

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

5 **Technical field**

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.

10 The invention also relates to the production method of 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 surface of the rotating charged electrode, at the same time the nanofibres created in this electric field are carried to the
15 counterelectrode and they deposit on the surface designated to it.

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
20 layer from polymeric nanofibres produced through electrostatic spinning of polymer solution in electric field created through the difference of potentials 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
25 the polymer solution into the electric field for spinning. Through the electrostatic spinning the mentioned textiles are produced from various polymers soluble in the water solution or the non-water solution.

30 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 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-
10 term and gradual releasing of such substances.

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
15 compounds are toxic for the human organism, thus having the undesirable 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
20 negligible. Silver in a suitable form may be prepared in various substrates like 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
25 odour due to bacteria.

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
30 achieved through a lower quantity of active substance in the carrier or through 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.

WO 2004/044281 A2 discloses production of nanofibres through
15 electrostatic spinning of solutions of various polymers and mixtures of polymers, while the polymer solution for production of nanofibres may contain e.g. metal oxide, silver, particles containing carbon, carbon nanotubes and their combinations.

WO 01/27365 A1 discloses a device for production of nanofibres
20 through electrostatic spinning of solutions of various polymers with different additives, which are a part of solution before spinning and after spinning they become a part of nanofibres in an unchanged form.

The journal SYNTHETIC METALS, vol. 137, 2003, page 973-974 publishes an article Q.B.YANG at all: Preparation and chrakterization of PAN
25 nanofibre containing AG nanoparticles via electrospinning", which describes preparation of a mixed solution of polymer with a silver salt (silver nitrate), reduction of silver salt in solution by means of hydrazine (hydrazinum hydroxide) upon formation of silver nano-particles in the solution and a consequent electrostatic spinning of the solution. Upon reduction of the silver
30 salt in solution, the created nano-particles of silver associate to a larger formations, which becomes evident e.g. by a black colour and by an increased thickness of nanofibres.

The objective of invention is to create a textile containing at least one layer of nanofibres which comprise nanoparticles of low-molecular substances, as e.g. silver and other metals of suitable properties, etc. having the smallest possible dimensions. The objective of invention is also to create a method for
5 production of a layer of such nanofibres.

The principle of invention

The objective of invention has been reached through a textile containing
10 at least one layer of polymeric nanofibres, that comprises nanoparticles of a low molecular substance, whereas the principle of the invention consists in that, the nanoparticles of low molecular substance are products of chemical reaction between the precursor of a low molecular substance dissolved in a polymer solution and the chemical agent applied to nanofibres after their
15 spinning, while the dimensions of nanoparticles of low molecular substance are smaller than the diameter of nanofibres.

Precursor of low molecular substance in the polymer solution being subject to spinning is dispersed in molecular respective ion manner. In this status it is being subject to spinning, and its concentration and particle
20 dimensions in nanofibres after spinning is close to its concentration in solution. Upon chemical reaction between the precursor of low molecular substance and the chemical agent applied to nanofibres after their spinning, the high viscosity of surroundings restricts motion of nanoparticles of low molecular substance being created and thus it prevents their gathering together.
25 Therefore in nanofibres small nanoparticles of low molecular substance are created.

According to the claim 2 it is advantageous if the precursor of low molecular substance is a metallic salt and the low molecular substance is metal. The nanofibres then contain mostly very small nanoparticles of
30 corresponding substance that they are able to release in long-term period, thus creating the required effect.

According to the claim 3 it is advantageous if the precursor of low molecular substance silver nitrate and the low molecular substance is silver.

5 The reduction of silver nitrate takes place though the particles of silver nitrate are deposited in nanofibres. No gathering of silver nanoparticles occurs here, which is apparent through the yellow colour.

10 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, which is at spinning seized together with polymer to the nanofibres being created, while after spinning the precursor contained in nanofibres is subject to acting of a suitable chemical agent, through which the precursor of low molecular substance is converted into a low molecular substance.

15

At the same time it is advantageous if the precursor of low molecular substance is metallic salt and the low molecular substance is metal.

20 In advantageous embodiment according to the claim 7 the precursor of low molecular substance is silver nitrate and the low molecular substance is silver.

Examples of embodiment

25 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
30 charged electrode is, with advantage, created with a cylinder according to CZ 294274 and to it analogical international application WO 2005/024101 Al.

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
25 reductant and the silver created is dispersed in the spinning solution. During 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
30 reduced metal into larger particles, and so the nanoparticles are created. The 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 gm², at the same time they contain 0,01 to 0,2 gm² 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 gm² 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.

5

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 bacteriological test were performed on the final product and according to the tests the product completely prevents bacteria, yeast and fungus to grow.

10

Example 4

In dimethylformamide solution, which contains eighteen percent of polyurethane of average molecular mass 120000 and one percent of silver 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 gm⁻² with diameter of nanofibres in the range from 100 to 500 nanometers.

15

20

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 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.

25

30

Claims

1. Textiles containing at least one layer of polymeric nanofibres of diameter to 600 nanometers produced through electrostatic spinning from
5 polymer solution, while the nanofibres comprise nanoparticles of low molecular substance, **characterised by that, the** nanoparticles of low molecular substance are products of chemical reaction between the precursor of low molecular substance dissolved in polymer solution and the chemical agent applied to nanofibres after their spinning, while the dimensions of
10 nanoparticles of low molecular substance are less than the diameter of nanofibres.

2. Textiles as claimed in the claim 1, **characterised by that the** precursor of low molecular substance is metallic salt, and the low molecular substance is metal.

15 3. Textiles as claimed in the claim 2, **characterised by that the** precursor of low molecular substance is silver nitrate and the low molecular substance is silver.

4. A method of creating the layer of nanofibres containing the nanoparticles of low molecular substance from the polymer solution through
20 electrostatic spinning in electric field created by difference of potentials between the charged electrode and the counterelectrode **characterised by that the** solution of polymer for spinning contains precursor of low molecular substance which is during spinning seized together with polymer to the nanofibres being created, while after spinning the precursor contained in
25 nanofibres is subject to acting of a suitable chemical agent, by means of which the precursor of low molecular substance is transformed into a low molecular substance.

5. A method as claimed in the claim 4, **characterised by that the.** acting to precursor for the purpose to create a low molecular substance is
30 preceded by netting of nanofibre polymer.

6. A method as claimed in the claim 4 or 5, **characterised by that the** precursor of low molecular substance is metallic salt and the low molecular substance is metal.

5 7. A method as claimed in the claim 6, **characterised by that the** precursor of low molecular substance is silver nitrate and the low molecular substance is silver.