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(54) Title: METHOD FOR PRODUCING A TEXTILE COMPOSITE, ESPECIALLY FOR OUTDOOR APPLICATIONS, WHICH CONTAINS AT LEAST ONE LAYER OF POLYMERIC NANOFIBERS, AND A TEXTILE COMPOSITE PREPARED BY THIS METHOD

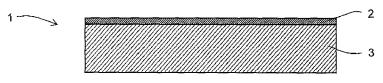


Fig. 1

(57) Abstract: The invention relates to a method for producing a textile composite, especially for outdoor applications, which contains at least one layer (2) of polymeric nanofibers deposited on a textile carrier layer (3), in which at least one hydrophobic agent in a liquid or plastic state is applied with plasma spraying to the textile carrier layer (3) after deposition of the layer (2) of polymeric nanofibers and after connecting the two layers by a binder, whereby the hydrophobic agent is applied to the textile carrier layer (3) from the side opposite the side where layer (2) of polymeric nanofibers has been deposited. The invention also relates to a textile composite (1), especially for outdoor applications, which contains a layer (2) of polymeric nanofibers deposited on a textile carrier layer (3), prepared by this method.





Method for producing a textile composite, especially for outdoor applications, which contains at least one layer of polymeric nanofibers, and a textile composite prepared by this method

### 5 Technical field

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The invention relates to a method for producing a textile composite, especially for outdoor applications, which contains at least one layer of polymeric nanofibers deposited on a textile carrier layer.

The invention also relates to a textile composite, particularly for outdoor applications, which contains a layer of polymeric nanofibers deposited on a textile carrier layer.

#### Background art

Nowadays, a number of the so-called outdoor textiles are known, which prevent penetration of water from the external environment, but at the same time they are permeable to water vapor from the internal environment. Most of them are based on using a hydrophobic material and/or applying hydrophobic surface treatment, or layering several identical or different layers on one another. Progressively also appear composites containing as one of its layers a layer of polymeric nanofibers, whose interfibrous spaces are due to their small dimensions hardly permeable to water, but allow vapor to pass through them easily on the principle of diffusion. Examples of such composites are, for instance, the composites described in US 2011092122 or US 2008184453. Their disadvantage is the fact that their polymeric nanofibers mutually move or slip upon hydrostatic load of water column of approximately 300 mm, as a result of which the spaces between them become larger, which allows penetration of water. Although the achieved value of hydrostatic resistance of these composites is higher than that of the outdoor textiles, for most outdoor applications it is not sufficient.

Partial solution to this problem is represented by the composites proposed, for example, in US 2008220676 or US 2009176056, in which a layer

of polymeric nanofibers is coated with a hydrophobic substance. Their disadvantage is the fact that the hydrophobic substance is deposited in droplets only on the surface of this layer, or on the surface of its nanofibers, but their interfibrous spaces are mostly free, and when a higher hydrostatic load is applied, approximately 1,300 mm of water column, then again mutual slippage of the individual nanofibers occurs and that leads to water penetration.

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To remove this problem, a method for increasing hydrophobic properties of a layer of polymeric nanofibers was disclosed in CZ PV 2011-306, which consists in that emulsion of a hydrophobic agent is applied to the layer of polymeric nanofibers by spraying. The drawback of this method is the fact that part of the hydrophobic agent is deposited purposefully in the interfibrous spaces of the layer of polymeric nanofibers and closes them, by which means it substantially reduces its vapor permeability and breathability. As a result, in spite of increased hydrostatic resistance of this layer, its real applicability is limited.

Another method for increasing hydrophobic properties of a layer of polymeric nanofibers was proposed in CZ PV 2012-325. This method consists in that the hydrophobic agent is applied to the layer of polymeric nanofibers in a liquid or plastic state by low pressure vacuum plasma spraying. In this manner, a uniform continuous film of the agent is formed on the surface of the polymeric nanofibers. The disadvantage of this process is the fact that the layer of polymeric nanofibers, having been treated in this manner, cannot be joined to other layers of material in the conventional manner, since its increased hydrophobic properties inhibit the penetration of a liquid binder into its structure and, consequently, there is no bonding between adjacent polymeric nanofibers. Due to this, the resulting composite is extremely predisposed to mechanical damage of the layer of nanofibers, or the layer separation, which considerably reduces its practical applicability.

The goal of the invention is to eliminate or at least reduce the disadvantages of the background art and provide a method which would enable to produce a textile composite, especially for outdoor applications, which would contain at least one layer of polymeric nanofibers connected to at least one

textile layer with sufficient resistance, while achieving at the same time high hydrostatic resistance, as well as vapor permeability and breathability.

The goal of the invention is also to provide a textile composite, especially for outdoor applications, which contains at least one layer of polymeric nanofibers prepared by this method.

# Principle of the invention

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The aim of the invention is achieved by a method for producing a textile composite, especially for outdoor applications, which contains at least one layer of polymeric nanofibers deposited on a textile carrier layer, whose principle consists in that after deposition of the layer of polymeric nanofibers and connecting the layers by a binder, at least one hydrophobic agent in a liquid or plastic state is applied by plasma spraying to the textile carrier layer, from the side opposite the side where the layer of polymeric nanofibers is deposited. In this process, the binder can penetrate into the inner structure of the layer of polymeric nanofibers which has not been pretreated, by which means this layer is reinforced and the resistance of its connection to the textile carrier layer increases. In addition, if the binder penetrates through its entire thickness of layer of polymeric nanofibers, it also protects it from abrasion from its outer side. The hydrophobic agent considerably increases the hydrophobic properties of the textile carrier layer, without reducing its vapor permeability and breathability due to the method of its application.

A suitable method for applying a binder to the textile carrier layer and/or layer of polymeric nanofibers is gravure printing, spraying or spray coating.

Should a need arise, prior to the application of the hydrophobic agent to the textile carrier layer by plasma spraying, the layer of polymeric nanofibers is overlaid by a cover layer - textile or non-textile, which is further connected to the layer of polymeric nanofibers and/or the textile carrier layer.

In another variant, the layer of polymeric nanofibers is overlaid by a cover layer after the application of the hydrophobic agent to the textile carrier layer.

So as to increase the hydrostatic resistance of the resulting composite, it is possible to apply a hydrophobic agent in a liquid or plastic state by plasma spraying to the cover layer formed by a textile prior to its connection to the layer of polymeric nanofibers and/or the textile carrier layer, and/or after it.

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In a special case, prior to the application of the hydrophobic agent to the textile carrier layer by plasma spraying, the layer of polymeric nanofibers is overlaid by the layer of polymeric nanofibers deposited on a textile carrier layer, whereby both textile carrier layers, prior to the application of the hydrophobic agent by plasma spraying to at least one of them, are connected to each other, preferably outside the area of the polymeric nanofibers deposited on them. Thus, a four-layer composite is formed, which consists of two mutually unconnected layers of polymeric nanofibers.

A suitable method for the application of the hydrophobic agent to the textile carrier layer or to the textile cover layer is low pressure vacuum plasma spraying. The amount of the hydrophobic agent is in this case up to 5 % of basis weight of the textile carrier layer, or the cover layer.

The aim of the invention is also achieved by a textile composite, especially for outdoor applications, which contains a layer of polymeric nanofibers deposited on a textile carrier layer, whose principle consist in that the layer of polymeric nanofibers and the textile carrier layer are connected by formations of a binder which extend into the inner structure of the layer of polymeric nanofibers, whereby on the fibers of the textile carrier layer is at least from one side formed a coating of at least one hydrophobic agent applied by plasma spraying. This enables to achieve a sufficiently resistant connection of the textile carrier layer and the layer of polymeric nanofibers, reinforcing the layer of polymeric nanofibers, as well as increasing the hydrostatic resistance of the textile carrier layer by plasma spraying, without reducing its vapor permeability and breathability.

The hydrophobic agent can be also applied to the layer of polymeric nanofibers by plasma spraying at least from one side.

If necessary, the layer of polymeric nanofibers is overlaid by a cover layer, which is connected to the layer of polymeric nanofibers and/or to the textile carrier layer by formations of the binder, thereby increasing the overall resistance of the textile composite and protection of the layer of polymeric nanofibers. In another variant of embodiment, the layer of polymeric nanofibers is overlaid by a cover layer, preferably textile, which is connected to the textile carrier layer by sewing or needling.

In order to increase the hydrostatic resistance of the entire composite, a coating of at least one hydrophobic agent applied by plasma spraying is created also on the fibers of the textile cover layer.

In yet another variant of embodiment, the layer of polymeric nanofibers is overlaid by a layer of polymeric nanofibers, deposited on a textile carrier layer.

The experiments proved that the most suitable material for the textile carrier layer was fleece, which constitutes the upper layer in the products prepared from the composite according to the invention.

Suitable hydrophobic agents for the application by plasma spraying include especially fluorinated carbohydrate-based hydrophobic agents, silicone-based hydrophobic agents and/or alkane-based hydrophobic agents. These agents are applied to the fibers of the textile carrier layer, or to the fibers of the cover layer in an amount of up to 5 % of basis weight of the textile carrier layer, or the basis weight of the cover layer.

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# **Description of drawings**

In the enclosed drawings, Fig. 1 schematically represents a cross-section of a variant of a textile composite according to the invention, Fig. 2 a cross-section of the second variant of a textile composite according to the invention and Fig. 3 a cross-section of the third variant of a textile composite according to the invention.

#### **Examples of embodiment**

In the method for producing a textile composite  $\underline{1}$  (Figs. 1 and 3), especially for outdoor applications, which contains at least one layer  $\underline{2}$  of polymeric nanofibers according to the invention, first a semi-finished product is

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formed, which contains at least one layer 2 of polymeric nanofibers and at least one textile carrier layer 3 formed by a standard textile fabric (knitted, woven, non-woven), whereby after connecting these layers 2, 3 by a suitable binder, e.g. fusible, at least one hydrophobic agent in a liquid or plastic state is applied to the textile carrier layer 3 by plasma spraying. This agent is at the same time deposited at least on the impacting parts of the surface of the individual fibers of the textile carrier layer 3, or on their entire surface, where it creates a continuous coating, thereby increasing substantially the hydrostatic resistance of this layer 3. Due to the fact that during plasma spraying it is on principle a very small amount of the hydrophobic agent that is applied, the inter-fibrous spaces of the textile carrier layer 3 cannot be filled up, or blocked, and so the textile carrier layer 3 retains substantially unchanged vapor permeability and breathability. If during the application of the hydrophobic agent a certain part of it penetrates through the entire thickness of the textile carrier layer 3, it is deposited at least on the impacting side of unillustrated formations of the binder connecting the textile carrier layer 3 and the layer 2 of polymeric nanofibers, and optionally also at least on the impacting side of the polymeric nanofibers, by which menas the hydrostatic resistance the layer 2 of polymeric nanofibers is further increased.

The resulting composite <u>1</u> thus combines the textile carrier layer <u>3</u>, having a considerably increased hydrostatic resistance, but also having the original high vapor permeability and breathability, with the layer <u>2</u> of polymeric nanofibers, which has thanks to its inner structure a high hydrostatic resistance, as well as vapor permeability and breathability, and whose hydrostatic resistance can be also increased as a side effect.

Furthermore, both layers  $\underline{2}$ ,  $\underline{3}$  of the textile composite  $\underline{1}$  (optionally in combination with at least one additional layer of a suitable material) can be connected by a commonly used method using a commonly used binder (binders), e.g., fusible, which can freely penetrate into their inner structure and in the case of the layer  $\underline{2}$  (layers) of polymeric nanofibers also through its entire thickness, making the connection of the layers  $\underline{2}$ ,  $\underline{3}$  of the composite  $\underline{1}$  sufficiently resistant, whereby, in addition, the layer  $\underline{2}$  (layers) of polymeric nanofibers is reinforced by the binder which penetrated into its inner structure.

At the same time, the binder, which penetrated through the entire thickness of the layer  $\underline{2}$  of polymeric nanofibers, protects this layer  $\underline{2}$  from its outer side from abrasion, which allows to wash the composite  $\underline{1}$  according to the invention in a conventional manner, without causing mechanical damage to the layer  $\underline{2}$  (layers) of polymeric nanofibers or its separation from the carrier layer  $\underline{3}$  of the composite  $\underline{1}$  and loss of the favorable parameters of the textile composite  $\underline{1}$ , all that even if the layer  $\underline{2}$  of polymeric nanofibers is applied to the surface of this composite  $\underline{1}$ , without being overlaid by another layer or material, when it constitutes, e.g., the lining of the finished product.

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A suitable textile carrier layer <u>3</u> is substantially any fabric of any type (woven, nonwoven, knitted) made from synthetic and/or natural fibers, preferably hydrophobic or with hydrophobic surface treatment, which has sufficient vapor permeability and breathability for the intended application of the textile composite <u>1</u>. During the experiments it was especially fleece that proved to be very suitable material. In products prepared from the textile composite <u>1</u> according to the invention, the textile carrier layer <u>3</u> made from fleece constitutes the upper layer.

A suitable material of the nanofibers is preferably hydrophobic, easily spinnable polymer, such as polyamide 6 (PA6), polyamide 6.6 (PA6.6), polyurethane (PUR), polyvinyl alcohol (PVA), polyester (PES) or polyvinylidene fluoride (PVDF), etc., and copolymers or mixtures of at least two of them, whereby the basis weight of the layer **2** of polymeric nanofibers according to the requirements and intended application usually ranges from 3 to 20 g/m², or is even higher. In addition, the layer **2** of polymeric nanofibers can be provided with a suitable antimicrobial treatment, e.g. in the form of impregnation with an antimicrobial substance and/or in the form of an antimicrobial substance (substances) embedded in the material of polymeric nanofibers, etc., or with another treatment which increases its utility value and provides the required function.

In order to obtain uniform properties of the final composite <u>1</u> it is favourable if the layer <u>2</u> (layers) of polymeric nanofibers is as uniform as possible, both in the direction of its width and in the direction of its length or also its thickness. At present, the highest evenness is achieved by producing it by

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nozzle-less electrostatic spinning, in which a polymer solution or melt is spun in an electric field created between a collecting electrode and a spinning electrode of elongated shape – composed, for example, of a cylinder (see, e.g., EP 1673493) or a string (see, e.g., EP 2059630 or EP 2173930). This principle is commercially employed in the technology Nanospider<sup>TM</sup> of the company Elmarco. Moreover, the layer **2** of polymeric nanofibers can be deposited directly to the textile carrier layer **3**, which is used as a substrate material for depositing nanofibers during electrostatic spinning, whereby for connecting these layers **2**, **3** by a binder, which can be also, e.g., the material of one or both these layers **2**, **3**, and, optionally, also after adding at least one more layer, the hydrophobic agent is applied to the textile carrier layer **3** by plasma spraying.

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In other variants it is possible to prepare the layer <u>2</u> of polymeric nanofibers by another method for producing polymeric nanofibers, for example, by using a static spinning electrode formed, e.g., by a needle, a tube, a nozzle, or a group of needles, tubes or nozzles, a listel, a string, etc., or movable spinning electrodes formed, e.g., by a rotating disc, spiral, ring, a rewinding belt according to CZ 2008-529, etc., whereby the solution for spinning is spun from the surface of this spinning electrode, or its spinning element/elements.

Another suitable method for producing a layer of polymeric nanofibers is, e.g., electrical spinning according to CZ 304137, wherein an electrical field for spinning is created between a spinning electrode, to which a high AC voltage is brought, and air ions and/or gas ions created and/or brought to its vicinity. According to the current phase of AC voltage on the spinning electrode are formed polymeric nanofibers with an electric charge of opposite polarity and/or segments with an electric charge of opposite polarity, which after their formation due to the action of electrostatic forces create a voluminous structure, which moves freely in the direction of the gradient of the electric fields away from the spinning electrode.

However, apart from electrostatic or electric spinning, it is possible to use also centrifugal spinning for producing polymeric nanofibers, when the solution for spinning is extruded by the centrifugal force through the holes formed in the

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casing of a rotating body in the shape of a disc (e.g. in the sense of DE 102005048939) or a cylinder (e.g. in the sense of JP 2008127726).

For connecting the textile carrier layer 3 and the layer 2 of polymeric nanofibers and, optionally, also another layer (layers) of the composite 1, any binder can be used, e.g. fusible, or a mixture of at least two binders, which are applied to the surface of at least one or both layers being connected by any of the known methods - preferably, e.g., by the method of gravure printing, spraying or spray coating, etc., when points of the binder and/or its planar and/or linear formations are applied to the layer/the layers, e.g. in the form of a regular or irregular grid. In another alternative or in combination with the binder applied, the material of one or both layers being connected can also be used as a fusible binder. In a preferred embodiment, the textile carrier layer 3 contains bicomponent fibers, e.g. sheath-core bicomponent fibers, or of any other known type, which contain sections made of polypropylene and polyethylene, whereby the polyethylene is during the bonding of the layers melted and after solidification it connects the textile carrier layer 3 to the layer 2 of polymeric nanofibers and, if needed, also to another layer (other layers) of the composite <u>1</u>.

If the layer  $\underline{2}$  of polymeric nanofibers is overlaid by a cover layer  $\underline{4}$  (see, e.g., Fig. 2), the cover layer  $\underline{4}$  can be connected to the layer  $\underline{2}$  of polymeric nanofibers and/or to the textile carrier layer  $\underline{3}$  during the bonding of the layer  $\underline{2}$  of polymeric nanofibers with the textile carrier layer  $\underline{3}$  by a binder applied to one of the layers, or additionally in the following step, or it can be connected to the textile carrier layer  $\underline{3}$  by another method, e.g. by sewing or needling and the like.

Subsequently, a suitable hydrophobic agent in a liquid or plastic state e.g. a polymeric fluorinated carbohydrate-based hydrophobic agent, or a silicone-based hydrophobic agent and/or an alkane-based hydrophobic agent, etc., or a combination thereof, is applied by plasma spraying to the textile carrier layer 3 of a semi-finished product thus prepared. For this purpose, it is advisable to use especially low pressure vaccum plasma, whereby the conditions of the application are selected according to the properties of the materials used and the requirements for the finished product. The pressure

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usually ranges from 70 to 150 militorr and the temperature is in the range from the ambient temperature, or room temperature, i.e. approximately from 18 °C, to the lowest melting temperature of the material of one of the layers of the composite 1 being produced. The process of the application itself is then carried out according to the requirements for the depth of the penetration of the hydrophobic agent into the inner structure of the textile carrier layer 3 and/or for its amount approximately for a period of 3 to 6 minutes in the required part of its area. The semi-finished product is during the application of plasma spraying either static, or it moves, e.g., rotates, or rewinds, etc., so as to achieve the required penetration of the hydrophobic agent and its deposition on the required part of the surface of the fibers of the textile carrier layer 3. For most of the intended applications, it is sufficient to perform only a single-step application of the hydrophobic agent, but, in case of need, its application can be repeated, or it can be performed at least once complementarily from the side of the layer 2 of polymeric nanofibers. The amount of the hydrophobic agent applied is then according to the requirements and the materials used approximately up to 5 % basis weight of the textile carrier layer 2.

If the layer  $\underline{2}$  of polymeric nanofibers is overlaid by a cover layer  $\underline{4}$  (different from or the same as the textile carrier layer  $\underline{3}$ ), it is possible to apply the hydrophobic agent both to the textile carrier layer  $\underline{3}$ , and the cover layer  $\underline{4}$ , whereby to each of them it is possible to apply a hydrophobic agent from its outer side, whereby the hydrophobic agent can be of another type and/or it can be applied in a different amount and/or with different parameters of applying, or it is possible to leave the cover layer  $\underline{4}$  without plasma spraying, or optionally only with plasma spray penetrating through the other layers  $\underline{2}$ ,  $\underline{3}$  of the textile composite  $\underline{1}$ . If the hydrophobic agent is applied to the cover layer  $\underline{4}$ , its amount is up to approximately 5 % of basis weight of the cover layer  $\underline{4}$  according to the requirements and the materials used.

The most simple variant of the textile composite <u>1</u> according to the invention is a composite <u>1</u> which contains a textile carrier layer <u>3</u> with at least one hydrophobic agent applied by plasma spraying, whereby to one of the surfaces of the textile carrier layer <u>3</u> is applied a layer <u>2</u> of polymeric nanofibers, which is firmly connected to it by point and/or linear and/or planar formations of

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a binder. Nevertheless, for a number of real applications for outdoor use it is advantageous to supplement this variant with at least one more layer of a suitable material - a textile layer, or, possibly, also non-textile layer (e.g. made of foil, paper, etc.), namely especially for achieving the required properties and also for the protection of the layer 2 of polymeric nanofibers from mechanical damage or from abrasion. This layer (these layers) is/are at the same time connected to at least one layer 2, 3 of a textile composite 1 or to all its layers 2, 3, for example, by means of a binder and/or by sewing, or by another appropriate method. If this layer (these layers) is/are connected to it/them by means of a binder, then it preferably undergoes plasma spraying together with it/them; if this layer (these layers) is/are connected to it/them in another method, e.g. by sewing, needling, etc., undergoing of plasma spraying is not necessary. In another variant of embodiment, the layer 2 of polymeric nanofibers can be reinforced by a network or a grid of at least one polymer printed at least on one of its surfaces (preferably on the surface away from the textile carrier layer 3), e.g. in the sense of CZ 27368, which further increases resistance and the protection of the layer 2 of polymeric nanofibers.

Fig. 3 shows another variant of a textile composite <u>1</u> according to the invention. In this variant, the textile composite <u>1</u> contains two textile carrier layers <u>3</u>, <u>30</u>, each of which has a layer <u>2</u>, <u>20</u> of polymeric nanofibers deposited on one of its surfaces by means of a binder, whereby both the textile carrier layers <u>3</u>, <u>30</u> are facing each other by layers <u>2</u>, <u>20</u> of polymeric nanofibers, and are connected to each other, preferably outside these layers <u>2</u>, <u>20</u>, e.g. along their circumferences. Furthermore, the entire textile composite <u>1</u>, or at least one of its carrier layers <u>3</u>, <u>30</u> before formation of the textile composite <u>1</u>, can undergo plasma spraying, whereby if the hydrophobic agent is applied to both carrier layers <u>3</u>, <u>30</u>, it is possible to apply a different hydrophobic agent, or a different amount of the hydrophobic agent to each of them. The textile carrier layers <u>3</u>, <u>30</u> can be identical, or they can differ, e.g., by the material and/or the diameter of the nanofibers and/or basis weight and/or thickness, or by another parameter. This also applies to the layer of polymeric nanofibers <u>2</u>, <u>20</u>.

The textile composite <u>1</u> according to the invention is intended especially for the production of outdoor clothing and other outdoor textile products.

Listed below are illustrative specific examples of the textile composite <u>1</u> according to the invention. Nevertheless, these examples are merely illustrative, whereby, as is apparent to a person skilled in the art, other variants of the textile composite <u>1</u> according to the invention may differ from these examples, for example, by the material and/or the parameters of the individual layers <u>2</u>, <u>20</u>, <u>3</u>, <u>30</u>, <u>4</u>, and/or by the binder used, and/or by the hydrophobic agent, and/or by the conditions of plasma spraying, or they may be supplemented with other textile or non-textile layers.

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#### Example 1

A planar layer of nanofibers of polyamide 6 (PA6) with a basis weight of 4 g/m² was formed on a device for electrostatic spinning equipped with a spinning electrode composed of a rotating cylinder according to EP 1673493. This layer was connected to a textile carrier layer consisting of a polyamide (PA) woven fabric having a basis weight of 45 g/m² by means of polyurethane (PU), which was applied to the textile carrier layer in an amount of 10 g/m². After their connection, a fluorinated carbohydrate-based hydrophobic agent was applied to the carrier layer from the opposite side by plasma spraying with low pressure vacuum plasma of a roll-to-roll type at a winding speed of the formed semi-finished product of 1 m/min. Thus, a two-layer textile composite was formed according to the invention, having a final permeability of 2.5 l/m²/s, vapor permeability Ret 3.1 Pa.m².W¹¹ and hydrostatic resistance of 10,000 mm of water column.

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This textile composite was afterwards washed 3 times in a conventional manner in a washing machine, whereby its parameters were maintained to a considerable extent, being still sufficient for outdoor use: permeability being 2.2 l/m²/s, vapor permeability being Ret 4.1 Pa.m².W¹¹ and hydrostatic resistance being 8,000 mm of water column.

### Example 2

The layer of polymeric nanofibers of a composite according to example 1 was after plasma spraying of a hydrophobic agent overlaid by a cover layer consisting of a polyester (PL) woven fabric with a basis weight of 28 g/m², to whose surface was applied polyurethane in an amount of 10 g/m². Connecting all the layers resulted in the formation of a three-layer textile composite according to the invention, having a final permeability of 3.18 l/m²/s, vapor permeability Ret 3.0 Pa.m².W¹¹ and hydrostatic resistance of 12,000 mm of water column.

This textile composite was afterwards washed 3 times in a conventional manner in a washing machine, whereby its parameters were maintained to a considerable extent, being still sufficient for outdoor use: permeability was 3.18 l/m²/s, vapor permeability Ret was 2.9 Pa.m².W¹¹ and hydrostatic resistance was 11,590 mm of water column.

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#### Example 3

A planar layer of nanofibers of polyamide 6 (PA6) having a basis weight of 3 g/m² was formed in the same manner as in Example 1. This layer was connected to a textile carrier layer consisting of a cotton woven fabric having a basis weight of 45 g/m² by means of polyurethane (PU), which was applied to the textile carrier layer in an amount of 10 g/m². After their connection, a fluorinated carbohydrate-based hydrophobic agent was applied to the textile carrier layer from the opposite side by plasma spraying with low pressure vacuum plasma of a roll-to-roll type at a winding speed of 1 m/min. Subsequently, the layer of polymeric nanofibers was overlaid by a cover layer consisting of a polyester (PL) woven fabric having a basis weight of 28 g/m², to whose surface was applied polyurethane in an amount of 10 g/m². Connecting all the layers resulted in the formation of a three-layer textile composite according to the invention having permeability 2,2 l/m²/s, vapor permeability Ret 4,1 Pa.m².W¹¹ and hydrostatic resistance of 21,000 mm of water column.

This textile composite was afterwards washed 3 times in a conventional manner in a washing machine, whereby its parameters were maintained to a

considerable extent, being still sufficient for outdoor use: permeability was 2.20 l/m²/s, vapor permeability Ret was 3.9 Pa.m².W¹¹ a hydrostatic resistance was 18,100 mm of water column.

### 5 Example 4

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A planar layer of nanofibers of polyamide 6 (PA6) having a basis weight of 3 g/m² was formed in the same manner as in Example 1. This layer was connected to a textile carrier layer consisting of a cotton woven fabric having a basis weight of 45 g/m² by means of polyurethane (PU), which was applied to the textile carrier layer in an amount of 10 g/m². After their connection a fluorinated carbohydrate-based hydrophobic agent was applied to the carrier layer by plasma spraying with low pressure vacuum plasma of a roll-to-roll type at a winding speed of 1 m/min. Thus, a two-layer textile composite was formed according to the invention having permeability 2.98 l/m²/s, vapor permeability Ret 3.5 Pa.m².W⁻¹ a hydrostatic resistance of 17,320 mm of water column.

This textile composite was afterwards washed 3 times in a conventional manner in a washing machine, whereby its parameters were maintained to a considerable extent, being still sufficient for outdoor use: permeability was 2.98 l/m²/s, vapor permeability Ret was 3.5 Pa.m².W¹¹ and hydrostatic resistance was 15.200 mm of water column.

## Example 5

A planar layer of nanofibers of polyamide 6 (PA6) having a basis weight of 3 g/m² was formed in the same manner as in Example 1. This layer was connected to a textile carrier layer consisting of a polyester (PL) woven fabric having a basis weight of 45 g/m² by means of polyurethane (PU), which was applied to textile carrier layer in an amount of 10 g/m². After their connection a fluorinated carbohydrate-based hydrophobic agent was applied to the carrier layer by plasma spraying with low pressure vacuum plasma of a roll-to-roll type at a winding speed of 1 m/min. Thus, a two-layer textile composite according to the invention was formed, having a permeability of 4.11 l/m²/s, vapor

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permeability Ret 2.0 Pa.m<sup>2</sup>.W<sup>-1</sup> and hydrostatic resistance of 5000 mm of water column.

This textile composite was afterwards washed 3 times in a conventional manner in a washing machine, whereby its parameters were maintained to a considerable extent, being still sufficient for outdoor use: permeability was 4.11 l/m²/s, vapor permeability Ret was 1.9 Pa.m².W¹¹ and hydrostatic resistance was 4,000 mm of water column.

### Example 6

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A planar layer of nanofibers of polyamide 6 (PA6) having a basis weight of 4 g/m² was formed on a device for producing polymeric nanofibers on the basis of centrifugal spinning. This layer was connected to a textile carrier layer consisting of a polyamide (PA) woven fabric having a basis weight of 45 g/m² by means of polyurethane (PU), which was applied to the textile carrier layer in an amount of 10 g/m². After their connection, a fluorinated carbohydrate-based hydrophobic agent was applied to the carrier layer by plasma spraying with low pressure vacuum plasma of a roll-to-roll type at a winding speed of 1 m/min. Thus, a two-layer textile composite was formed according to the invention, having a final permeability of 3.25 l/m²/s, vapor permeability of Ret 4.3 Pa.m².W¹ and hydrostatic resistance of 4,500 mm of water column.

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#### **PATENT CLAIMS**

- 1. A method for producing a textile composite, especially for outdoor applications, which contains at least one layer (2) of polymeric nanofibers deposited on a textile carrier layer (3), **characterized in that** after the layer (2) of polymeric nanofibers is deposited on the textile layer (3) and these layers (2), (3) are connected to each other by a binder, at least one hydrophobic agent in a liquid or plastic state is applied by plasma spraying to the textile carrier layer (3) from the side opposite the side where the layer (2) of polymeric nanofibers has been deposited.
- 2. The method according to Claim 1, **characterized in that** the binder for connecting the textile carrier layer (3) and the layer (2) of polymeric nanofibers is applied to the textile carrier layer (3) and/or to the layer (2) of polymeric nanofibers by gravure printing, spraying or spray coating.
- 3. The method according to Claim 1, **characterized in that** prior to the application of the hydrophobic agent to the textile carrier layer (3) by plasma spraying, the layer (2) of polymeric nanofibers is overlaid by a cover layer (4), which is connected to the layer of polymeric nanofibers (2) and/or the textile carrier layer (3).
- 4. The method according to Claim 1, **characterized in that** after applying the hydrophobic agent to the textile carrier layer (3) by plasma spraying, the layer (2) of polymeric nanofibers is overlaid by a cover layer (4), which is connected to the layer of polymeric nanofibers (2) and/or the textile carrier layer (3).
- 5. The method according to Claim 3 or 4, **characterized in that** the hydrophobic agent in a liquid or plastic state is applied to the cover layer (4) made of a textile by plasma spraying before it is connected to the layer of polymeric nanofibers (2) and/or the textile carrier layer (3), and/or after this connection.

6. The method according to Claim 1, **characterized in that** the layer (2) of polymeric nanofibers, prior to the application of the hydrophobic agent by plasma spraying to the textile carrier layer (3), is overlaid by a layer (20) of polymeric nanofibers deposited on a textile carrier layer (30), whereby both textile carrier layers (3, 30) are connected to each other prior to the application of the hydrophobic agent by plasma spraying to at least one of them.

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- 7. The method according to Claim 6, **characterized in that** both the textile carrier layers (3, 30) are connected to each other outside the area of the layers (2, 20) of polymeric nanofibers deposited on them.
- 8. The method according to any of Claims 1, 3, 4, 5 or 6, **characterized** in that the hydrophobic agent is applied to the textile carrier layer (3), or to the cover layer (4) formed by a textile by plasma spraying with low pressure vacuum plasma.
  - 9. The method according to any of Claims 1, 3, 4, 5 or 6, **characterized** in that the hydrophobic agent is applied to the textile carrier layer (3), or to the cover layer (4) in an amount of up to 5 % basis weight of the textile carrier layer (3) or the cover layer (4) respectively.
  - 10. A textile composite (1), especially for outdoor applications, which contains a layer (2) of polymeric nanofibers deposited on a textile carrier layer (3), **characterized in that** the layer (2) of polymeric nanofibers and the textile carrier layer (3) are connected by formations of a binder, which extend into the inner structure the layer (2) of polymeric nanofibers, whereby on the fibers of the textile carrier layer (3) is formed at least from one of their sides a coating of at least one hydrophobic agent applied by plasma spraying.
- 11. The textile composite (1) according to Claim 10, **characterized in that** a coating of at least one hydrophobic agent applied by plasma spraying is formed on the nanofibers of the layer (2) of polymeric nanofibers from at least one of their sides.
- 12. The textile composite according to Claim 10 or 11, **characterized in**30 **that** the layer (2) of polymeric nanofibers is overlaid by a cover layer (3), which

is connected to the layer (2) of polymeric nanofibers and/or to the textile carrier layer (2) by formations of a binder.

- 13. The textile composite according to Claim 12, **characterized in that** the cover layer (2) is composed of a textile.
- 5 14. The textile composite according to Claim 12, **characterized in that** the cover layer (2) and the textile carrier layer (3) are connected by sewing or needling.
  - 15. The textile composite according to Claim 12, 13 or 14, **characterized** in that on the fibers of the cover layer (4) at least from one side is formed a coating of at least one hydrophobic agent applied by plasma spraying.

- 16. The textile composite according to Claim 10 or 11, **characterized in that** the layer (2) of polymeric nanofibers is covered by the layer (20) of polymeric nanofibers deposited on a textile carrier layer (30).
- 17. The textile composite according to any of Claims 10 to 16, characterized in that the textile carrier layer (3, 30) is formed by a layer of fleece.
  - 18. The textile composite according to Claim 10, 11 or 15, **characterized** in that the hydrophobic agent is a fluorinated carbohydrate-based agent, a silicone-based agent or an alkane-based agent.
- 19. The textile composite according to any of Claims 10, 11, 15 or 18, characterized in that the hydrophobic agent is applied to the fibers of the textile carrier layer (3, 30), or to the fibers of the cover layer (4) in an amount of up to 5% of the basis weight of the textile carrier layer (3, 30), or of the basis weight of the cover layer (4) respectively.

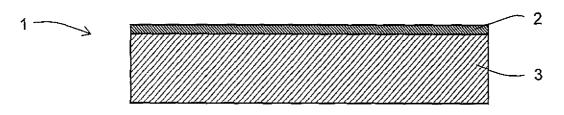


Fig. 1

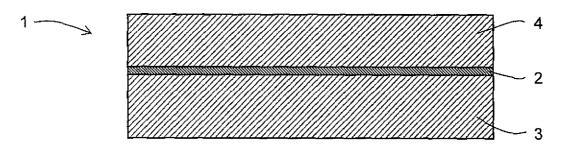


Fig. 2

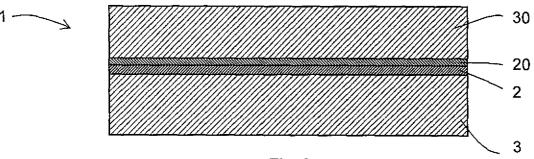


Fig. 3

#### INTERNATIONAL SEARCH REPORT

International application No PCT/CZ2016/000026

A. CLASSIFICATION OF SUBJECT MATTER INV. D06M10/02 D06M1

D06N3/00

D06M10/08 D06M10/10 D06M17/00

D06M23/08

ADD.

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

#### **B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

D06M D06N

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

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

EPO-Internal, WPI Data

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.				
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See patent family annex.

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- "&" document member of the same patent family

24/06/2016

Date of the actual completion of the international search Date of mailing of the international search report

17 June 2016

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Magrizo, Simeon

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