 0.1 and 20% by dry weight compared with the dry weight of said nonwoven with the balance to 100 percent comprising synthetic and/or natural fibers, the long fibers having a length of at least 5 mm and being selected from synthetic and/or natural fibers, and the nonwoven being impregnated with the NFC for its entire thickness.

2. The wet-laid nonwoven according to claim 1, ***characterized* in that** it comprises synthetic fibers in an amount of between 0 and 90% by dry weight compared with the dry weight of said nonwoven.

3. The wet-laid nonwoven according to claim 1 or 2, ***characterized* in that** it comprises natural fibers in an amount of up to 99% by dry weight compared with the dry weight of said nonwoven.

4. The wet-laid nonwoven according to any one of claims 1 to 3, ***characterized* in that** it has a tensile strength in the machine direction greater than 5 Nm/g, and tear resistance in the machine direction greater than 5 mNm^2/g.

5. The wet-laid nonwoven according to any one of claims 1 to 3, ***characterized* in that** the synthetic fibers are chosen from the group comprising glass, carbon, silicon, ceramic, metallic, polymeric fibers, synthetic fibers derived from cellulose, and their mixtures.

6. The wet-laid nonwoven according to any one of claims 3 or 5, ***characterized* in that** the natural fibers are cellulose fibers chosen from the group comprising fibers from wood pulp, cotton fibers, sisal fibers, abaca fibers, kenaf fibers, jute fibers, bagasse fibers, hemp fibers, flax fibers and their mixtures.

7. The wet-laid nonwoven according to any one of claim 6, ***characterized* in that** the natural fibers are cellulose fibers refined to less than 21 °SR.

8. The wet-laid nonwoven according to any one of claims 1 to 7, ***characterized* in that** it has a bulk between 2 and 6 cm^3/g.

9. A method of manufacturing the wet-laid nonwoven according to any one of claims 1 to 8, in which method a suspension of synthetic and/or natural fibers is deposited on a foraminous surface of a fiber web machine, ***characterized* by** adding nanofibrillar cellulose (NFC) to the suspension before, during or after depositing the suspension on the foraminous surface such that the nonwoven is impregnated with NFC for its entire thickness.

10. The method of manufacturing the wet-laid nonwoven according to claim *9****characterized*** **by** adding the NFC to one of the synthetic fiber suspension, to the natural fiber suspension and to a suspension of their mixture prior to depositing the suspension on the foraminous surface.

11. The method of manufacturing the wet-laid nonwoven according to claim 9 or *10,* ***characterized* by** applying the NFC onto the suspension deposited on the foraminous surface.

12. The method of manufacturing the wet-laid nonwoven according to any one of claims 9 to 11, ***characterized* by** impregnating the wet-laid nonwoven with the nanofibrillar cellulose after the formation of the nonwoven.

13. The method of manufacturing the wet-laid nonwoven according to claims 9 or *12,* ***characterized* by** drying the nonwoven before the impregnation thereof with the nanofibrillar cellulose.

14. The method of manufacturing the wet-laid nonwoven according to any one of claims 9 - 13, ***characterized* by** soaking the wet-laid nonwoven with a solution comprising at least one additive before drying of the nonwoven the additive being at least one of nanofibrillar cellulose, pigments, inorganic fillers (titanium, calcium carbonate, kaolin,

etc.) binders, wet and/or dry strengthening agents, dispersants, and retention agents

15. The method of manufacturing the wet-laid nonwoven according to claim 9, ***characterized*** **in that** the nanofibrillar cellulose is added, in the form of a suspension in water, in the headbox.

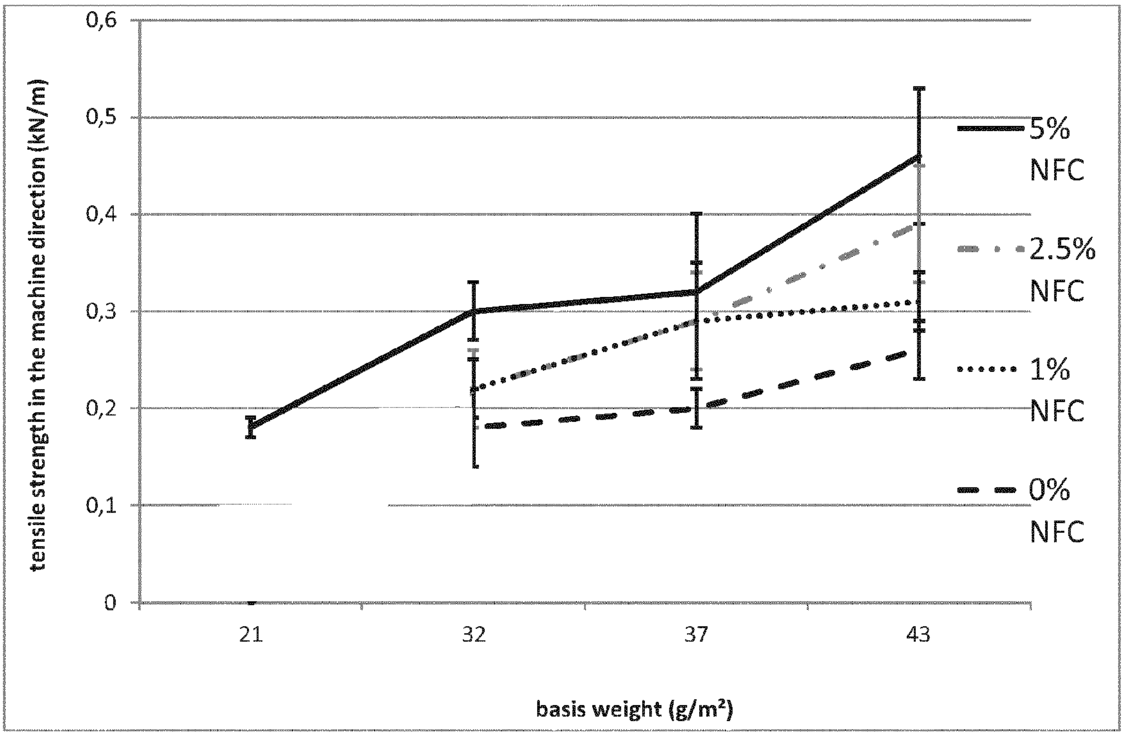
0,6
0,5
0,4
0,3
0,2
0,1
0
tensile strength in the machine direction (kN/m)
21
32
37
43
basis weight (g/m²)
5% NFC
2.5% NFC
1% NFC
0% NFC

Fig. 1

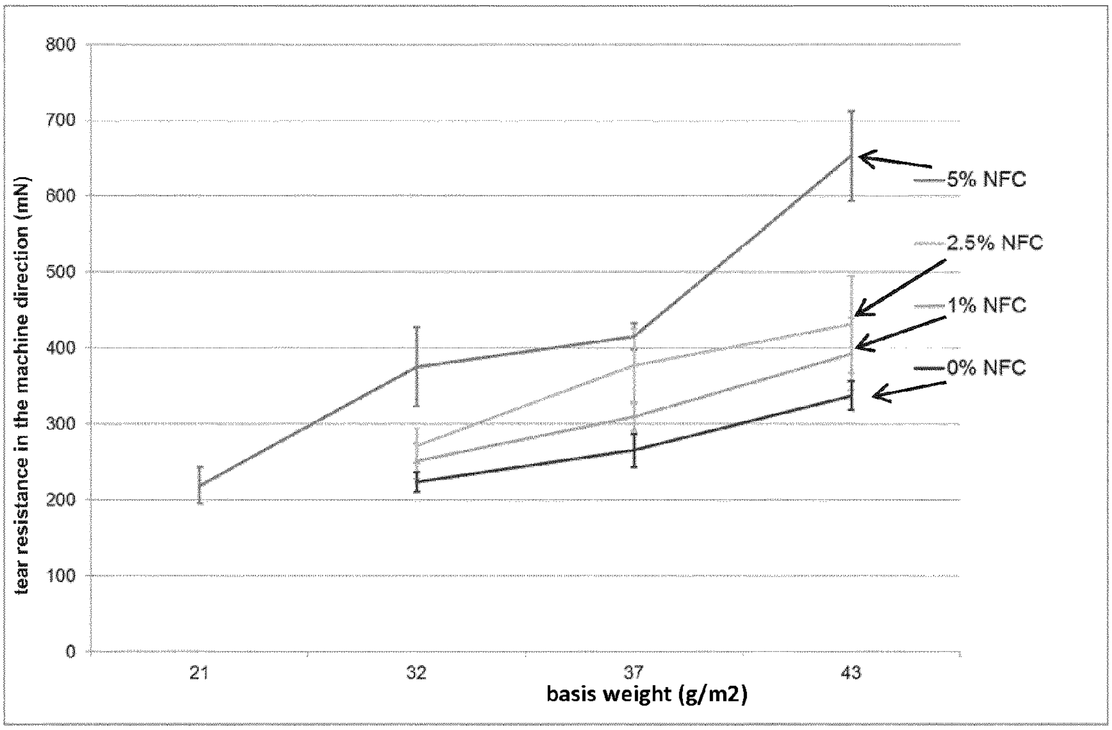
800
700
600
500
400
300
200
100
0
tear resistance in the machine direction (mN)
21
32
37
43
basis weight (g/m2)
5% NFC
2.5% NFC
1% NFC
0% NFC

Fig. 2

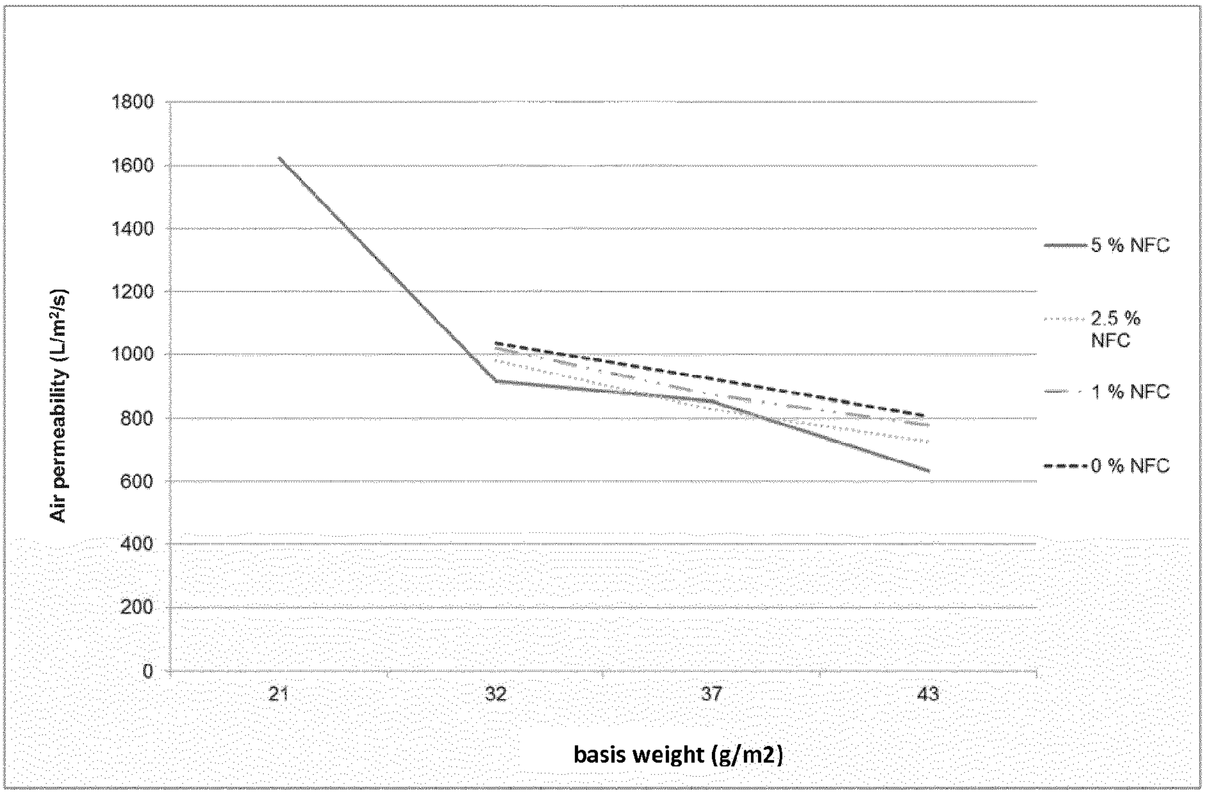
1800
1600
1400
1200
1000
800
600
400
200
0
Air permeability (L/m²/s)
21
32
37
43
basis weight (g/m2)
5 % NFC
2.5 % NFC
1 % NFC
0 % NFC

Fig. 3

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EUROPEAN SEARCH REPORT

Application Number
EP 14 16 0857

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	17 June 2014	Ponsaud, Philippe

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X : particularly relevant if taken alone
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