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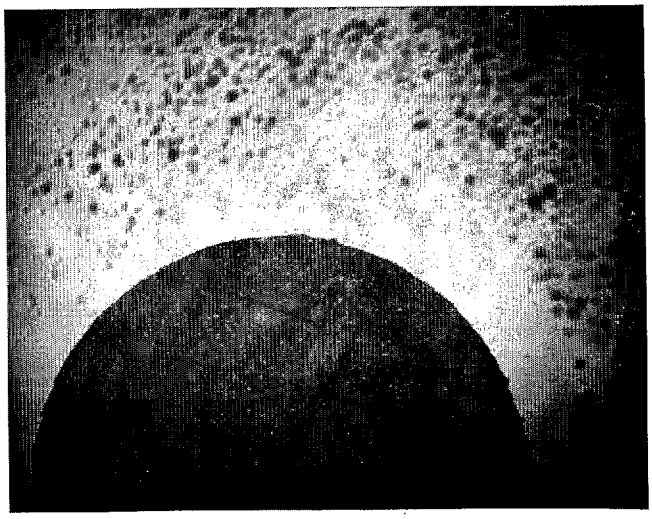
(54) **Title:** FORMATION COMPRISING AT LEAST ONE NANOFIBRE LAYER AND METHOD OF NANOFIBRE LAYER PRODUCTION



(57) **Abstract:** The invention relates to the formation comprising at least one nanofibre layer having diameter to 600 nm produced through electrostatic spinning of polymer solution. The layer of polymer nanofibres comprises particles of photodynamic sensitizer, at the same time the nanofibres are isotropic spread in a transparent and porous layer of surface weight from 0,01 g/m^2 to 15 g/m^2. Next to this, the invention relates to the production method of nanofibre layer through electrostatic spinning of polymer solution in electric field created by difference of potentials between the spinning electrode and collecting electrode, while the nanofibres produced in this electric field are carried to the collecting electrode and they deposit on a surface designated to it. The polymer solution for spinning contains particles of photodynamic sensitizer, which are during spinning seized together with polymer into the nanofibres being produced, in which these particles are anchored inside or on the surface.

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Formation comprising at least one nanofibre layer and method of nanofibre layer production

Technical field

The invention relates to the formation comprising at least one nanofibre layer having diameter to 600 nm produced through electrostatic spinning of polymer solution.

The invention also relates to the production method of nanofibre layer through electrostatic spinning of polymer solution in electric field created by difference of potentials between the spinning electrode and collecting electrode, while the nanofibres produced in this electric field are carried to the collecting electrode and they deposit on a surface designated to it.

Background art

Production of textiles containing one or more layers of polymer nanofibres arranged on a substrate material, which is usually also textile, is for example disclosed in US 2003/0190383 A1 or WO 2005/024101 A1. According to US 2003/0190383 A1 the nanofibres are produces through electrostatic spinning of polymer solution by means of spinning electrode containing a system of nozzles, from which the polymer solution is forced out against the collecting electrode, while electrodes are connected to opposite poles of a high voltage source.

WO 2005/024101 A1 discloses electrostatic spinning of polymer solution by means of rotating spinning electrode of an oblong shape positioned by a section of its circumference in polymer solution and connected to one pole of high voltage source, while against the free section of circumference of the spinning electrode there is arranged the collecting electrode connected to an opposite pole of high voltage source.

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 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.

Singlet oxygen $^1O_2$ is an energetically richer and highly reactive form of molecular oxygen, which plays a role in many chemical and biological processes. Singlet oxygen may be photo-generated on basis of photosensitized reactions. These are the reactions of sensitizers initiated by light, by means of whose light excitation an absorbed energy is transferred to oxygen under creation of $^1O_2$. Sensitizers are very active already at very low concentrations, one molecule of a sensitizer by a repeated transfer of energy may produce many molecules of $^1O_2$.

In chemical synthesis the $^1O_2$ is being used as a strong and selectively acting oxidizer. The main reactions are represented by three types of addition to the bound C=C – en-reaction, 2+2 cycloaddition , 4+2 cycloaddition and oxidation of sulphides[i,ii,iii]. From the synthetic point of view, the en-reaction and 4+2 cycloaddition reactions are the most important and they lead to creation of allylic hydroperoxides, endoperoxides and intermediators for syntheses of products like allylalcohols, epoxyalcohols, diols, saturated polyols and others. An example is photooxygenation of allylalcohol 4-methyl-3-penten-2-ol to β-hydroperoxyalcohol, which after conversion provides 1,2,4-trioxan showing antimalarial activity[iv]. Industrially exploited photooxidation of (-)-citronellol

provides a cyclic terpenoid, which is an important component used in production of perfumes.

In connection with increasing occurrence of bacterial strains resistant to antibiotics, other bactericidal and bacteriostatic methods become to be important e.g. so called photodynamic inactivation of bacteria, viruses, yeast and protozoon (photodynamic antimicrobial chemotherapy, PACT)[v]. The property of sensitizers causing photoinactivation *in vitro* as well as *in vivo* is generally designated as photodynamic phototoxicity or photocytotoxicity. The principle consists in a strong cytotoxic acting of photogenerated $^1O_2$.

The photosensitized generation of $^1O_2$ occurs usually in a liquid phase. This does not enable a simple separation of sensitizer from the processed object or products of reaction after its completion. If the sensitizer is anchored on a fixed carrier, it may be easily separated from products of reaction and used repeatedly.

Chemical possibly catalytic acting of solid substances is increasing with specific surface of active substances. If the active substance is bound to a carrier, at increasing surface of the carrier, the required effect may be achieved with smaller quantity or with lower concentration of active substance in the carrier.

The goal of the invention is to produce a transparent nanofibrous layer with a great specific surface permeable for oxygen and light, which would comprise a photodynamic sensitizer in a solid state in a quantity sufficient to generate the $^1O_2$ upon exposure of a daylight or artificial light.

Principle of the invention

The goal of the invention has been reached by a formation comprising at least one layer of nanofibres according to the invention, whose principle consists in that, the layer of polymer nanofibres comprises particles of photodynamic sensitizer, at the same time the nanofibres are isotropic spread in a transparent and porous layer of surface weight from 0,01 g/m^2 to 15 g/m^2.

The porous and transparent layer of nanofibres enables access for light and oxygen O_2 to particles of photodynamic sensitizer deposited in and on the nanofibres. Upon exposure of such layer of polymeric nanofibres to a light radiation due to a contact of oxygen contained in the air or in solution with particles of photodynamic sensitizer the $^1O_2$ is generated, which is effective in an immediate vicinity of sensitizer, i.e. in a layer of nanofibres and its close vicinity.

The particles of photodynamic sensitizer are anchored inside and/or on a surface of nanofibres. As a result of transparency and nanoporosity of the layer both oxygen as well as the light get to these particles without problems and the $^1O_2$ is generated.

As a result of a great specific surface of nanofibrous layer it is sufficient if the particles of photodynamic sensitizer in nanofibres are contained in the quantity 0,0001 to 0,01 g of sensitizer to 1 g of nanofibre layer. Low quantity of photodynamic sensitizer reduces a theoretic possibility of contamination of chemical or biological surroundings by the sensitizer and reduces economic costs.

For usage in an air as well as water environment the nanofibres are produced from polyurethane of polyacrylonitrile, polystyrene, polyvinyl alcohol or other polymer, the photoactive particle is 5,10,15,20-tetraphenyl-21H,23H-porfin (TPP) and/or C_{60} or other photodynamic sensitizer.

For some applications according to the invention it is advantageous, if the layer of polymeric nanofibres comprising particles of photodynamic sensitizer is deposited on a substrate material. Textile, paper, metal foil, plastic foil or combination of these materials may be the substrate material. By using the substrate material the strength of formation is increased, at the same time the possibilities of applicability are greater.

As a suitable substrate material e.g. the wallpaper may be used, through its application in illuminated areas, in which many people are present, the danger of transfer of infectious disease may be limited .

To enlarge the spectral range of light absorption it is further advantageous, if the nanofibre layer is formed by at least two layers of nanofibres, out of which each comprises other photodynamic sensitizer.

For a certain usage of formation according to the invention it is also advantageous, if the nanofibre layer is formed by at least two layers of nanofibres of different polymers.

The principle of method for production of nanofibre layer according to the invention consists in that the polymer solution for spinning contains particles of photodynamic sensitizer, which are during spinning seized together with polymer into the nanofibres being produced, in which these particles are anchored inside or on the surface.

Another procedure for production of nanofibre layer according to the invention is adsorption of photodynamic sensitizer to the surface of nanofibres from solution in a solvent , which does not dissolve the used nanofibres.

Description of the drawing

Example of embodiment of textile according to the invention will be described in the following text. Documentation of effects of the textile according to the invention is supported by the pictures on enclosed drawings, where the Fig. 1 shows absorption UV-VIS spectrum of detection iodine agent for singlet oxygen $^1O_2$ in presence of a textile with layer of polymeric polyurethane nanofibres comprising non-polar sensitizer 5,10,15,20-tetraphenyl -21H,23H-porfin (TPP designated also as *meso*-tetraphenylporphyrin) in period of 0 to 60 minutes of exposure by 250 W halogen lamp, while the lower curve is valid for the time 0 minutes and the upper curve for the time 60 minutes, the Fig. 2 linear increase of absorbance of photoproduct I_3^- in dependence on time during exposure of nanofibrous textile with TPP in iodine detection agent, the Fig. 3 linear production I_3^- during exposure of textile with a layer of nanofibres comprising sensitizer TPP in iodine detection agent, the Fig. 4 shows a photo of textile sample with layer of polymer polyurethane nanofibres comprising

sensitizer TPP, the Fig. 5 schematic representation of production of endoperoxide and its thermolysis.

Examples of embodiment

The production method of nanofibre layer through electrostatic spinning of polymer solution in electric field created by difference of potentials between the spinning electrode and collecting electrode according to the invention and the textile comprising a layer of nanofibres according to the invention will be described on an example of embodiment, at which the polymer solution into electric field for spinning is delivered through the rotating spinning electrode, which by a section of its circumference is dipped into the polymer solution and through its surface it brings the polymer solution into electric field for spinning. With advantage, the spinning electrode is at the same time formed by a cylinder according to CZ 294274 and to it analogical international application WO 2005/024101 A1 or it may be formed by another suitable rotatably mounted body of an oblong shape. Through electrostatic spinning the mentioned textiles are produced from various polymers soluble in water or non-water solution. The diameter of produced nanofibres is less than 600 nanometers, usually in the range from 50 to 600 nanometers and produced nanofibres are deposited into a layer of nanofibres on a substrate material, which passes between the spinning electrode and collecting electrode. The substrate material may be e.g. textile, paper, plastic foil, metal foil or a combination of these materials. Through electrostatic spinning also a separate layer of nanofibres may be produced without depositing on a substrate material.

Under suitable circumstances together with polymer also the photodynamic sensitizer may undergo the spinning process, which is soluble in the same solvent as the polymer undergoing spinning. For example, the sensitizer zincic complex of TPP (ZnTPP) is a suitable photodynamic sensitizer or in examples of embodiment the shown non-polar photodynamic sensitizer 5,10,15,20-tetraphenyl-21H,23H-porfin (TPP, designated also as *meso*-tetraphenylporphyrin), while both photodynamic sensitizers may be used simultaneously possibly with other suitable photodynamic sensitizers, so that

the incident light is absorbed more efficiently in the whole spectral range. The suitable polymers are e.g. polyurethane, polyvinylalcohol, polyacrylonitrile, polystyrene and others. According to present experience based on numerous experiments it is obvious, that all polymers capable of electrostatic spinning are suitable polymers, while the chemical composition of polymer influences periods of life of excited triplet statuses of sensitizer and of a produced singlet oxygen $^1O_2$. The life period of $^1O_2$ is very important because it conditions its photooxidation and photodesinfection effect. The experiments further showed that upon exposure of nanofibrous layer the $^1O_2$ is produced by a sensitizer inside the nanofibres as well as by a sensitizer anchored on surface of nanofibres, as it was proven, that oxygen can get through the polymer also to the encapsulated sensitizer inside the nanofibres. Nevertheless the sensitizer is more affected inside nanofibres. Similarly, the photodynamic sensitizers may be selected from a whole range of known sensitizers according to their sensitivity to a respective part of spectra of incident light, while the basic property of the used sensitizer is its solubility in solution of polymer being subject to spinning, or at least a capability to diffuse in polymer solution into such small particles, which upon electrostatic spinning may be seized together with polymer into the nanofibres being produced.

The particles of photodynamic sensitizer are during electrostatic spinning carried out by a surface of rotating spinning electrode together with polymer and in electric field together with polymer they are seized to the collecting electrode and they remain deposited in nanofibres as a part of them. At the same time sensitizers are anchored inside and/or on the surface of nanofibres. Concentration of photodynamic sensitizer in produced nanofibrous layer is close to concentration of sensitizers in the spinning solution, so that quantity of sensitizer in nanofibrous layer may be exactly determined in advance and it may be maintained on a very lower level. Textiles with such a modified layer of nanofibres have a high specific surface and the photodynamic sensitizer is in this way distributed on a large area. The surface weight of nanofibrous layer varies from 0,01 g/m^2 to 15 g/m^2. Nanofibrous layer is transparent and porous, which enables access for light and oxygen (including oxygen dissolved in

solutions) to particles of photodynamic sensitizer bound in nanofibres and anchored on surface of nanofibres and as a result of this production of singlet oxygen $^1O_2$, to effective production of which a very low concentration of sensitizer is necessary. Inside and on surface of nanofibres there are anchored the molecules of sensitizer with the content of 0,0001 g to 0,01 g in 1 g of polymer, of which the nanofibres are produced. It is advantageous if the ratio of nanofibres having diameter 50 to 200 nm is as great as possible, respectively if the nanofibres of nanofibrous layer are the thinnest, because with decreasing thickness of nanofibres the specific surface of nanofibre layer is increasing. The particles of sensitizer at these diameters of nanofibres are positioned more on surface of nanofibres, thus better accessible for light and oxygen and less influenced by the polymer.

The advantage of a low concentration of sensitizer is lowering of possibility of contamination of chemical or biological environment by the sensitizer and decrease in economical costs. Porous structure of nanofibre layer simultaneously restricts an access of high-molecular substances and microbes to the surface covered by nanotextile. A short life period of singlet oxygen $^1O_2$ with a short diffusion ratio ensures a local (*in situ*) acting of singlet oxygen $^1O_2$ in the vicinity of sensitizer, this is inside the nanofibrous layer and in its vicinity, and as a result of this the singlet oxygen does not act as toxicant in a more distant surroundings of nanofibrous layer.

The nanotextile, whose nanofibrous layer contains inside and/or on surface of nanofibres the anchored particles of photodynamic sensitizer, has a strong photooxidant efficiency, a high photodisinfecting and long-term antimicrobial efficiency and it is sterile on the light. The microorganizms do not create resistance to the singlet oxygen $^1O_2$ as e.g. to antibiotics, while the succession of sensitivity of individual microorganizms to $^1O_2$ is frequently opposite than the succession of sensitivity to ionising radiation. For example the *Deinococcus radiodurans*, is extremely resistant to ionising radiation, but highly sensitive to $^1O_2$.

Together with polymer and photodynamic sensitizer it is possible to subject to spinning also a suitable semicyclic aromatic substrate, which together with $^1O_2$ creates a thermally restricted stable endoperoxide, which through a slight warming decomposes back to original molecule of polycyclic aromatic substrate and oxygen with high content of $^1O_2$ in the meaning of backward reaction shown in the Fig. 5. Such polycyclic aromatic substrates create precursors of endoperoxides and they represent the carriers or secondary sources of $^1O_2$. A suitable precursor of endoperoxide for example is 1,4-dimethylnaphtalene (DMN), which creates endoperoxide decomposing already at slightly increased temperature with dissolution half-time of $t_{1/2} \approx 5$ hrs at 25 ^{0}C.[vi]

The photodynamic sensitizer may be applied onto the layer of nanofibres by dipping the layer of nanofibres in a solution, which contains sensitizer and which does not contain a solvent chemically affecting the used nanofibres, while the adsorption of photodynamic sensitizer takes place on a surface of nanofibrous layer.

Similarly a suitable precursor of endoperoxide may be applied on a layer of nanofibres by dipping the layer of nanofibres in a solution. Such precursor is dissolved in a solution, which does not contain a solvent affecting the nanofibres of the dipped layer. By dipping the layer of nanofibres in the solution an adsorption of precursor of endoperoxide takes place on a surface of nanofibre layer. The solution may be common with the photodynamic sensitizer.

Example 1

In a fifteen percent solution of polyurethane (PU) in dimethylformamide the non-polar photodynamic sensitizer TPP is dissolved in a concentration 0.0001-0,01 g of TPP to 1 g of PU. This solution is subject to electrostatic spinning in above mentioned manner, while the particles or molecules of TPP in the course of electrostatic spinning process are seized together with solution of polyurethane. The nanofibres being produced of a diameter of 50 to 600 nm are deposited on a surface of substrate material formed by a polypropylene

microfibrous layer produced through the spun-bond technology of a surface weight of 18 g/m^2. Through this the non-woven textile is produced which comprises the layer of nanofibres. Surface weight of the nanofibrous layer comprising TPP is 1 g/m^2. To attain a greater thickness or a greater surface weight of nanofibre layer it is possible to apply on a substrate material the nanofibres in several one after another arranged electrostatic spinning devices and so the surface weight up to 15 g/m^2 may be achieved. In the same manner another sensitizer e.g. ZnTPP may be used.

The nanofibres of a nanofibrous layer are formed of polyurethane and in them or on their surface there is installed the non-polar photodynamic sensitizer TPP or ZnTPP in concentration 0,0001- 0,01 g to 1 g of polyurethane.

To reach better affects in water surroundings, the nanofibrous layer containing TPP was modified by a surface active substance, e.g. 0,6 % dodecylsulphonate sodium. Through this the totally hydrophobic textile turned to become hydrophile textile, through which the photodisinfecting effect of nanofibrous layer of textile towards bacteria in water is increased. The reason is acting of $^1O_2$ to a very short distance, this is basically in situ and due to higher wettability a better access of water to the sensitizer.

Example 2

In solution of polyacrylonitrile (PAN) the TPP is dissolved in concentration 0,01 g of TPP to 1 g of PAN and the solution is subject to electrostatic spinning. The nanofibres being produced are deposited on surface of non-woven microfibrous textile of a surface weight of 20 g/m^2. On surface of nanofibres and in their diameter there is anchored the non-polar photodynamic sensitizer TPP .

Example 3

In solution of polyacrylonitrile (PAN) the TPP is dissolved in concentration 0,005 g of TPP to 1 g of PAN and the solution is subject to electrostatic spinning. The nanofibres being produced are deposited on surface

of non-woven microfibrous textile produced by means of spun-bond technology of a surface weight of 15 g/m^2. According to technological conditions of electrostatic spinning the nanofibres having diameter of 50 to 600 nm are produced. On surface of nanofibres and in their cross-section there is anchored the non-polar sensitizer TPP.

Example 4

In a spinning chamber of the device for production of nanofibres through electrostatic spinning there are several spinning devices arranged one after another.

The first spinning device contains the PU solution with the ZnTPP sensitizer in determined concentration and on the substrate material it deposits a first layer of PU nanofibres with this sensitizer.

The second spinning device contains the PAN solution with TPP in determined concentration and on the substrate material it deposits a second layer of PAN nanofibres with TPP.

The third spinning device contains solution of polyvinylalcohol with netting means and with TPP or other suitable sensitizer in determined concentration and on the substrate material it deposits a third layer of nanofibres of polyvinylalcohol with TPP.

The composed nanofibrous layer much more efficiently absorbs the incident light in a broader spectral range.

The number of nanofibrous layers is nevertheless limited by technological possibilities of a concrete spinning chamber respectively of a spinning machine. At the same time it is advantageous to combine the layers of nanofibres with various photodynamic sensitizers and to select these sensitizers so that the incident light is absorbed in the largest possible spectral range.

Example 5

In a twelve percent water solution of polyvinylalcohol (PVA) the $ZnTPPS_4$ sensitizer is dissolved in concentration 0,001 g of $ZnTPPS_4$ to 1 g of PVA. Simultaneously in the solution the system of cross-linking agents of polyvinylalcohol – phosphoric acid and glyoxal is dissolved. This solution is subject to electrostatic spinning in the above mentioned manner. The nanofibres being produced are deposited on a suitable substrate material, e.g. on non-woven textile of microfibres produced by means of spun-bond technology. Through electrostatic spinning the nanofibrous layer of a surface weight of 2 g/m^2 is produced which consequently is subject to netting by warming to the temperature of 140 °C for a period of 5 minutes. In the same manner another porphyrin sensitizer may be used.

Through this the non-woven textile with nanofibrous layer is produced, whose nanofibres are made of polyvinylalcohol (PVA) and they comprise inbuilt sensitizer $ZnTPPS_4$ having concentration of 0,001 g of $ZnTPPS_4$ in 1 g of polyvinylalcohol.

The non-woven textile according to this example of embodiment does not generate $^1O_2$ in a dry surroundings, but after dipping into water the $ZnTPPS_4$ is released from the textile into the water, and $ZnTPPS_4$ after then generates $^1O_2$ in the water. This property seems to be desirable for some applications, in which it is required that the $^1O_2$ is not produced in a dry surroundings.

Example 6 – Demonstration of photooxidative effect of nanofibrous layers with porphyrin sensitizers

A section with dimensions of 1 x 2 cm was cut of the non-woven textile containing a layer of nanofibres comprising TPP according to example 1. This section of textile was positioned on an inner wall of silica burette having dimensions of 1 x 1 x 3 cm containing 2 ml of iodine detection solution for singlet oxygen $^1O_2$ and radiated with halogen lamp, as represented in the Fig.

3. In consequence of contact of oxygen O_2 in detection solution with TPP in nanofibres under presence of light the $^1O_2$ is generated. Reaction of such photogenerated $^1O_2$ with I^- in a water surroundings through a complicated mechanism produces I_3^- in presence of catalyzer $(NH_4)_2MoO_4$[vii]. Concentration of I_3^- (product of photooxidation) being produced may be observed in its absorption strip at 351 nm, as it is obvious from the Fig.1. and Fig. 2.

The arrow in the Fig. 1 indicates an increase of absorbance I_3^- in the time of radiation. Concentration of I_3^- is proportional to photoproduction $^1O_2$.

As represented in the Fig. 2 a linear increase of absorbance of I_3^- during radiation indicates a very equal photoproduction $^1O_2$ on a layer of nanofibres comprising TPP during exposure of textile with layer of nanofibres with TPP in iodine detection agent.

Photosensitized reactions require presence of sensitizer, oxygen and light. Under above mentioned experimental conditions the generation of $^1O_2$ (respectively of I_3^-) is ceased in absence of light , as represented in the Fig. 3a. During exposure of textile with nanofibres with TPP in iodine detection agent the I_3^- (thus also $^1O_2$) is being produced, and this production stops in the dark. Photoproduction of I_3^- is also not observed under presence of 0.01M NaN_3, physical extinguisher $^1O_2$ in detection agent or in absence of oxygen O_2, if e.g. the detection solution is saturated by an inert gas. To the contrary, presence of D_2O, in the detection solution increases photoproduction of I_3^-.

Example 7

The nanofibrous layer with PVA nanofibres was dipped into 1% solution of TPP in chloroform. After 20 minutes the layer was taken out and dried freely on the air. By radiation of the layer with adsorbed TPP a generation of $^1O_2$, was demonstrated similarly as at the example 6.

Example 8 – Demonstration of bactericidal effect of nanofibrous layers with porphyrin sensitizers

From nanofibrous textile comprising a layer of nanofibres with photodynamic sensitizer according to example 1 the disks of 0,5 cm radius were cut off and positioned on two bacterial agar plates, the working bacterial plate and the checking bacterial plate. Both bacterial plates contained the X-gal (5-bromo-4-chloro-3-indolyl-ß-D-galactpyranosid) and in the whole surface they were inoculated by E-coli bacteria (type DH5α with plasmide pGEM11Z), producing the beta galactsidase. This enabled to visualise the bacterial colonies, because the bacterial enzyme splits off sugar under production of indol colouring agent, by which the bacterial colony receives the blue-green colour. The disks from the same nanofibrous textile without sensitizer were also positioned on bacterial plates. These disks exercised the function of negative checking.

After then, the working bacterial plate was radiated by a cold white light (power of the source 150 W) from a distance of 15 cm for a period of 15 minutes. The checking bacterial plate (B) was maintained in the dark. After irradiation of the working bacterial plate, both plates were incubated 18 hours at 37° C in incubator. The bacterial plates with disks with grown bacterial colonies were documented by means of photos.

No bacterial colonies grew on the disks from the nanofibrous textile comprising a layer of nanofibres with photodynamic sensitizer on the working bacterial plate irradiated by light. The colonies did not grow either in the vicinity, cca 0,5 mm, of these disks, as represented in the Fig. 4 and in the Fig. 4a. Photo in the Fig. 4a documents the photodisinfecting action of nanofibrous textile with a layer of nanofibres, which comprise the TPP in concentration 0,01 g of TPP to 1 g of polyurethane. After irradiation the colonies of E-coli bacteria of a blue-green colour are noticeable on an agar surface outside the surface of the disk and its vicinity. This means, that on surface of the disk and in its vicinity there are a sterile and photo disinfecting surroundings.

On the contrary, plenty of bacterial colonies grew on the rest of agar surface of the working bacterial plate and on the disks from nanofibrous textile with layer of nanofibres without sensitizer.

On the checking bacterial plate, which was not exposed to the light, the bacterial colonies grew on the whole surface including the disks, that means both the disks from nanofibrous textile with layer of nanofibres without sensitizer, and the disks from nanofibrous textile with layer of nanofibres with sensitizer.

Through further experiments it was revealed, that the same results are reached also at exposure of samples by a daylight or other suitable light.

The nanofibrous layer according to sample 1, 2, 3 or 4 is applied to the right side of wallpaper in a surface weight 0,01 to 15 g/m^2. The surface weight at the same time is controlled especially according to the intensity of light, which is supposed to be in a place where the wallpaper will be used, so that the transillumination of the whole nanofibrous layer is achieved. The wallpaper may be of any material, for example of paper, textile, of their combination and with any surface finish, which however must allow fixation of layer of nanofibres and sufficient access of light and oxygen.

Generally the nanofibrous layer with content of photodynamic sensitizer may be applied on any substrate enabling application and a following fixation of nanofibrous layer, e.g. on a paper strip, plastic or metal foil, and especially on a suitable textile. The advantage of textile as a substrate material is air permeability and translucence, so that the substrate material does not restrict effect possibilities of nanofibrous layer with a content of photodynamic sensitizers.

The nanofibrous layer may be produced separately and consequently either used as it is or deposited on any suitable body shaped for a particular purpose and to create in this way a three-dimensional formation.

Example 9

The nanotextile is formed by the PUR nanofibres, which comprise the encapsulated photosensitizer TPP in a quantity 0,1 % by weight and precursor of endoperoxide, which is formed by 1,4-dimethylnaphthalene (DMN) in a

quantity 14 % by weight. Such nanotextile produces the $^1O_2$ on light. A portion of produced $^1O_2$ peroxidizes the inbuilt DMN. The created endoperoxide is gradually decomposed thermally upon release of the $^1O_2$. The photooxidation and photodisinficting effect of nanotextile is thus intensified by oxidation/disinfecting effect of the $^1O_2$ produced in the dark. Oxidation or disinfecting effect may be thus monitored by usage of methodics shown in examples 6 to 8.

Applicability

The textile comprising at least one layer of nanofibres containing the photodynamic sensitizer is applicable in chemistry for preparation of specific products of reaction of a number of substrates with photogenerated $^1O_2$.

Next to this, the textile according to the invention is applicable in a human and veterinary medicine for a wide spectra of applications requiring sterile or sterilising medical material (plasters, bandages, upper part of surgical mouth-screens and other surgical textiles), which simultaneously prevents access and growing of bacteria, cilia and fungus.

The textile according to the invention may be also used in other e.g. industrial artistic (e.g. artificial ageing of surfaces) or cosmetic applications, making use of a local, oxidative effect of the $^1O_2$ especially in the surface.

Another possibility of application is for example photodegradation of aromatic pollutants by means of the photogenerated $^1O_2$

Another possibility of application is preservation of sterile surfaces, non-oxidizing chemicals being subject to bacterial decomposition, agricultural products (e.g. seeds of plants), foodstuffs or potable water.

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CLAIMS

1. The formation comprising at least one nanofibre layer having diameter to 600 nm produced through electrostatic spinning of polymer solution, **characterised by that the** layer of polymer nanofibres comprises particles of photodynamic sensitizer, at the same time the nanofibres are isotropic spread in a transparent and porous layer of surface weight from 0,01 g/m^2 to 15 g/m^2.

2. The formation according to the claim 1, **characterised by that the** particles of photodynamic sensitizer are anchored inside and/or on surface of the nanofibres.

3. The formation according to any from the previous claims, **characterised by that the** particles of photodynamic sensitizer in nanofibres of nanofibre layer are contained in the quantity 0,0001 g to 0,01 g of sensitizer to 1 g of nanofibre layer.

4. The formation according to any from the previous claims, **characterised by that the** nanofibres are produced of polyurethane or PAN and the particles of photodynamic sensitizer are from 5,10,15,20-tetraphenyl-21H,23H-porfin (TPP) and/or of zinzic complex of TPP (ZnTPP).

5. The formation according to any from the previous claims, **characterised by that the** layer of polymer nanofibres comprises the precursor of endoperoxide.

6. The formation according to the claim 5, **characterised by that the** precursor of endoperoxide is 1,4-dimethylnaphthalene (DMN).

7. The formation according to any from the previous claims, **characterised by that the** layer of polymer nanofibres is deposited on a substrate material.

8. The formation according to the claim 7, **characterised by that the** substrate material is textile or paper or plastic foil or the metal foil or a wallpaper.

9. The formation according to any from the previous claims, **characterised by that the** layer of nanofibres is formed by at least two layers of nanofibres, out of which each comprises different photodynamic sensitizer.

10. The formation according to any from the previous claims, **characterised by that the** layer of nanofibres is formed by at least two layers of nanofibres produced from different polymers.

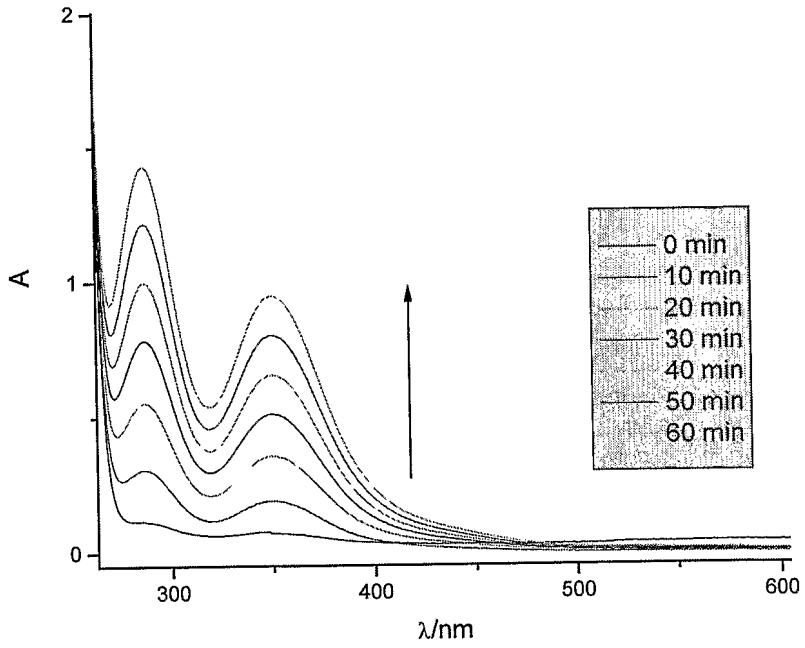
11. The production method of nanofibre layer through electrostatic spinning of polymer solution in electric field created by difference of potentials between the spinning electrode and collecting electrode, while the nanofibres produced in this electric field are carried to the collecting electrode and they deposit on a surface designated to it, **characterised by that the** polymer solution for spinning contains particles of photodynamic sensitizer, which are during spinning seized together with polymer into the nanofibres being produced, in which these particles are anchored inside or on the surface.

12. The method according to the claim 11, **characterised by that the** polymer solution for spinning comprises particles of precursor of endoperoxide, which are during spinning seized together with polymer into the nanofibres being produced, in which they are anchored inside or on the surface.

13. The method of production of nanofibre layer according to the claims 1 to 4, **characterised by that the** layer of nanofibres is dipped into the solution, which contains photodynamic sensitizer and which does not contain a solvent affecting the used nanofibres, while the adsorption of photodynamic sensitizer takes place to a surface of nanofibres.

14. The method according to the claim 13, **characterised by that the** layer of nanofibres is dipped into the solution containing the precursor of endoperoxide and not containing a solvent affecting the used nanofibres, while the adsorption of precursor of endoperoxide takes place to the surface of nanofibres.

15. The method according to the claim 12 or 14, **characterised by that the** precursor of endoperoxide is 1,4-dimethylnaphthalene (DMN).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400
500
600
λ/nm
0 min
10 min
20 min
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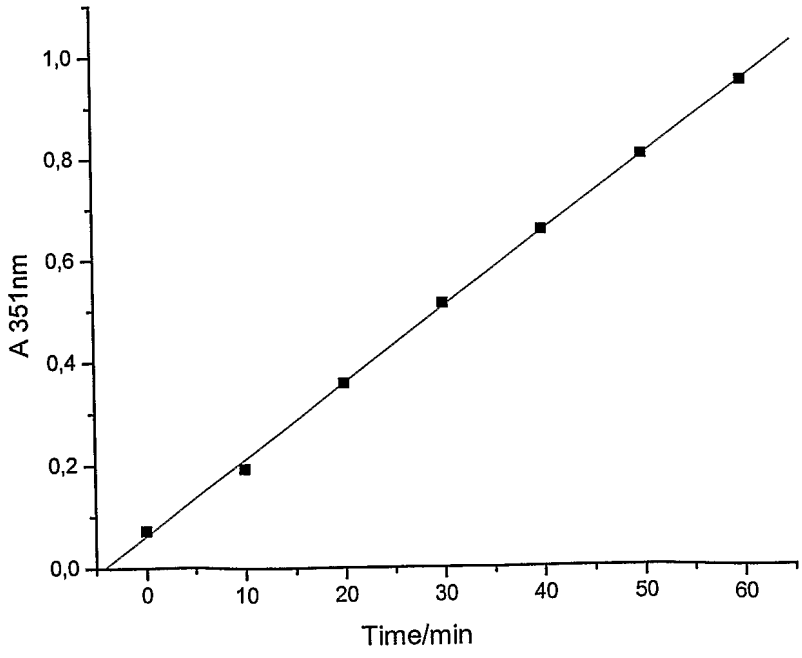
40 min
50 min
60 min

Fig. 1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60
Time/min

Fig. 2

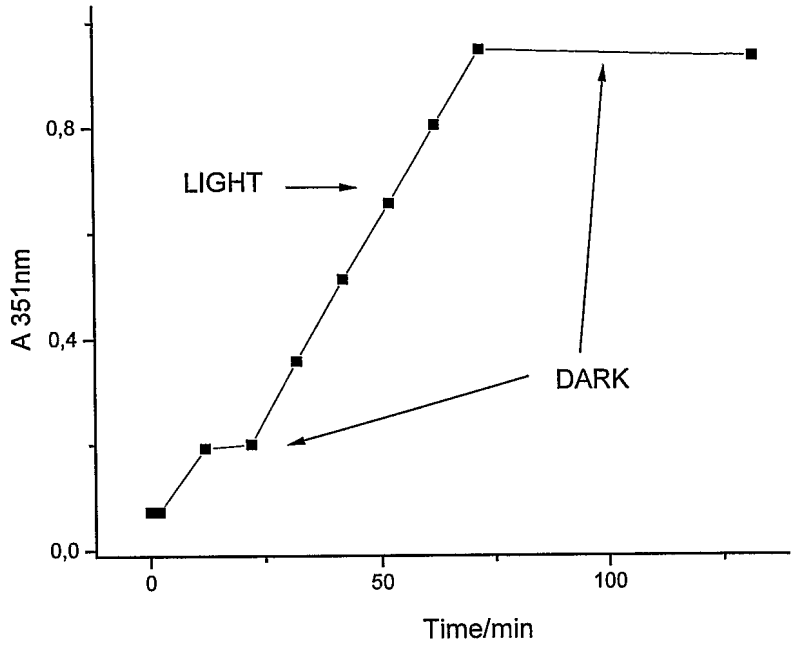

Fig. 3

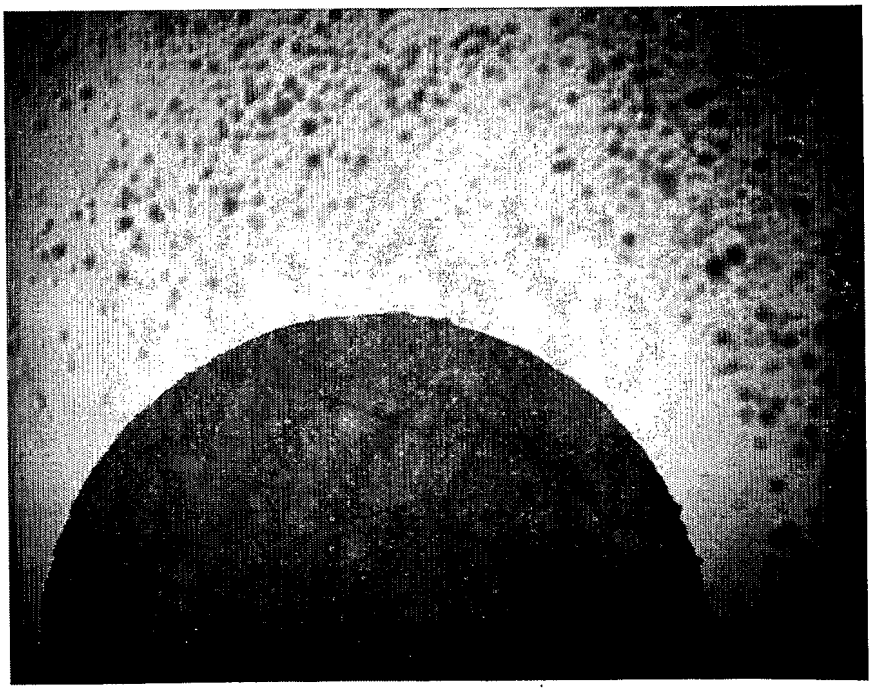

Fig. 4