

Textiles containing at least one layer of polymeric nanofibres and method of production of the layer of polymeric nanofibres from the polymer solution through electrostatic spinning

Technical field

5 The invention relates to the textile containing at least one layer of polymeric nanofibres having diameter to 600 nanometres produced through electrostatic spinning of the polymer solution.

 The invention also relates to the production method of the layer of nanofibres from the polymer solution through electrostatic spinning in electric
10 field created by difference of potentials between the charged electrode and the counterelectrode, at which the solution of polymer is brought into the electric field for spinning through the surface of the rotating charged electrode, at the same time the nanofibres created in this electric field are carried to the counterelectrode and they deposit on the surface designated to it.

15 **Background art**

 From the CZ 294274 and to it analogical international application WO 2005/024101 A1 it is known to produce the textiles containing at least one layer from polymeric nanofibres produced through electrostatic spinning of polymer solution in electric field created through the difference of potentials
20 between the charged cylindrical electrode, positioned in rotation manner, and the counterelectrode, at the same time the charged cylindrical electrode is with portion of its perimeter sunk in polymer solution, through its surface it brings the polymer solution into the electric field for spinning. Through the electrostatic spinning the mentioned textiles are produced from various
25 polymers soluble in the water solution or the non-water solution.

 The textiles containing at least one layer of polymeric nanofibres are used, next to others, in health practice, e.g. to cover the wounds because thanks to the small dimensions of poruses they prevent the bacteria to penetrate into the wound, and simultaneously enable the liquid products of the
30 healing process to go away and the access of air to the wound.

Other known textiles used in health practice sometimes contain physiologic active substances which are released from them in a controlled speed and support the healing process. On the finished textile these substances are deposited through dipping the textile into the solution of the
5 respective substance and through its consequent drying, when the quantity of the substance that gets stuck on the textile is very difficult to control, respectively it is difficult to deposit very small quantity of the active substance which restricts usage of such textiles. Even more difficult is to effect the long-term and gradual releasing of such substances.

10 Because of its antiseptic and antimicrobial effect a lot of substances with antiseptic and antimicrobial effects are used in the health practice. An example represent the dissociative compounds of heavy metals, especially of silver, with high antimicrobial effectiveness. At the same time, these compounds are toxic for the human organism, thus having the undesirable
15 side effects. Better results are achieved with metallic silver which is only a slightly soluble and dissociative in surrounding of body liquids. The concentration of ions created in such a way is sufficient to achieve the antimicrobial effect, at the same time the rate of undesirable side effects is negligible. Silver in a suitable form may be prepared in various substrates like
20 the textile formations or the polymer membranes through reduction of silver compounds. In these carriers, silver is present in the form of metallic particles, whose magnitude is in micrometers as to numerical order. A similar form of silver is used also in textile materials, e.g. in socks, to prevent creation of odour due to bacteria.

25 From the studies of colloid status of substance it is known that chemical or catalytic acting of solid matters is being increased with specific surface of active substances. At decreasing dimensions of particles of active substance in the carrier, the necessary proportion of effect of this substance may be achieved through a lower quantity of active substance in the carrier or through
30 a lower concentration of active substance in the carrier. By a way of reduction of metallic salts in water solutions, e.g. at photographic techniques, the metal particles of dimensions larger than one micrometer are created. These

particles are of a black colour. A lot of patents and published papers deals with procedures for preparation of metallic nanoparticles with characteristic dimension under one micrometer. According to US 5759230 such particles may be prepared through reduction of silver salts in alcoholic solutions. The
5 procedures according to US6110254 and 6660058 use reduction on the interphase of two-solvent systems, possibly with usage of suitable surface-active substances. The paper of K. Šišková and the team published in conference proceedings Nano03, Brno 2003 and Nano04, Brno 2004 describe usage of laser beam for preparation of nanoparticles of silver. The silver
10 nanoparticles may be used with advantage for their high activity and the minimum toxicity. Nevertheless their production according to the above mentioned procedures is demanding and does not solve the positioning of these particles into suitable carrying substrates.

The objective of invention is to propose a suitable carrier, respectively a
15 carrying substrate for nanoparticles of low-molecular substances, as e.g. silver and other metals of suitable properties, salts, physiological active substances, etc. The objective of invention is also to create a method for production of such carrier.

The principle of invention

20 The objective of invention has been reached through a textile containing at least one layer of polymeric nanofibres, whereas the principle of the invention consists in that the dimensions are smaller than the diameter of nanofibres, at the same time the particles of low molecular substance are deposited in polymer of nanofibre.

25 The polymeric nanofibres contain particles of low-molecular substance dissolved or dispersed in electrostatic spinning solution of polymer before spinning. Or they contain the polymeric nanofibres of particle of low molecular substance which was created after fibrillation through a consequent chemical reaction of the original low molecular substance dissolved in electrostatic
30 spinning solution of polymer before spinning. The low molecular substance is deposited directly in polymeric nanofibres of the layer and its concentration is

close to the concentration of the low molecular substance in the solution of polymer during spinning process. The resulting concentration of active substance in nanofibres of the layer may be controlled exactly.

According to the claim 2 it is advantageous if the particles of low molecular substance are created by at least one substance from the group of metals, salts, dyes, physiological active substances, odours, indicators and catalyzers. The nanofibres then contain mostly very small quantity of corresponding substance that they are able to release in long-term period, thus creating the required effect.

The dimensions of particles of low molecular substance are smaller than the diameter of nanofibres, whereas according to the claim 3 it is advantageous if these particles are of dimensions from 5 to 100 nanometers, which enables their depositing in the nanofibres.

According to the claim 4 the nanofibres in the layer of textile may be created by a polymer which undergoes the electrostatic spinning from the water solution and subsequently is reticulated, in which the particles of low molecular substance were dissolved or dispersed before the spinning. The nanofibres of this textile usually contain low-molecular substances soluble in water, which may be after netting treated by a way of chemical reaction in other water solution. At the same time the nanofibres may, according to the claim 5, contain particles of metal created through a following chemical reaction of salt particles of metal contained in nanofibres before the netting process.

Salt particles of metal deposited in nanofibres may consist of the silver nitrate from which through a following reduction the silver particles are created, at the same time the reduction takes place though the particles of silver nitrate are deposited in nanofibres.

According to the claim 7 the nanofibres are in the textile layer created by a polymer which is subject to the electrostatic spinning from the non-water solution. The fine particles of the low molecular substance may be dispersed in the non-water solution.

At the same time the nanofibres contain the metal particles dispersed in the non-water solution being subject to electrostatic spinning before the spinning or during its course.

According to the claim 9 the metallic particles are the particles of silver.

5 The principle of production method of layer of nanofibres from the polymer solution through electrostatic spinning consists in that, the polymer solution for spinning contains the particles of low-molecular substance having dimensions smaller than the diameter of nanofibres, which are at spinning seized together with polymer to the nanofibres being created.

10 At the same time the particles of low molecular substance are created by at least one substance from the group of metals, salts, dyes, physiological active substance, odours, indicators, e.g. reacting to pH and the catalysts.

The polymer solution for spinning is water solution in which, together with polymer and a substance causing polymer netting, the low molecular
15 substance is dissolved, that the nanofibres should contain after spinning, or the low molecular substance containing a substance, that the nanofibres should contain after spinning, and which will be created through a following chemical reaction of the original low molecular substance dissolved in polymer solution being subject to electrostatic spinning. The low molecular substance
20 may be as well dispersed in the water solution.

The low molecular substance dissolved in water solution of polymer is, with advantage, the metallic salt which, after completion of netting, is treated with solution of a suitable substance and through a consequent chemical reaction the required low molecular substance is created in nanofibres.

25 According to the claim 14 it is advantageous, if the low molecular substance dissolved in the water solution of polymer is the silver nitrate, from which by acting of an reduction agent after completion of netting the metallic silver is created in nanofibres.

30 Another variant of the method according to the invention is that the polymer solution for spinning is the non-water solution in which the low molecular substance is dispersed together with polymer, that the nanofibres

should contain after spinning, or the low molecular substance containing the substance which the nanofibres should contain after spinning, and which will be created through consequent chemical reaction of the original low molecular substance dispersed in polymer solution being subject to electrostatic spinning. The low molecular substance may be also dissolved in the non-water solution.

The low molecular substance may be, with advantage, the silver which will be obtained through reduction of the silver nitrate contained in non-water solution of polymer.

10 **Examples of embodiment**

During creation of nanofibres from the polymer solution through electrostatic spinning in electric field created by a difference of potentials between the charged electrode positioned in rotational manner and the counterelectrode, at the same time the charged electrode is with a part of its perimeter dipped in polymer solution and through its surface it brings the polymer solution into the electric field for spinning. At the same time the charged electrode is, with advantage, created with a cylinder according to CZ 294274 and to it analogical international application WO 2005/024101 A1. Using the electrostatic spinning the mentioned textiles are made of various polymers soluble in water or non-water solution. The diameter of nanofibres is less than 600 nanometers, usually in the range from 100 to 600 nanometers.

Under a suitable circumstances, it is possible to perform electrostatic spinning not only of respective polymer from polymer solution or of mixture of polymers, but with the polymer also the low molecular substances dissolved or dispersed in the same solvent as the polymer. The particles of low molecular substance are at the electrostatic spinning carried by a perimeter of the rotating charged cylindrical electrode together with polymer into the electric field for spinning, where at creating the nanofibres are seized by polymer and they stay deposited in nanofibres, when the size of particles of low molecular substance usually varies from 5 to 100 nanometers and is lower than the diameter of nano-fibre in which it is deposited. Concentration of low molecular

substance in the layer of nanofibres being created may be close to concentration in the solution subject to spinning.

The particles of low molecular substance are created at least of one substance from the group of metals, salts, dyes, physiological active
5 substances, odours, indicators and catalyzers.

First of all, the manner of production of layer of nanofibres according to the invention shall be described for the low molecular substance created by metallic particles, e.g. silver and the water solution of polymer. For example, from the polyvinyl alcohol the water solution of polyvinyl alcohol is prepared,
10 which further contains a netting agent and soluble silver salt, with advantage the silver nitrate. During the spinning process the particles of silver nitrate are seized together with polymer into the nanofibres being created. After fibrillation the polymer is transferred to the three-dimensional insoluble form through activating the netting agent using heat. After then the silver nitrate is reduced
15 through a known manner upon acting of solution of a known reductant, e.g. by water solution of black-and-white photographic developer. The reduction of silver nitrate is running in a common manner, though the silver nitrate is deposited in polymer of nanofibre, and after reduction the nanofibres of nanofibre layer contain the particles of silver having dimensions of 5 to 100
20 nanometers.

In case of polyurethane the non-water solution of dimethylformamide is subject to electrostatic spinning, at the same time the silver nitrate is dissolved in this solution, which is reduced out of it still in this solution using suitable reductant and the silver created is dispersed in the spinning solution. During
25 the electrostatic spinning these particles of silver are seized together with polymer and deposited in nanofibres.

A low concentration of metallic ions in the basic polymer and the restricted moveability of reacting agents prevents agglomeration of atoms of reduced metal into larger particles, and so the nanoparticles are created. The
30 final product – textile containing at least one layer of nanofibres does not have the black colour, but a colour which is brown up to yellow. Finally the layer of

nanofibres is deprived of the soluble products of chemical reactions using water and after then is dried and sterilised.

Such layer of nanofibres of polyvinyl alcohol or polyurethane with particles of silver anchored in nanofibres features a high and long-term antimicrobial efficiency and prevents bacteria, fimbria and fungus to grow. The surface weight of textiles is only 0,5 to 2 gm⁻², at the same time they contain 0,01 to 0,2 gm⁻² metallic silver. This quantity is significantly lower than at the up to now used products, hence adequately lower is also loading of human organism with side toxic effects.

Specific examples of production of nano-fibre layer from polymer solution and the textiles containing at least one layer of polymer nanofibres are described in below shown examples.

Example 1

Twelve percent water solution of polyvinyl alcohol of average molecular mass 100000, thirty percent water solution of polyacrylic acid of average molecular mass 70000 and the four percent water solution of silver nitrate is being mixed in the volume ratio 5 : 1 : 1. After homogenisation the mixed solution is subject to spinning through the process of electrostatic spinning according to CZ 294274 to the layer of nanofibres of surface weight of 2 gm⁻² with diameters of nanofibres in the range from 150 to 500 nanometers. The layer of nanofibres is exposed to the temperature of 150 °C during 30 minutes, at the same time the netting reaction is running and the nano-fibre material becomes indissoluble in water. Then the water solution of black-and-white photographic developer sold in the CR under the METOL designation is acting on the layer of nanofibres, through which the silver nitrate reduces and particles of silver having dimensions from 10 to 100 nanometers are created inside the polymeric nanofibres.

Example 2

The layer of nanofibres is produced in the same manner as in example 1 from mixture of the same substances in the ratio 5 : 1 : 0,2. After reduction of silver nitrate deposited in nanofibres during spinning, the particles of silver having dimensions from 5 to 50 nanometers are created in nanofibres.

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Example 3

The layer of nanofibres is being produced in the same manner as in example 1 while the reductant of silver nitrate deposited in nanofibres during spinning shall be the two percent water solution of ascorbic acid. The
10 bacteriological test were performed on the final product and according to the tests the product completely prevents bacteria, yeast and fungus to grow.

Example 4

In dimethylformamide solution, which contains eighteen percent of polyurethane of average molecular mass 120000 and one percent of silver
15 nitrate, through equivalent of acetaldehyde, if standing during 4 hours at the temperature of 20 °C, the metallic silver shall be reduced. The solution will be mixed after then, homogenized, and the fine suspension created will be subject to spinning through the process of electrostatic spinning according to CZ 294274 to the layer of nanofibres with surface weight approximately 10
20 gm⁻² with diameter of nanofibres in the range from 100 to 500 nanometers.

The silver nitrate may be in the polymer solution superseded with another metallic salt, e.g. of copper or with another low-molecular substance from the group of metals, salts, dyes, physiologically active substances, odours, indicators and catalysts, at the same time the nanofibres of the layer
25 produced through the electrostatic spinning contain the corresponding low molecular substance, mostly in a very small quantity, and they are able, as the need may be, to release it in a controlled way. From the dyes it is possible to use the two percent water solution of Saturn red upon spinning of the water solution of polymer

Claims

1. Textiles containing at least one layer of polymeric nanofibres of diameter to 600 nanometers produced through electrostatic spinning from polymer solution **characterised by that , the** polymeric nanofibres contain particles of low molecular substance having dimensions less than the diameter of nanofibres, at the same time the particles of low molecular substance are deposited in polymer of nano-fibre.
2. Textiles as claimed in the claim 1, **characterised by that the** particles of low molecular substance are created by at least one substance from the group of metals, salts, dyes, physiologically active substances, odours, indicators and catalysts.
3. Textiles as claimed in any of the claims 1 or 2, **characterised by that** the low molecular substances contained in nanofibres have dimensions from 5 to 100 nanometers.
4. Textiles as claimed in any of the claims 1 to 3, **characterised by that the** nanofibres are created by polymer subjected to electrostatic spinning from the water solution and consequent netting, in which the particles of low molecular substance were dissolved or dispersed before spinning.
5. Textiles according to claim 4, **characterised by that the** nanofibres contain particles of metal created by the subsequent chemical reaction of particles of metallic salt contained in nanofibres before netting.
6. Textiles according to claim 5, **characterised by that the** nanofibres contain the particles of silver created by the consequent reduction of silver nitrate contained in nanofibres before netting.
7. Textiles as claimed in any of the claim 1 to 3, **characterised by that the** nanofibres are crated by polymer subjected to electrostatic spinning from the non-water solution.

8. Textiles as claimed in the claim 7, **characterised by that the** nanofibres contain the particles of metal dispersed in non-water solution which is subjected to electrostatic spinning.

9. Textiles as claimed in the claim 8, **characterised by that the metal**
5 particles are particles of silver.

10. A method of creating the layer of nanofibres from the polymer solution through electrostatic spinning in electric field created by difference of potentials between the charged electrode and the counterelectrode at which the solution of polymer is brought into the electric field for spinning through the
10 surface of the rotating charged electrode, at the same time the nanofibres created in this electric field are carried to the counterelectrode and they deposit on the surface designated to it, **characterised by that the** solution of polymer for spinning contains particles of low molecular substance of dimensions less than the diameter of nanofibres which are during spinning
15 seized together with polymer to the nanofibres being created.

11. A method as claimed in the claim 10, **characterised by that the** particles of low molecular substance are created at least by one substance from the group metals, salts, dyes, physiologically active substances, odours, indicators and catalysts.

20 12. A method as claimed in the claim 10 or 11, **characterised by that the** polymer solution for spinning is a water solution in which together with polymer and the polymer netting substance the low molecular substance is dissolved, which the nanofibres should contain after spinning or the low molecular substance containing the substance which the nanofibres should
25 contain after spinning, and which will be created through the consequent chemical reaction of the original low-molecular substance dissolved in the polymer solution being subject to electrostatic spinning.

13. A method as claimed in the claim 12, **characterised by that the** low molecular substance dissolved in water solution of polymer is a salt of metal
30 and which, after completion of netting, is treated with solution of a suitable

substance and through a consequent chemical reaction the required low molecular substance is created in nanofibres.

14. A method according to the claim 13, **characterised by that the** low molecular substance dissolved in the water solution of polymer is the silver
5 nitrate, from which by acting of an reduction agent after completion of netting the metallic silver is created in nanofibres.

15. A method as claimed in the claim 10 or 11, **characterised by that the** polymer solution for spinning is a non-water solution in which the low molecular substance is dispersed together with polymer, that the nanofibres
10 should contain after spinning, or the low molecular substance containing the substance which the nanofibres should contain after spinning, and which will be created through consequent chemical reaction of the original low molecular substance dispersed in polymer solution being subject to electrostatic spinning.

15 16. A method as claimed in the claim 15, **characterised by that the** low molecular substance is silver.

17. A method as claimed in the claim 16, **characterised by that the** non-water solution of polymer for spinning contains the silver nitrate from which the metallic silver will be obtained before spinning.