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(54) Title: METHOD FOR TREATING AN ARTICLE MADE OF FIBROUS MATERIAL, ARTICLE OBTAINED BY SAID METHOD AND MEDICAL AND/OR HEALTH CARE AND/OR PERSONAL CARE DEVICE COMPRISING SAID ARTICLE

(57) Abstract: The present invention refers to a method for treating an article (9) made of fibrous material, able to provide said article (9) with antibacterial and/or antifungal properties by the application on a surface (9p) of said article (9) of particles of a method oxide. The method according to the present invention comprises the first step of generating said particles by flame synthesis of said particles from a precursor compound. The method according to the present invention then comprises the second step of depositing said particles in a controlled manner on a surface (9p) of said article (9) by means of thermophoresis. The present invention further refers to a medical and/or health care and/or personal care device comprising an article (9) made of fibrous material treated by means of the method comprising the aforesaid first step and second step.

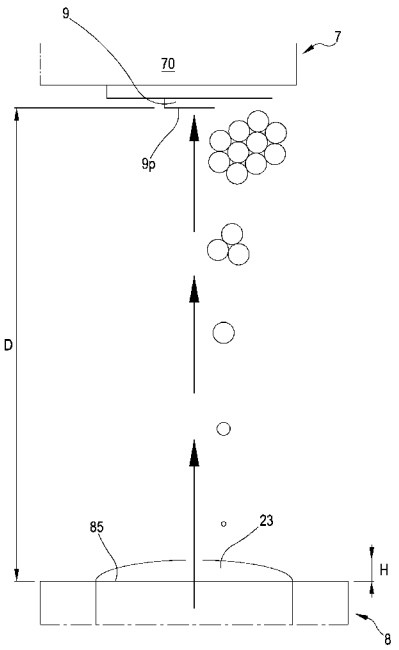


FIG.3

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# "METHOD FOR TREATING AN ARTICLE MADE OF FIBROUS MATERIAL, ARTICLE OBTAINED BY SAID METHOD AND MEDICAL AND/OR HEALTH CARE AND/OR PERSONAL CARE DEVICE COMPRISING SAID ARTICLE"

## DESCRIPTION

The present invention relates to a method for treating an article made of fibrous material, able to provide said article with antibacterial and/or antifungal properties by means of the application on the surface of said article of particles of a titanium-based compound, preferably titanium dioxide ($TiO_2$) The present invention further relates to an article obtained by means of said method and a medical and/or health care and/or personal care device comprising said article.

In environments such as hospitals it is extremely important to contrast the proliferation of fungi and bacteria, inasmuch as they are pathogenic factors especially for in-patients, out-patients and health care professionals. Among the devices that are most at risk of facilitating such proliferation are those made of fabric (for example sheets or white coats, but also disposable devices such as gauze or bandages), wherein fungi and bacteria can become ensconced and reproduce very rapidly. Over the years, consequently, progressively more attention has been paid to the development of technical solutions that would make it possible to reduce the vulnerability of fabric devices to the lodging and proliferation of fungi and bacteria.

Among these technical solutions, some of those deemed to be of greatest interest use titanium dioxide, in view of the undoubted cleansing and sanitising properties of this material. Known technical solutions wherein titanium dioxide particles are used entail their local application. To the surfaces of the fabrics to be treated, a solution of titanium dioxide in a solvent is applied. The solvent is then made to evaporate and particles of titanium dioxide thus remain positioned on the treated surfaces.

While such local application of particles of titanium dioxide improves the hygiene of the fabrics, it has undoubted critical issues. In the first place, application of the solvent and the subsequent applying of heat can damage the fabrics. In the second place, the process that allows the local application of titanium dioxide is poorly repeatable and is distinguished by a rather low efficiency. In the third place, titanium dioxide particles, following the evaporation of the solvent, remain on fabrics in agglomerated form.

This latter critical issue certainly constitutes the most significant one. Agglomerates of titanium dioxide particles, being all of large size and differing from one another in structure and geometry, cannot arrange themselves on the surface of the fabrics, to constitute a continuous, uniform coating layer. Between the agglomerates, wide interstices are created, i.e. wide areas that in fact are not treated and thus are highly susceptible being attacked by fungi and bacteria and hence to facilitate their proliferation. Moreover, because of their significant mass, agglomerates of titanium dioxide particles are easily removed by a mechanical action. Therefore, a simple friction of the fabrics after the local application of titanium dioxide particles causes their detachment and consequently the loss of all the fabric cleansing and sanitisation benefits. Lastly, because of the interstices between agglomerates, the chemical agents that come in

contact with the fabrics (for example in a subsequent washing treatment) have facilitated paths to infiltrate between the titanium dioxide particles and hence to cause their detachment by chemical action.

The document DE102012003943A1 describes a method for applying a nano-layer with antimicrobial capabilities on a substrate of fabric, paper or generally of a fibrous materials, under atmospheric pressure conditions (thus avoiding the complexity and costs of vacuum processes). In the nano-layer is present a metal or a metal oxide (preferably ZnO, but also TiO2) in the form of nanoparticles generated by flame synthesis starting from a precursor compound. A nano-layer of metal or metal oxide nanoparticles can be applied to a garment for patients with lesions, to make it dermo-compatible and protective.

A purpose of the present invention is to solve the aforesaid drawbacks noted in relation to the prior art, in particular in relation to the local application of titanium dioxide particles.

Another purpose of the present invention is to make available a method for treating an article made of fibrous material (for example an article made of fabric or paper) distinguished by high hygiene.

Another purpose of the present invention is to make available a method for treating an article made of fibrous material that makes said article particularly capable of contrasting the proliferation of fungi and bacteria, both immediately after the execution of the treatment, and after the treatment as time goes by.

Another purpose of the present invention is to make available a method for treating an article made of fibrous material wherein the effectiveness of the treatment is not then compromised by mechanical actions (for example, friction) which the article undergoes after the treatment.

Another purpose of the present invention is to make available a method for treating an article made of fibrous material wherein the effectiveness of the treatment is not as easily compromised by the chemical agents with which the article comes in contact after the treatment (the article is then able to maintain appreciable resistance to fungi and bacteria even after undergoing some washing treatments).

Another purpose of the present invention is to attenuate the biological hazard to which are subject, in a hospital environment, both patients and health care professionals.

Another purpose of the present invention is to obtain sterile articles for the treatment, for example, of wounds with exudate, configured to minimise the risk of fungal or bacterial infections through the wounds.

These and other purposes are achieved by means of the method for treating an article made of fibrous material, by means of the fibrous article and by means of the medical and/or health care and/or personal care device according to one or more of the following aspects.

A first aspect of the invention refers to a method for treating an article made of fibrous material, adapted to provide said article with antibacterial and/or antifungal properties by means of the application on a surface of said article of particles of a metal oxide, preferably of a titanium- or zinc- or iron- or silver-based oxide, still more preferably titanium dioxide (TiO2), said method comprising the steps of:

i) generating said particles through Flame Synthesis of said particles from a precursor compound, preferably titanium tetraisopropoxide (TTIP) and/or titanium tetrachloride (TiCl4), and

ii) depositing in a controlled manner said particles on a surface of said article (9) by thermophoresis.

A second aspect of the invention, dependent on the first aspect, refers to a method for treating an article made of fibrous material, wherein said flame synthesis occurs by means of a reactor to which said precursor compound is carried and wherein said surface of said article is exposed to the output section of said reactor.

A third aspect of the invention, dependent on the second aspect, refers to a method for treating an article made of fibrous material, wherein the exposure of said surface of said article to said output section of said reactor is a periodic exposure wherein a first exposure phase is alternated with a second non-exposure phase, the duration of said first exposure phase being appreciably shorter than the duration of said second non-exposure phase.

A fourth aspect of the invention, dependent on the third aspect, refers to a method for treating an article made of fibrous material, wherein said duration of said first exposure phase is shorter than 1 second, preferably shorter than 0.1 seconds, yet more preferably approximately 0.02 seconds.

A fifth aspect of the invention, dependent on the third aspect or on the fourth aspect, refers to a method for treating an article made of fibrous material, wherein the duration of said periodic exposure is between 10 seconds and 10 minutes, preferably between 1 minute and 5 minutes, still more preferably between 150 seconds and 180 seconds.

A sixth aspect of the invention, dependent on any aspect between the third aspect and the fifth aspect, refers to a method for treating an article made of fibrous material, wherein said periodic exposure is obtained by rotation of a carousel, said article being applied to said carousel so as to assure the exposure of said surface of said article to said output section of said reactor.

A seventh aspect of the invention, dependent on any aspect between the second aspect and the sixth aspect, refers to a method for treating an article made of fibrous material, wherein said precursor compound is carried to said reactor by means of a solution of said precursor compound in a solvent, preferably ethanol.

An eighth aspect of the invention, dependent on any aspect between the second aspect and the seventh aspect, refers to a method for treating an article made of fibrous material, wherein said precursor compound is carried to said reactor in aerosol form, said aerosol being preferably generated by means of a vibrating orifice aerosol generator (VOAG).

A ninth aspect of the invention, dependent on the eighth aspect, refers to a method for treating an article made of fibrous material, wherein said aerosol is mixed in said reactor with a fuel, preferably ethylene premixed with air.

A tenth aspect of the invention, dependent on any aspect between the second aspect and the ninth aspect, refers to a method for treating an article made of fibrous material, wherein said precursor compound is carried to said reactor by saturation of a dispersion medium, preferably air, of said precursor compound and/or of said solution of said precursor compound in said solvent.

An eleventh aspect of the invention, dependent on any aspect between the second aspect and the tenth aspect, refers to a method for treating an article made of fibrous material, wherein the temperature of the flame at said output section

of said reactor is between 1000 K and 2500 K, preferably between 1500 K and 2000 K, still more preferably between 1700 K and 1800 K and/or wherein the temperature difference between said article and the flame at said output section of said reactor is between 400 K and 2200 K, preferably between 400 K and 1700 K, still more preferably between 400 K and 1500 K.

A twelfth aspect of the invention, dependent on any of the preceding aspects, refers to a method for treating an article made of fibrous material, wherein said step i) is preceded by the preliminary step of regulating the numerousness of said particles and/or the coalescence of said particles and/or the possible agglomeration of said particles and/or the crystalline group of said particles.

A thirteenth aspect of the invention, dependent on the twelfth aspect, refers to a method for treating an article made of fibrous material, wherein in said preliminary step an adjustment of the distance of said surface of said article from said output section of said reactor is carried out, in particular of the component of said distance orthogonal to said output section of said reactor, an increase of said distance determining an increase of the size of said particles and/or the passage of said particles from the condition of non-agglomeration to the condition of agglomeration.

A fourteenth aspect of the invention, dependent on the twelfth aspect or on the thirteenth aspect, refers to a method for treating an article made of fibrous material, wherein in said preliminary step an adjustment of the concentration of said precursor compound in said solution is carried out, an increase of said concentration determining an increase of the numerousness of said particles and/or of the size of said particles and/or the passage of said particles from the condition of non-agglomeration to the condition of agglomeration.

A fifteenth aspect of the invention, dependent on any aspect between the twelfth aspect and the fourteenth aspect, refers to a method for treating an article made of fibrous material, wherein in said preliminary step an adjustment of the stoichiometry of the flame is carried out, in particular by adjustment of the quantity of comburent and/or of fuel sent into said reactor, a change of the stoichiometry of the flame determining a change of the quantity of oxygen present in the environment of the reactor and hence of the crystalline group of said particles.

A sixteenth aspect of the invention, dependent on any of the preceding aspects, refers to a method for treating an article made of fibrous material, wherein said particles are deposited on said surface of said article in the non-agglomeration condition.

A seventeenth aspect of the invention, dependent on any of the preceding aspects, refers to a method for treating an article made of fibrous material, wherein said particles are deposited on said surface of said article in a size of between 1 nm and 50 nm, preferably between 3 nm and 10 nm, still more preferably between 4 nm and 5 nm.

An eighteenth aspect of the invention, dependent on any of the preceding aspects, refers to a method for treating an article made of fibrous material, wherein said particles are deposited on said surface of said article crystallised in the tetragonal crystalline system, preferably in the form of anatase.

A nineteenth aspect of the invention, dependent on any of the preceding aspects, refers to a method for treating an article made of fibrous material, further comprising the step of:

iii) irradiating said surface of said article with an ultraviolet radiation (UV).

A twentieth aspect of the invention, dependent on the nineteenth aspect, refers to a method for treating an article made of fibrous material, wherein the duration of said step iii) is between 1 minute and 20 minutes, preferably between 3 minutes and 10 minutes, still more preferably approximately 5 minutes.

A twenty-first aspect of the invention refers to an article made of fibrous material treated by means of the method according to any of the preceding aspects.

A twenty-second aspect of the invention, dependent on the twenty-first aspect, refers to an article made of fibrous material, wherein said fibrous material comprises a synthetic material, preferably polypropylene and/or viscose, or cotton or paper.

A twenty-third aspect of the invention, dependent on the twenty-first aspect or on the twenty-second aspect, refers to an article of fibrous material, wherein said fibrous material comprises a nonwoven fabric (NWF).

A twenty-fourth aspect of the invention, dependent on the twenty-first aspect, refers to an article of fibrous material, wherein said fibrous material comprises a ceramic material or a metallic material.

A twenty-fifth aspect of the invention refers to a medical and/or health care and/or personal care device, for example a sheet, a white coat, a mask, a bonnet, a bandage, a gauze, comprising an article according to any of the aspects of the twenty-first aspect to the twenty-fourth aspect.

The aspects of the present invention will become more readily apparent from the detailed description that follows, which will refer to the figures accompanying the following description, in which:

- Figure 1 schematically shows a system configured to implement the method according to the present invention;

- Figure 2 is an axonometric view of a component of the system in Figure 1;

- Figure 3 schematically shows a detail of the system in Figure 1;

- Figures 4a - 4c show magnified views of the same detail of a textile article respectively before being treated thermally, after being treated thermally for a first time interval and after being treated thermally for a second time interval;

- Figures 5a - 5c show magnified view of the detail of a textile article of Figure 4a after being thermally treated for the aforesaid first time interval;

- Figures 6a - 6c show magnified view of the detail of a textile article of Figure 4a after being thermally treated for the aforesaid second time interval;

- Figures 7a and 7b show, in the form of histograms, the effectiveness of the method according to the present invention in relation to a particular fungus (Candida albicans);

- Figures 8a and 8b show, in the form of histograms, the effectiveness of the method according to the present invention in relation to a particular Gram-positive bacterium (Staphylococcus aureus);

- Figures 9a and 9b show, in the form of histograms, the effectiveness of the method according to the present invention in relation to a particular Gram-negative bacterium (Pseudomonas aeruginosa) and

- Figures 10a and 10b show, in the form of histograms, the effectiveness of the method according to the present invention in relation to a particular fungus (Candida albicans) by comparison with the effectiveness of the method according to the prior art in relation to the same fungus.

The idea at the basis of the present invention is to make an article made of fibrous material particularly high performing with regard to its resistance to fungi and/or bacteria, applying a coating layer on the outer surface thereof, exploiting the physical phenomenon of thermophoresis to deposit, on said surface, particles of a metal oxide generated by flame synthesis.

The method according to the invention is therefore suitable to provide an article of fibrous material with antibacterial and/or antifungal properties by means of two distinct steps and carried out in succession with a time separation of the order of milliseconds.

In the first step of the method, the metal oxide particles are generated by flame synthesis starting from a precursor compound. In an advantageous embodiment of the present invention, the metal oxide of which particles are generated by flame synthesis is a titanium or zinc or iron or silver oxide. For example, the metal oxide of which particles are generated by flame synthesis is titanium dioxide (TiO2): in this case, titanium tetraisopropoxide (TTIP) and/or titanium tetrachloride (TiCl4) can be used.

In the second step of the method, the metal oxide particles generated are deposited by thermophoresis on a surface of the article, thus providing the article with the desired antibacterial and/or antifungal properties.

For the implementation of the present invention, the system 1 of Figure 1 can conveniently be used. Said system comprises a reactor 8 which, appropriately powered, makes possible to flame synthesise the particles of metal oxide for subsequent deposit on an article 9 of fibrous material. The reactor 8 is in particular a burner configured to generate a flame of sufficiently high temperature (of the order of 1800 k, or even higher) able to cause the synthesis of the metal oxide particles starting from the precursor compound, the latter having been carried to the reactor 8.

The article 9 is advantageously a medical and/or health care and/or personal care device, for example a device suitable to be used in hospital environments. In particular, the article 9 can comprise a sheet, a white coat, a mask, a bonnet, a bandage or a gauze. The article 9 can be a device usable a multiple number of times (having been adequately treated between one use and the next) or a disposable device. The fibrous material constituting the article 9 can comprise a synthetic material, preferably polypropylene and/or viscose, or cotton or paper. Alternatively, the fibrous material constituting the article 9 can comprise a nonwoven fabric (NWF). As an additional alternative, the fibrous material constituting the article 9 can comprise a ceramic material or a metallic material.

In the example illustrated in Figure 1, the reactor 8 is a honeycomb burner comprising two concentric tubes (inner tube 1 and outer tube 2) made of stainless steel that ends in an output section 8s from which the flame 23 is freed outside. To stabilise the flame 23 that is freed from the output section 8s and thus obtain a uniform radial effect, a cylinder of silicon carbide or of mullite (also with honeycomb configuration) is positioned in the upper part of the inner tube 1.

The flow of gas inside the reactor 8 can ideally be mono-dimensional (the flow develops mainly along the direction of development of the reactor 8) and laminar, the velocities of the gases being maintained intentionally low (approximately

0.1 m/s), to obtain at the output a stable, ideally unidirectional flow. The ideal unidirectionality of the flow of gas that traverses the output section 8s of the reactor 8 ensures that, arranging the article 9 so that the surface 9p thereof to be treated is exposed to the output section 8s, the particles of metal oxide that are generated by flame synthesis reach the surface 9p to be deposited thereon by thermophoresis, thus assuring a small dispersion of the particles and consequently a high efficiency of the treatment.

Observing the system of Figure 1, it is noticeable that the region upstream of the reactor 8 is occupied by a chamber 3 that is supplied with the precursor compound. The precursor compound is advantageously supplied through a solution of said precursor compound in a solvent. If titanium tetraisopropoxide (TTIP) and/or titanium tetrachloride ($TiCl_4$) is used as a precursor compound, to obtain the synthesis of titanium dioxide ($TiO_2$) particles, ethanol can conveniently be used as a solvent.

In an embodiment of the present invention, the precursor compound is supplied to the reactor 8 in aerosol form. Therefore the system 1 comprises an aerosol generator 4 which, in the example represented by way of non-limiting explanation in Figure 1, is of the vibrating orifice type. Said aerosol generator 4, developed on the basis of the studies by Berglund and Liu, is able to create monodispersed particles with size below 0.2 mm. An aerosol generator suitable for being used in the system 1 is marketed by TSI Incorporated ® with the code 3450:

http://www.tsi.com/uploadedFiles/_Site_Root/Products/Literature/Spec_Sheets/3450VibOr1930086RevA.pdf

The chamber 3 is supplied with the solution comprising the precursor compound and with a dispersing air flow coming from an appropriate supply 3a. The function of this air flow is to prevent or significantly to limit, inside the chamber 3, the coalescence of the particles of solution released in aerosol form in the chamber 3. The dispersing air flow, preferably saturated with particles of solution, then drags the particles of solution and contributes to convey them inside the reactor 8, where the particles of solution are then mixed to particles of a suitable fuel, for example a mixture of ethylene and air.

In an additional embodiment of the present invention (alternative or complementary with the preceding one), the precursor compound is supplied to the reactor by saturation of a dispersing medium, preferably air, of the precursor compound and/or of the solution of the precursor compound in the solvent.

Returning to the architecture of the system 1 represented in Figure 1, it is observed that the chamber 3 performs both the role of mixing chamber of the solution of the precursor compound in the solvent, because this solution tends to disperse uniformly in the dispersing air flow inside the chamber 3, and the role of solvent evaporation chamber, because the solvent in the chamber 3 starts to evaporate from the solution and therefore to free the precursor compound.

Immediately downstream of the chamber 3, in the system 1 the reactor 8 is supplied with the fuel and with the comburents necessary for generating the flame 23. In the example shown in Figure 1, it can be appreciated that, immediately downstream of the chamber 3, a supply 8x is provided, configured to supply a premixed mixture of fuel and comburent into the reactor 8. As a fuel, it is possible to use for example ethylene, coming from a first sub-supply 8y, and air, coming from a second sub-supply 8z. In this regard, it can be appreciated that the connection point between the first sub-supply 8y and the second sub-supply 8z is arranged at an adequate distance with respect to the point of

supply of the mixture in the reactor 8. In this way, the fuel and the comburent are allowed to adequately mix together, so as to assure optimal flammability of the mixture. Moreover, regulating the quantities of fuel and/or comburent sent to the reactor 8 it is possible to modify the stoichiometry of the flame 23, obtaining conditions of excess fuel with respect to the stoichiometric, conditions of excess comburent with respect to the stoichiometric, or stoichiometric conditions according to the need.

By means of the architecture of the system 1 of Figure 1, a mixture is created, within the reactor 8, of fuel (ethylene, but also the ethanol freed from the solution with the precursor compound) and comburent (air and/or oxygen) that is quite homogeneous and that transports within it homogeneously dispersed particles of precursor compound. To raise the temperature of the aforesaid mixture along the reactor 8, between the inner tube 1 and the outer tube 2 is advantageously installed an electrical resistor 5 configured to heat the inner tube 1 and hence by convection the flow within the reactor 8.

The temperature distribution in the reactor 8 is such that the maximum temperature is recorded at the flame 23, where temperatures of the order of 1700 K - 1800 K can be reached, i.e. the optimal temperature for completion of the synthesis of the metal oxide, in particular titanium dioxide (TiO2) starting from the precursor compound. More generally, the temperature of the flame 23 at the output section 8s of the reactor 8 is between 1000 K and 2500 K, preferably between 1500 K and 2000 K, still more preferably between 1700 K and 1800 K. Comparing the temperature of the flame 23 at the output section 8s of the reactor 8, it is observed that the difference between said temperature is between 400 K and 2200 K, preferably between 400 K and 1700 K, still more preferably between 400 K and 1500 K. Since the precursor compound is carried in the flow ideally in the form of monodispersed particles, it is appreciated that the metal oxide particles that are created by flame synthesis are also monodispersed and have size of the order of 1 nm (de facto having zero mass).

To obtain an appropriate insulation of the flame 23 from the surrounding air, preventing the flame 23 from being perturbed or the mixture from being polluted by external contaminants, a flow of inert gas is released starting from the annular section 23k that surrounds the output section 8s. As an inert gas, a noble gas, for example argon, coming from an appropriate supply 10, is advantageously used. A sort of gas blade is thus created, which performs an effective function of protecting the flame 23 from the exterior. The flame 23 thus obtained has a carpet conformation, a blue coloration and a height H of the order of 1 mm.

Once they are created by flame synthesis, the metal oxide particles move away from the reactor 8 until they are deposited by thermophoresis on the surface 9p of the article 9 made of fibrous material to be treated, said surface being exposed to the output section 8s of the reactor 8. Figure 3 shows what occurs to the metal oxide particles between their flame synthesis and their deposit on the surface 9p of the article 9.

In a first time interval starting from their creation (diameter 1 nm or smaller), the metal oxide particles tend at first to become larger by coalescence. Therefore, the size of the particles grows until reaching at first a value of 3 nm - 4 nm and then a value of 20 nm - 30 nm. Once a critical size is reached, in a second time interval the physical phenomenon of coalescence ceases to the advantage of the concurrent physical phenomenon of agglomeration. Metal oxide

particles, then, instead of further increasing their size, tend to agglomerate forming clusters of metal oxide particles that are mutually diversified in terms of mass, dimensions and geometry.

Figure 3 therefore shows how, changing the distance D between the flame 23 and the surface 9p of the article 9 to be treated, the size of the metal oxide particles that will be deposited by thermophoresis on said surface 9p will consequently change as well. In addition, adjusting the distance D between the flame 23 and the surface 9p, so that it is smaller or larger than the critical distance starting from which the physical phenomenon of the agglomeration prevails over coalescence, the metal oxide particles will be deposited on the surface 9p of the article 9 mainly in the condition of non-agglomeration or mainly in the agglomeration condition.

Concerning the deposit of the metal oxide particles on the surface 9p, it is stressed that thermophoretic force does not depend on the mass of the particles, but only on the temperature difference between the temperature of the metal oxide particles (which are approximately at the temperature of the flame 23) and the temperature of the surface 9p of the article 9 (which is at ambient temperature or slightly above ambient temperature). Hence, although the metal oxide particles can differ from each other in terms of size and/or can be differently aggregated together, reach the surface 9p substantially with the same speed, therefore assuring an adequate uniformity of the coating layer of the surface 9p and consequently the desired increase of the antifungal and/or antibacterial properties of the article 9.

To provide the article 9 with the best antifungal and/or antibacterial properties, there is an interest in minimising the distance D between the flame 23 and the surface 9p of the article 9, so that metal oxide particles of the smallest possible size can be deposited on the surface 9p. In this way, the creation on the surface 9p of a coating layer that is as uniform, continuous and thin as possible is facilitated, so as to enhance the benefits of the method for treating the article 9 according to the present invention. In any case, it is preferable to prevent the distance D between the flame 23 and the surface 9p of the article 9 from exceeding the critical distance starting from which the agglomeration between the metal oxide particles prevails over coalescence. If agglomerates are deposited on the surface 9p, the substantial continuity of the coating layer would be compromised, so that areas susceptible to becoming lodging and proliferation areas for fungi and/or bacteria. Additionally, the possible deposit of agglomerates on the surface 9p would create evident non-uniformity in the application of the metal oxide to the article 9 and would also make it necessary to use a quantity of metal oxide particles that is markedly greater than the quantity necessary for the creation of a thin and uniform layer.

From what is described and illustrated in Figure 3, it follows that, to increase the effectiveness of the treatment method, it is absolutely advantageous to reduce the distance D between the flame 23 and the surface 9p of the article 9. On the other hand, however, said distance D must be sufficient to prevent the flame 23 from burning the article 9 made of fibrous material or that otherwise it is not possible to prevent the flame 23 from compromising the characteristics of the article 9.

To preserve the article 9 of fibrous material from possible damages due to its exposure to the flame 23, the method of the present invention can advantageously provide for the exposure of the surface 9p of the article 9 to the output section 8s of the reactor 8 to be achieved by means of a process of periodic exposure. Therefore a first phase in which the surface 9p of the article 9 is exposed to the output section 8s of the reactor 8 is then followed by a second phase

in which the surface 9p of the article 9 is not exposed to the output section 8s of the reactor 8. The duration of the first exposure phase is appreciably shorter than the duration of the second non-exposure phase. In this way, it is possible to contain the heating of the surface 9p to less than 100 K (advantageously to approximately 50 K), so that the article 9 is not burned by the flame 23 and to avoid alterations of the characteristics of the fibrous material constituting the article 9. Advantageously, the duration of the first phase of exposure is shorter than 1 second, preferably shorter than 0.1 seconds, still more preferably approximately 0.02 seconds.

To allow an adequate quantity of metal oxide particles to be deposited on the surface 9p of the article 9, the aforesaid periodic exposure continues until a predetermined time threshold is reached. Advantageously, the periodic exposure of the surface 9p of the article 9 to the output section 8s of the reactor 8 has a duration $t_{des}$ between 10 seconds and 10 minutes, preferably between 1 minute and 5 minutes, still more preferably between 150 seconds and 180 seconds.

In the example illustrated by way of non-limiting explanation in Figure 1, the periodic exposure of the surface 9p of the article 9 to the output section 8s of the reactor 8 is obtained by rotation of a carrousel 7, shown in detail in the axonometry of Figure 2. The carrousel 7 is configured so as to allow the application of the article 9 thereon and further to allow that the surface 9p of the article 9 thus applied to the carrousel 7 is adequately exposed to the output section 8s of the reactor 8. Advantageously, the carrousel 7 is configured to support the article 9 in a position located frontally to the output section 8s of the reactor 8, so that the metal oxide particles that are released by the reactor 8 (and that maintain, even after traversing the output section 8s, a direction of flow substantially parallel to the axis of the reactor 8) can more efficiently and easily reach the surface 9p.

The carrousel 7 comprises a table 70 that extends along a plane that is substantially parallel to the plane of lay of the output section 8s of the reactor 8. In the example represented in Figure 2, the table 70 has nearly circular shape. Although this shape is deemed to be the preferred shape, other shapes are nonetheless possible for the table 70 of the carrousel 7, for example a polygonal shape.

The table 70 is configured to rotate around its own axis. For this purpose, the table 70 is splined to a shaft 76 to which is coupled an electric motor 85. Table 70 then has at least a pair of slots 77 substantially parallel to each other, which extend along a substantially radial direction. The function of the slots 77 is to allow the article 9 to be stably supported by the table 70 of the carrousel 7. The article 9 is positioned adjacently to the surface of the carrousel 7 oriented towards the reactor 8 so that the two flaps of the article 9 are inserted into the slots 77. To the carrousel 7 are then applied fastening plates (not shown in Figure 2) that lock the flaps of the article 9, thus assuring that the article 9 is not applied loosely to the table 70 of the carrousel 7. Advantageously, the table 70 comprises a plurality of slots 77 (preferably equally distanced from each other) that make it possible to apply to the carrousel 7 a plurality of articles to be treated simultaneously.

According to the present invention, alternative devices to the carrousel 7 can be used to allow the periodic exposure of the surface 9p of the article 9 to the output section 8s of the reactor 8. Purely by way of explanatory but non-limiting example, one can mention, as alternatives to the carrousel 7, a wheel with orthogonal axis to the reactor 8 and supports for the articles obtained on the outer surface of the wheel or a roller mechanism configured to make the article 9 travel in closed loop trajectories.

An alternative embodiment of the present invention then a configuration is provided for the system 1 (in particular for the reactor 8) which makes it possible to generate the particles of a metal oxide by means of flame synthesis, changing the flow rates of fuel and of comburent sent to the reactor 8 and establishing (instead of laminar flow conditions) conditions of premixed flame or of flame with diffusion in turbulent flow.

Figures 4a to 4c are photographic images of a detail of an article 9 made of fibrous material applied to the carrousel 7 and subjected to periodic exposure to the flame 32 described above, the fibrous material constituting the article 9 shown in the Figures being in particular a nonwoven fabric (NWF). Figure 4a shows said detail before subjecting the article 9 to periodic exposure to the flame 32. Figure 4b shows said detail after subjecting the article 9 to periodic exposure to the flame 32 for a duration $t_{des}$ equal to 150 seconds. Figure 4c shows said detail after subjecting the article 9 to periodic exposure to the flame 32 for a duration $t_{des}$ equal to 180 seconds. From a comparison between the three photographic images, it is readily apparent that the fibres that comprise the article 9 were not burned by periodic exposure to the flame 23 and that they have retained, without significant alteration, their own geometric and/or dimensional and/or mechanical characteristics.

Advantageously, the system 1 shown in Figure 1 comprises an electronic control unit, operatively connected to sensor devices and actuator devices. As sensor devices installable in the system 1 can be mentioned temperature sensors (adapted for example to measure the temperature of the flame 32) and/or chemical concentration sensors (adapted for example to measure the quantity of oxygen and/or of precursor compound inside the reactor 8). As actuator devices, instead, one can mention the actuators associated to the various supplies of the reactor 8 and/or the vibrating orifice of the aerosol generator 4. The function of the electronic control unit is to control the implementation of the method according to the invention by means of the system 1. An additional function of the electronic control unit is to assure that the design parameters match the desired parameters, to obtain the desired characteristics and/or values for the metal oxide particles that are deposited on the surface 9p of the article 9. There can be numerous adjustments in the system 1 allowed by the electronic control unit. For example, starting from the reading of the temperature of the flame 23, the electronic control unit can intervene on the electrical resistor 5 to increase and/or decrease the thermal power delivered by it and hence to increase and/or decrease the temperature of the flame 23.

In an embodiment of the present invention (not shown in the Figures accompanying the present description), the electronic control unit, to obtain for example the desired size of the metal oxide particles on the surface 9p of the article 9, can control actuating means interposed between the reactor 8 and the carrousel 7. The actuating means allow the reactor 8 and the carrousel 7 (and consequently the surface 9p of the article 9 and the output section 8s of the reactor 8) to approach or move away from each other, thus determining a decrease or an increase of the dimensions of the metal oxide particles deposited on the surface 9p. The actuating means can comprise, for example, a telescopic element applied to the shaft 76 to approach or remove the table 70 to and from the electric motor 85 and/or a carriage integral with the reactor 8 that allows it to slide along a fixed rail substantially parallel to the reactor 8, approaching it to or removing it from the table 70. The actuating means are operatively connected to the electronic control unit, so that the latter can finely control and/or adjust the distance between the table 70 and the output section 8s of the reactor 8 (and consequently the distance between the surface 9p of the article 9 and the output section 8s of the reactor 8).

Advantageously, the electronic control unit allows the system 1 to implement a preliminary step to the method according to the invention, in which an adjustment is made to the numerousness of the metal oxide particles and/or the coalescence of the metal oxide particles and/or the possible agglomeration of the metal oxide particles and/or the crystalline group of the metal oxide particles. In particular:

i) the numerousness of the metal oxide particles that are deposited on the surface 9p of the article 9 can be adjusted by intervening on the duration $t_{des}$ of the periodic exposure of the article 9 to the flame 32 (for example by prolonging said duration $t_{des}$ from 150 seconds to 180 seconds, a higher number of metal oxide particles are deposited on the surface 9p, and consequently an improvement of the antifungal and/or antibacterial properties of the article 9, with the disadvantage of a longer treatment time and of higher consumption of precursor compound), but also intervening on the concentration of the precursor compound in the solution (starting from a reference concentration titanium tetraisopropoxide (TTIP) and/or of titanium tetrachloride (TiCl4) in ethanol, said reference concentration being for example equal to 0.3 M, the numerousness of the metal oxide particles that are deposited on the surface 9p can be increased adopting a higher concentration than the reference concentration, or reduced adopting a lower concentration than the reference concentration);

ii) the size of the metal oxide particles that are deposited on the surface 9p of the article 9 can be adjusted intervening on the distance between the surface 9p of the article 9 and the output section 8 of the reactor 8, or alternatively only on the component of said distance orthogonal to the output section 8s of the reactor 8 (increasing the distance between the surface 9p and the output section 8s causes a progressive increase of the size of the titanium oxide particles, since they are allowed more time to grow through the coalescence phenomenon), but also intervening on the concentration of the precursor compound in the solution (starting from a higher concentration of precursor compound in the solution, for equal distance between the surface 9p and the output section 8s metal oxide particles of larger size are obtained, because the greater numerousness of particles promotes the coalescence phenomenon);

iii) the condition of agglomeration or non-agglomeration of the metal oxide particles can be determined intervening on the distance between the surface 9p of the article 9 and the output section 8s of the reactor 8: therefore, to avoid the emergence (to a significant extent) of the agglomeration phenomenon, the distance between the surface 9p and the output section 8s is set to such a value that the metal oxide particles are not allowed to agglomerate, but only to grow by coalescence, the value of the distance between the surface 9p and the output section 8s to be set being the smaller, the greater the concentration of the precursor compound in the solution, given that an increase in the concentration of the precursor compound in the solution aids the agglomeration for the metal oxide particles;

iv) the crystalline group of the metal oxide particles is determined adjusting the stoichiometry of the flame 32, in particular adjusting the quantity of fuel and/or of comburent in the reactor 8, so that, changing the flow rate of ethylene and/or of air and/or of oxygen coming from the supply 3a and/or from the sub-supplies 8y and 8z, the concentration of oxygen present in the reaction environment can be changed, thus promoting the formation of different crystalline groups. In the example of use of titanium dioxide particles, it is possible to obtain the crystallisation of said compound in the three main crystalline group, i.e. rutile when the flame is operated in conditions of excess fuel, anatase when the flame is operated in conditions of excess comburent, and brookite when the flame is operated in stoichiometric conditions.

Advantageously, the method according to the present invention is implemented to deposit on the surface 9p of the article 9 the metal oxide particles in the condition of non-agglomeration. Still more advantageously, metal oxide particles are deposited on the surface 9p of the article 9 in the condition of non-agglomeration and with a dimension between 1 nm and 50 nm, preferably between 3 nm and 10 nm, still more preferably between 4 nm and 5 nm. Advantageously, metal oxide particles are deposited on the surface 9p of the article 9 crystallised in the tetragonal crystalline system, preferably in the form of anatase.

The Figures from 5a to 5c and from 6a to 6c provide immediate views, obtained by scanning electron microscope (SEM), of the effects of the method according to the present invention when applied on the article 9 made of nonwoven fabric (NWF) of the Figures from 4a to 4c, the adjustment parameters listed above (distance between flame 23 and surface 9p, concentration of the precursor compound in the solution, quantity of comburent in the reactor 8) having been defined to obtain the deposit on the surface 9p of the article 9 of a homogeneous layer of particles of titanium dioxide (TiO2) crystallised in the form of anatase and having a size of approximately 4nm. The Figures from 5a to 5c refer to an article 9 treated with the method according to the present invention with a periodic exposure of duration $t_{des}$ equal to 150 seconds, while the Figures from 6a to 6c refer to an article 9 treated with the method according to the present invention with a periodic exposure of duration $t_{des}$ of 180 seconds. Figures 5b and 6b show the distribution of titanium respectively on the details of Figures 5a and 6a, while Figures 5c and 6c show the distribution of oxygen respectively on the details of Figures 5a and 6a. As is readily apparent from the views of the Figures from 5a to 5c and from 6a to 6c, titanium dioxide is uniformly deposited on the fibres of the article 9 with a periodic exposure of duration $t_{des}$ equal to 150 seconds, and still more with a periodic exposure of duration $t_{des}$ equal to 180 seconds.

To enhance the antifungal and/or antibacterial properties imparted to the article 9 by the generation of metal oxide particles, in particular titanium dioxide (TiO2), by flame synthesis starting from a precursor compound and subsequent deposit by thermophoresis of the metal oxide particles thus generated on the surface 9p of the article 9, the surface 9p of the article 9 can subsequently be irradiated with ultraviolet radiation (UV), advantageously for a duration between 1 minute and 20 minute, preferably between 3 minutes and 10 minutes, still more preferably approximately 5 minutes. In this way, fungi and/or bacteria are eradicated not only by the sanitising and/or cleansing effect of the titanium dioxide (TiO2) particles, but also by the universally recognised sterilising properties of ultraviolet rays. Ultraviolet (UV) radiation produces a synergic effect to that of the metal oxide particles.

Laboratory tests were carried out to assess the effectiveness of the method according to the present invention, concretely verifying the antifungal and/or antibacterial properties provided to the article 9. In these tests, microorganisms were directly inoculated on the article 9, said article being in particular a sterile gauze of nonwoven fabric (NWF). The ability of the microorganisms to adhere to the fibres of the article 9 was then measured, both immediately after inoculation (to verify the resistance of the article 9, treated with the method according to the present invention, to the aggression of fungi and/or bacteria), and after 18 hours (to verify the persistence of the antifungal and/or antibacterial properties provided to the article 9 by the method according to the present invention).

A first laboratory test was carried out to verify the antifungal properties provided to the article 9 by means of the method according to the present invention. The test was carried out using Candida albicans as test fungus. The results of this first test are immediately visible by means of the histograms of Figures 7a, 7b, 10a and 10b. From the histogram

represented in Figure 7a it is noted that, when a charge of Candida albicans exceeding 30000 CFU/mL is inoculated (first column), less than one tenth of this charge is then actually able to adhere to the article 9. Excellent results are already obtained with a periodic exposure to the flame 23 of duration $t_{des}$ equal to 150 seconds (second column). Still better results are obtained by following the treatment with irradiation with ultraviolet (UV) radiation for a duration of 5 minutes (third column), or prolonging the periodic exposure to a duration $t_{des}$ of 180 seconds (fourth column), or prolonging the periodic exposure to the flame 23 to a duration $t_{des}$ of 180 seconds and hence following the treatment with irradiation with ultraviolet (UV) radiation for a duration of 5 minutes (fifth column). From the histogram in Figure 7b it is appreciated that, while in the untreated sample the charge of Candida albicans reaches, after 18 hours, a value exceeding 50000 CFU/mL (first column), less than one tenth of said charge is found in the sample of article 9 treated with a periodic exposure to the flame 23 of duration $t_{des}$ equal to 150 seconds (second column). Still better results are found in the sample subjected to the treatment according to the present invention was followed by an irradiation with ultraviolet (UV) radiation for a duration of 5 minutes (third column), or in the sample in which the periodic exposure to the flame 23 was prolonged to a duration $t_{des}$ of 180 seconds (fourth column), or in the sample in which the periodic exposure to the flame 23 was prolonged to a duration $t_{des}$ of 180 seconds and then the treatment according to the invention was followed by an irradiation with an ultraviolet radiation (UV) for a duration of 5 minutes (fifth column).

Figures 10a and 10b represent, in the form of histograms, the effectiveness of the method according to the present invention in relation to the Candida albicans fungus, comparing it with the effectiveness of the method according to the present invention (local application of particles of titanium dioxide by evaporation of the solvent) in relation to the same fungus. Comparison between the second column and the third column in Figure 10 shows that the local application of titanium dioxide particles for a duration $t_{app}$ of 150 seconds is able nearly to halve the charge (second column), while a periodic exposure with the method according to the present invention for a duration $t_{des}$ equal to 150 seconds is able to reduce the charge by approximately ten times (third column). Comparison between the fourth column and the fifth column in Figure 10 shows that the local application of titanium dioxide particles for a duration $t_{app}$ of 180 seconds is able nearly to reduce to one third the charge (fourth column), while a periodic exposure with the method according to the present invention for a duration $t_{des}$ equal to 180 seconds is able to reduce the charge by approximately ten times (fifth column).

A second laboratory test was carried out to verify the antibacterial properties provided to the article 9 by means of the method according to the present invention, a Gram-positive bacterium (Staphylococcus aureus) being used for the second laboratory test. The results of this second test are immediately visible by means of the histograms of Figures 8a and 8b. From the histogram represented in Figure 8a it is noted that, when a charge of Staphylococcus aureus exceeding 55000 CFU/mL is inoculated (first column), less than one fifth of this charge is then actually able to adhere to the article 9. Excellent results are already obtained with a periodic exposure to the flame 23 of duration $t_{des}$ equal to 150 seconds (second column). Still better results are obtained by following the treatment with irradiation with ultraviolet (UV) radiation for a duration of 5 minutes (third column), or prolonging the periodic exposure to a duration $t_{des}$ of 180 seconds (fourth column), or prolonging the periodic exposure to the flame 23 to a duration $t_{des}$ of 180 seconds and hence following the treatment with irradiation with ultraviolet (UV) radiation for a duration of 5 minutes (fifth column). From the histogram in Figure 8b it is appreciated that, while in the untreated sample the charge of Staphylococcus

aureus reaches, after 18 hours, a value of approximately 80000 CFU/mL (first column), less than one quarter of said charge is found in the sample of article 9 treated with a periodic exposure to the flame 23 of duration $t_{des}$ equal to 150 seconds (second column). Still better results are found in the sample subjected to the treatment according to the present invention was followed by an irradiation with ultraviolet (UV) radiation for a duration of 5 minutes (third column), or in the sample in which the periodic exposure to the flame 23 was prolonged to a duration $t_{des}$ of 180 seconds (fourth column), or in the sample in which the periodic exposure to the flame 23 was prolonged to a duration $t_{des}$ of 180 seconds and then the treatment according to the invention was followed by an irradiation with an ultraviolet radiation (UV) for a duration of 5 minutes (fifth column).

A third laboratory test was carried out to verify the antibacterial properties provided to the article 9 by means of the method according to the present invention, a Gram-negative bacterium (Pseudomonas aeruginosa) being used for the second laboratory test. The results of this third test are immediately visible by means of the histograms of Figures 9a and 9b. From the histogram represented in Figure 9a it is noted that, when a charge of Pseudomonas aeruginosa of approximately 30000 CFU/mL is inoculated (first column), approximately one third of this charge is then actually able to adhere to the article 9. Interesting results are already obtained with a periodic exposure to the flame 23 of duration $t_{des}$ equal to 150 seconds (second column). Still better results are obtained by following the treatment with irradiation with ultraviolet (UV) radiation for a duration of 5 minutes (third column), or prolonging the periodic exposure to a duration $t_{des}$ of 180 seconds (fourth column), or prolonging the periodic exposure to the flame 23 to a duration $t_{des}$ of 180 seconds and hence following the treatment with irradiation with ultraviolet (UV) radiation for a duration of 5 minutes (fifth column). From the histogram in Figure 9b it is appreciated that, after 18 hours, less than half of said charge is found in the sample of article 9 treated with a periodic exposure to the flame 23 of duration $t_{des}$ equal to 150 seconds (second column). Still better results are found in the sample subjected to the treatment according to the present invention was followed by an irradiation with ultraviolet (UV) radiation for a duration of 5 minutes (third column), or in the sample in which the periodic exposure to the flame 23 was prolonged to a duration $t_{des}$ of 180 seconds (fourth column), or in the sample in which the periodic exposure to the flame 23 was prolonged to a duration $t_{des}$ of 180 seconds and then the treatment according to the invention was followed by an irradiation with an ultraviolet radiation (UV) for a duration of 5 minutes (fifth column).

The antifungal and/or antibacterial activity of metal oxide particles, in particular titanium dioxide (TiO2), created by flame synthesis and then deposited on the surface 9p of the article 9 by means of the physical phenomenon of thermophoresis is thus far higher than the antifungal and/or antibacterial activity of the particles of metal oxide, in particular of titanium dioxide (TiO2), obtained by local evaporation of a solvent. This benefit of the method according to the present invention is due to the smaller size of the particles together with the lower presence of agglomerates.

In addition to the fundamental advantage of markedly increasing the antibacterial and/or antifungal properties of the particles of metal oxide, in particular of titanium dioxide (TiO2), the present invention achieves additional important advantages. The method according to the invention does not produce effluents and therefore has a limited impact on the environment. The method according to the invention is easily used for mass production of fabrics with antifungal and/or antibacterial properties. The method according to the invention is fast and assures high efficiency. The method according to the invention is suitable for multiple implementations on different fibrous materials (fabric, paper, ceramic,

metal, synthetic and so on). The method according to the invention does not require pre-treatments and-or post-treatments of the fibrous material. The method according to the invention markedly improves the ability of the layer of titanium dioxide (TiO2) to withstand mechanical stresses (for example, friction and/or rubbing) and also appreciably improves the ability of the layer of titanium dioxide (TiO2) to withstand chemical agents (for example washing agents). Lastly, the method according to the invention does not alter the colour of the article to which the layer of titanium dioxide (TiO2) is applied.

The advantages listed above, together with additional significant advantages, are fully achieved by means of the method according to the present invention. These advantages are further achieved by an article made of fibrous material treated with the method according to the present invention, the fibrous material comprising a synthetic material, preferably polypropylene and/or viscose, or cotton or paper and/or comprising a nonwoven fabric (NWF) and/or comprising a ceramic material or a metallic material. Lastly, these advantages are achieved by a medical and/or health care and/or personal care device, for example a sheet, a white coat, a mask, a bonnet, a bandage, a gauze, comprising an article made of fibrous material treated with the method according to the present invention.

The present invention, lastly, can be subject to numerous possible variants. According to one among such variants, to make treatment of the article 9 made of fibrous material easier and faster, the exposure of the surface 9p of the article 9 to the output section 8s of the reactor 8 can be obtained by a continuous exposure process. In this case, while the surface 9p of the article 9 is exposed to the output section 8s of the reactor 8, a surface of the article 9 not exposed to the output section 8s (typically the surface of the article 9 opposite to the surface 9p, the article 9 being a fundamentally two-dimensional object) is subjected to cooling. Said cooling allows the achievement of equally significant advantages. In the first place, said cooling preserves the article 9 from possible damages due to its exposure to the flame 23, avoiding structural modifications to the fibres that comprise the article 9. In the second place, said cooling acts as promoter of the thermophoretic transport of the metal oxide particles. Said cooling not only determines an increase of the temperature difference between the flame 23 and the article 9, but also promotes the penetration of the metal oxide particles in the article 9, the latter being made of fibrous material. According to a first embodiment, said cooling can be obtained using a Peltier cell. According to a second embodiment, said cooling can be obtained using a water or liquid cooling circuit.

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## CLAIMS

1. Method for treating an article (9) made of fibrous material, able to provide said article (9) with antibacterial and/or antifungal properties by the application on a surface (9p) of said article (9) of particles of a method oxide,

said method comprising the steps of:

i) generating said particles by flame synthesis of said particles from a precursor compound and

ii) depositing in a controlled manner said particles on a surface (9p) of said article (9) by thermophoresis.

2. Method according to claim 1, wherein said metal oxide is a titanium- or zinc- or iron- or silver-based oxide.

3. Method according to claim 2, wherein said metal oxide is titanium dioxide (TiO2).

4. Method according to claim 3, wherein said precursor compound is titanium tetraisopropoxide (TTIP) and/or titanium tetrachloride (TiCl4).

5. Method according to any of the claims from 1 to 4, wherein said particles are deposited on said surface (9p) of said article (9) in the condition of non-agglomeration.

6. Method according to any of the claims from 1 to 5, wherein said particles are deposited on said surface (9p) of said article (9) in a dimension between 1 nm and 50 nm.

7. Method according to claim 6, wherein said particles are deposited on said surface (9p) of said article (9) in a dimension between 3 nm and 10 nm.

8. Method according to claim 7, wherein said particles are deposited on said surface (9p) of said article (9) in a dimension between 4 nm and 5 nm.

9. Method according to any of the claims from 1 to 8, wherein said particles are deposited on said surface (9p) of said article (9) crystallised in the tetragonal crystalline system.

10. Method according to claim 9, wherein said particles are deposited on said surface (9p) of said article (9) in the form of anatase.

11. Method according to any of the claims from 1 to 10, wherein said flame synthesis takes place by means of a reactor (9) to which said precursor compound is supplied and wherein said surface (9p) of said article (9) is exposed to the output section (8s) of said reactor (8).

12. Method according to claim 11, wherein the exposure of said surface (9p) of said article (9) to said output section (8s) of said reactor (8) is achieved by a process of periodic exposure in which a first phase of exposure is alternated to a second phase of non-exposure, the duration of said first phase of exposure being appreciably shorter than the duration of said second phase of non-exposure.

13. Method according to claim 12, wherein said duration of said first phase of exposure is shorter than 1 second.

14. Method according to claim 13, wherein said duration of said first phase of exposure is shorter than 0.1 seconds.

15. Method according to claim 14, wherein said duration of said first phase of exposure is approximately 0.02 seconds.

16. Method according to any of the claims from 11 to 15, wherein said process of periodic exposure has a duration ($t_{des}$) between 10 seconds and 10 minutes.

17. Method according to claim 16, wherein said process of periodic exposure has a duration ($t_{des}$) between 1 minutes and 5 minutes.

18. Method according to claim 17, wherein said process of periodic exposure has a duration ($t_{des}$) between 150 seconds and 180 seconds.

19. Method according to any of the claims from 11 to 18, wherein said method of periodic exposure comprises rotating a carrousel (7), said article (9) being applied to said carrousel (7) so as to assure the exposure of said surface (9p) of said article (9) to said output section (8s) of said reactor (8).

20. Method according to claim 11, wherein the exposure of said surface (9p) of said article (9) to said output section (8s) of said reactor (8) is achieved by a process of continuous exposure.

21. Method according to claim 20, wherein, in said process of continuous exposure, a surface of said article (9) not exposed to said output section (8s) is subjected to cooling.

22. Method according to claim 21, wherein said cooling uses a Peltier cell.

23. Method according to claim 21, wherein said cooling uses a water cooling or liquid cooling circuit.

24. Method according to any of the claims from 11 to 23, wherein said precursor compound is supplied to said reactor (8) through a solution of said precursor compound in a solvent.

25. Method according to claim 24, wherein said solvent is ethanol.

26. Method according to any of the claims from 11 to 25, wherein said precursor compound is supplied to said reactor (8) in aerosol form.

27. Method according to claim 26, wherein said aerosol is generated by means of a vibrating orifice aerosol generator (VOAG).

28. Method according to claim 26 or claim 27, wherein said aerosol is mixed in said reactor (8) with a fuel.

29. Method according to claim 28, wherein said fuel is ethylene pre-mixed with air.

30. Method according to any of the claims from 11 to 29, wherein said precursor compound is supplied to said reactor (8) by saturation of a dispersing medium of said precursor compound and/or of said solution of said precursor compound in said solvent.

31. Method as claimed in claim 30, wherein said dispersing medium is air.

32. Method according to any of the claims from 11 to 31, wherein the temperature of the flame (23) at said output section (8s) of said reactor (8) is between 1000 K and 2500 K.

33. Method according to claim 32, wherein the temperature of the flame (23) at said output section (8s) of said reactor (8) is between 1500 K and 2000 K.

34. Method according to claim 33, wherein the temperature of the flame (23) at said output section (8s) of said reactor (8) is between 1700 K and 1800 K.

35. Method according to any of the claims from 11 to 34, wherein the temperature difference between said article (9) and the flame (23) at said output section (8s) of said reactor (8) is between 400 K and 2200 K.

36. Method according to claim 35, wherein the temperature difference between said article (9) and the flame (23) at said output section (8s) of said reactor (8) is between 400 K and 1700 K.

37. Method according to claim 36, wherein the temperature difference between said article (9) and the flame (23) at said output section (8s) of said reactor (8) is between 400 K and 1500 K.

38. Method according to any of the preceding claims, wherein said step i) is preceded by the preliminary step of adjusting the numerousness of said particles and/or the coalescence of said particles and/or the possible agglomeration of said particles and/or the crystalline group of said particles.

39. Method according to claim 38, wherein in said preliminary step an adjustment of the distance (D) of said surface (9p) of said article (9) from said output section (8s) of said reactor (8) is carried out, an increase of said distance (D) determining an increase of the size of said particles and/or the passage of said particles from the condition of non-agglomeration to the condition of agglomeration.

40. Method according to claim 38, wherein in said preliminary step an adjustment of the component of the distance (D) of said surface (9p) of said article (9) from said output section (8s) of said reactor (8) is carried out, an increase of the component of said distance (D) determining an increase of the size of said particles and/or the passage of said particles from the condition of non-agglomeration to the condition of agglomeration.

41. Method according to any of the claims from 38 to 40, wherein in said preliminary step an adjustment of the concentration of said precursor compound in said solution is carried out, an increase of said concentration determining an increase of the numerousness of said particles and/or of the size of said particles and/or the passage of said particles from the condition of non-agglomeration to the condition of agglomeration.

42. Method according to any of the claims from 38 to 41, wherein in said preliminary step an adjustment of the stoichiometry of the flame (23) is carried out, a change of the stoichiometry of the flame (23) determining a change of the quantity of oxygen present in the environment of the reactor (8) and hence of the crystalline group of said particles.

43. Method according to claim 42, wherein said adjustment of the stoichiometry of the flame (23) is carried out by adjusting the quantity of comburent and/or of fuel supplied to said reactor (8).

44. Method according to any of the preceding claims, wherein conditions of pre-mixed flame or flame with diffusion in turbulent flow are established.

45. Method according to any of the preceding claims, further comprising the step of:

iii) irradiating said surface (9p) of said article (9) with an ultraviolet radiation (UV).

46. Method according to claim 45, wherein said step iii) has a duration between 1 minute and 20 minutes.

47. Method according to claim 46, wherein said step iii) has a duration between 3 minutes and 10 minutes.

48. Method according to claim 46, wherein said step iii) has a duration of approximately 5 minutes.

49. Article (9) made of fibrous material characterised in that it is treated by means of the method according to any of the preceding claims.

50. Article (9) according to claim 49, wherein said fibrous material comprises a synthetic material.

51. Article (9) according to claim 50, wherein said synthetic material is polypropylene and/or viscose.

52. Article (9) according to claim 49, wherein said fibrous material comprises cotton.

53. Article (9) according to claim 49, wherein said fibrous material comprises paper.

54. Article (9) according to claim 49, wherein said fibrous material comprises a nonwoven fabric (NWF).

55. Article (9) according to claim 49, wherein said fibrous material comprises a ceramic material.

56. Article (9) according to claim 49, wherein said fibrous material comprises a metallic material.

57. Medical and/or health care and/or personal care device, characterised in that it comprises an article (9) according to any of the claims from 49 to 56.

58. Device according to claim 57, characterised in that it comprises a sheet.

59. Device according to claim 57, characterised in that it comprises a white coat.

60. Device according to claim 57, characterised in that it comprises a mask.

61. Device according to claim 57, characterised in that it comprises a bonnet.

62. Device according to claim 57, characterised in that it comprises a bandage.

63. Device according to claim 57, characterised in that it comprises a gauze.

FIG.1

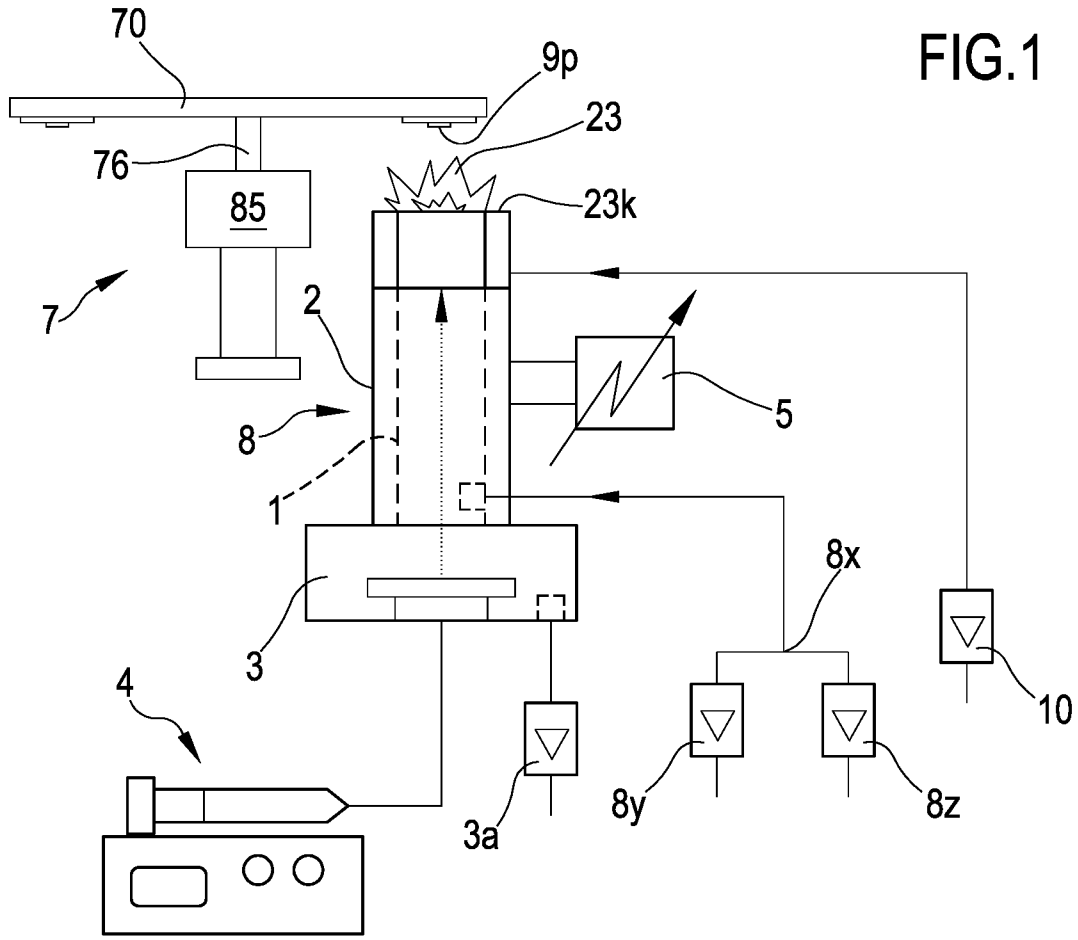
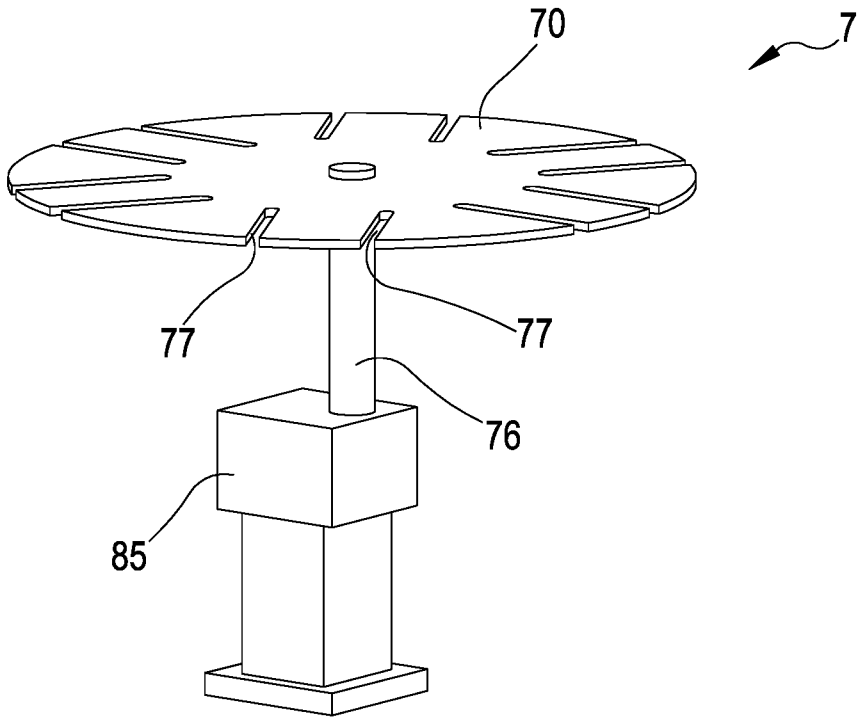



FIG.2



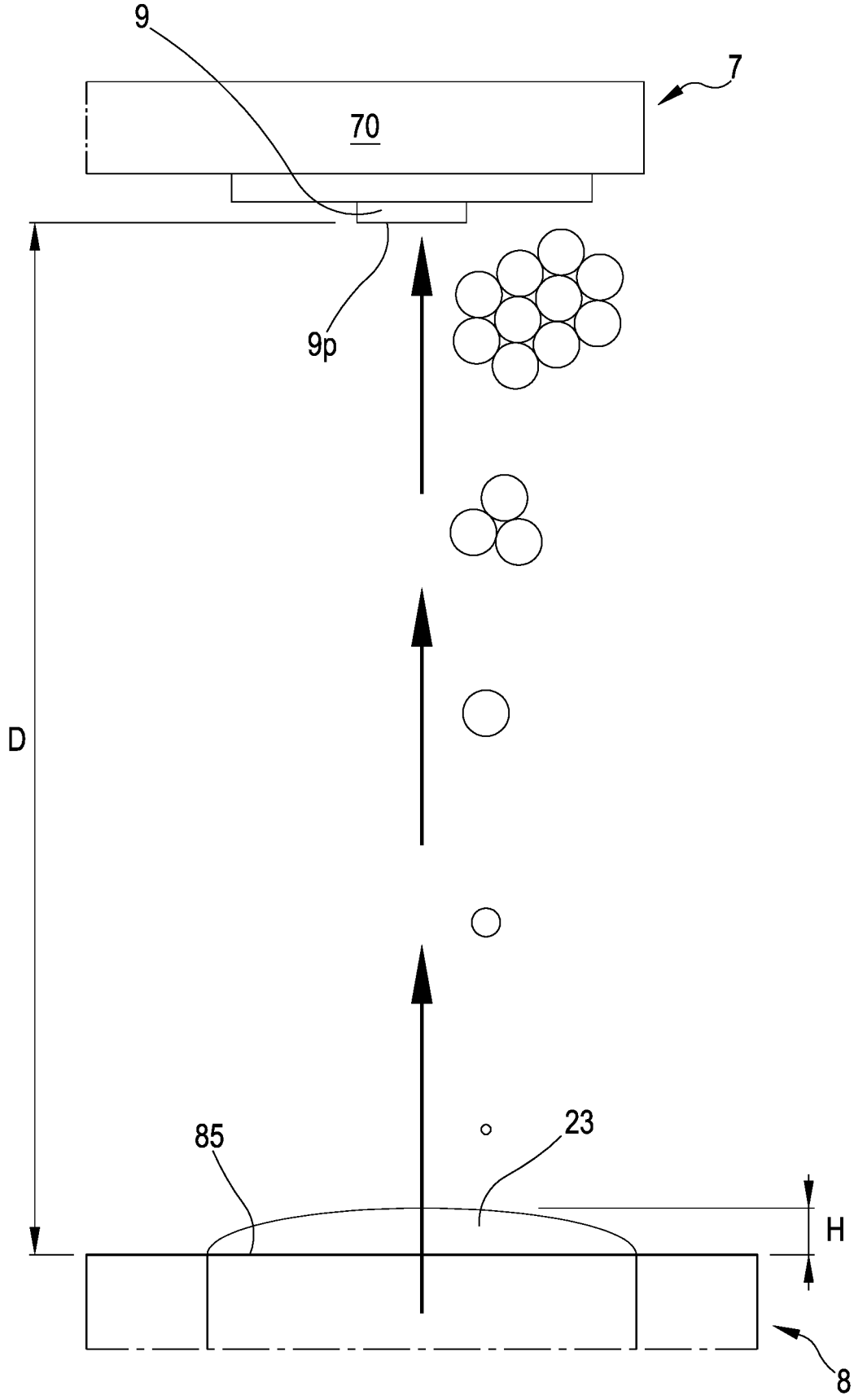



FIG.3

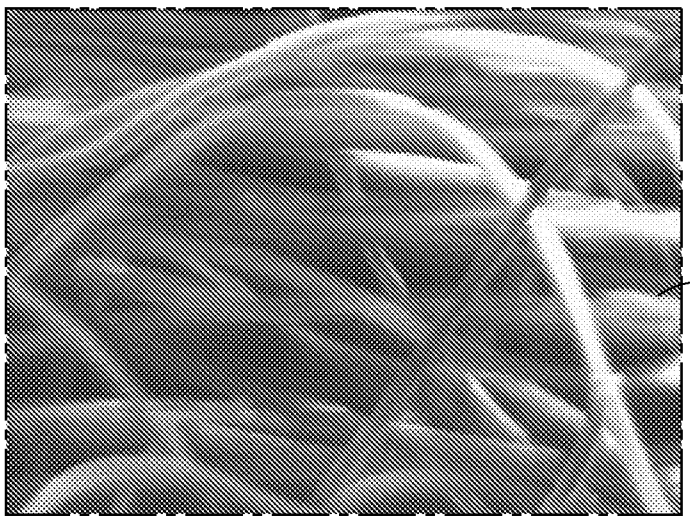



FIG.4a

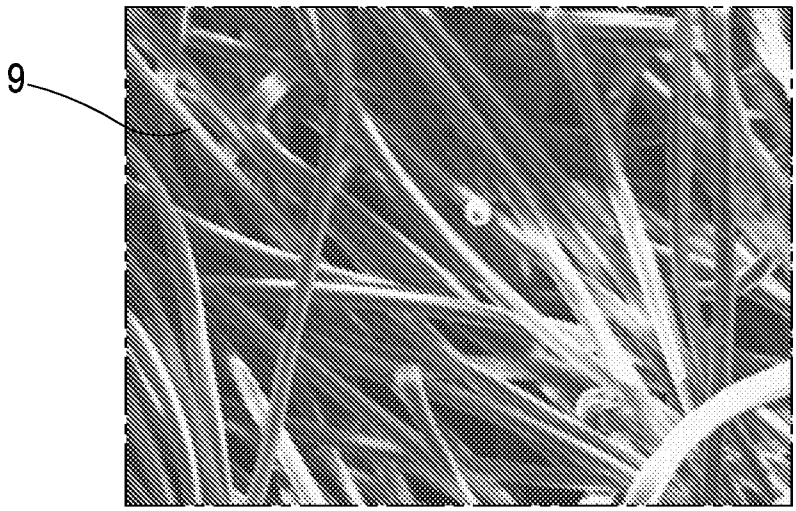



FIG.4b

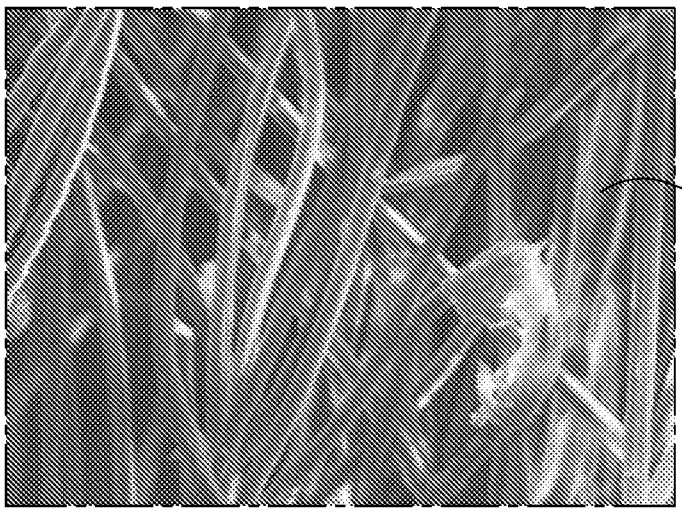



FIG.4c

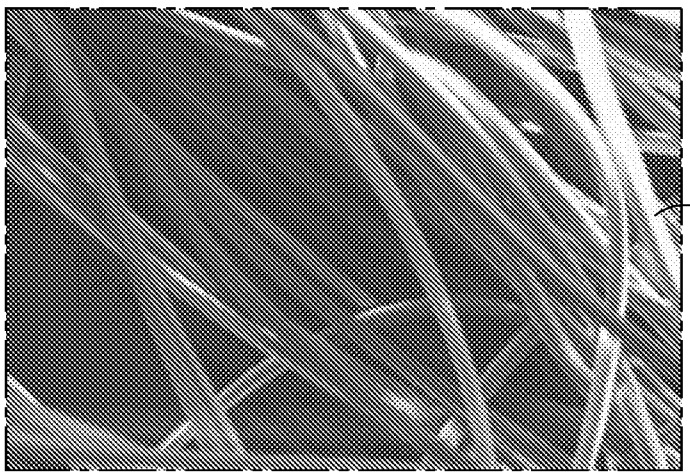



FIG.5a

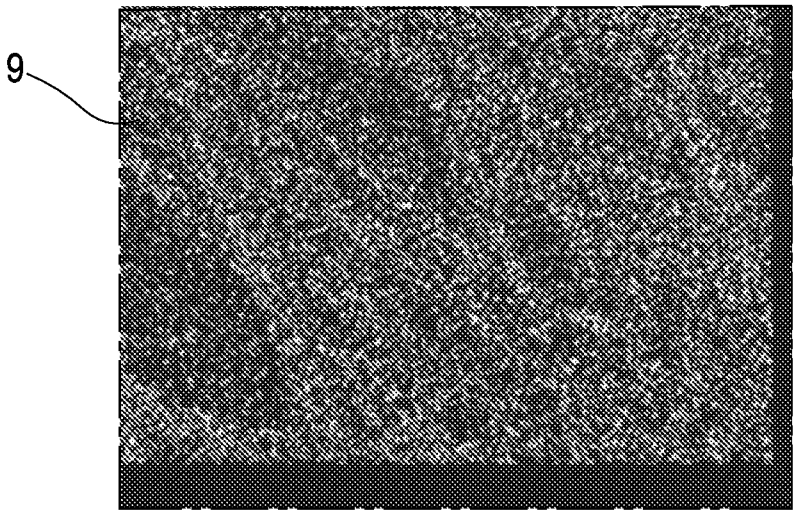



FIG.5b


FIG.5c

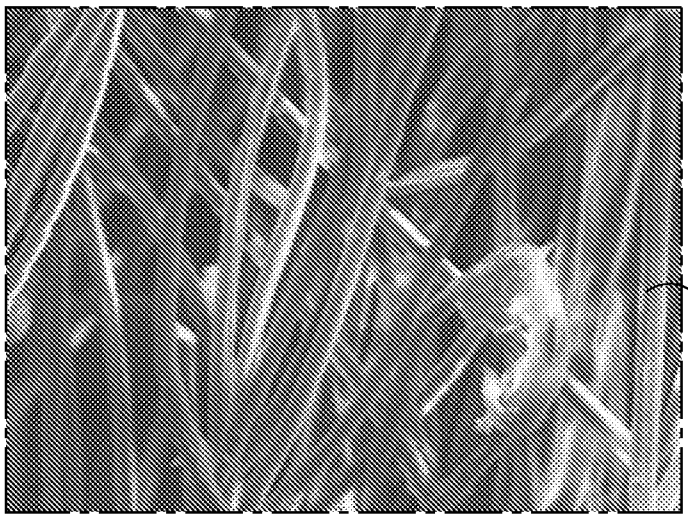



FIG.6a

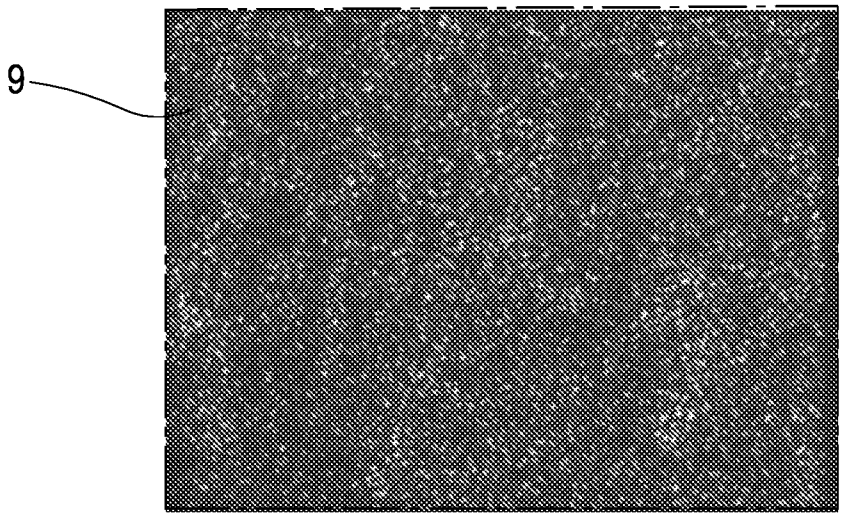



FIG.6b

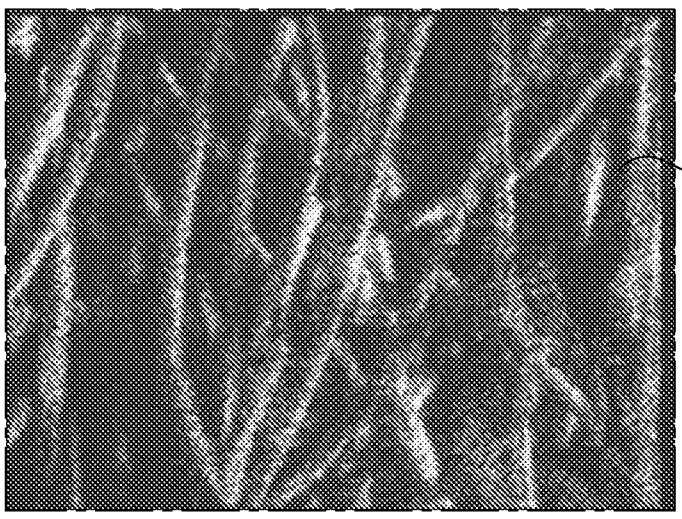



FIG.6c

FIG.7a

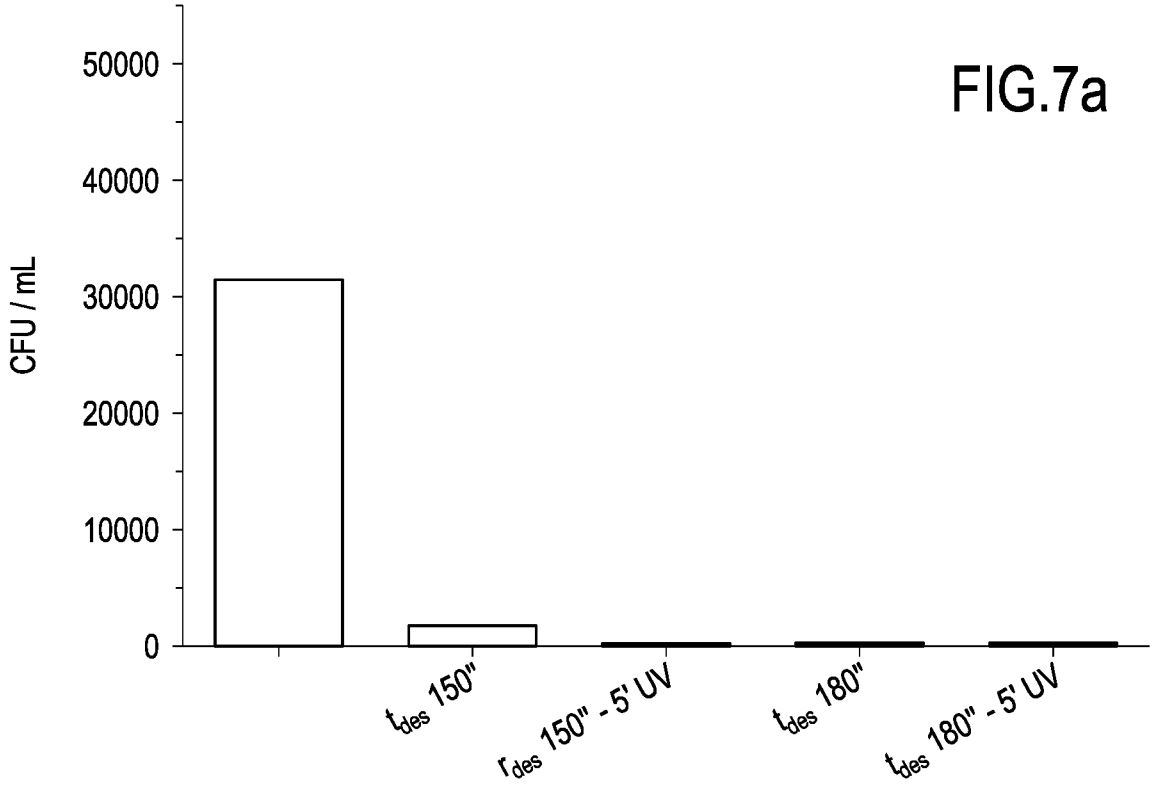
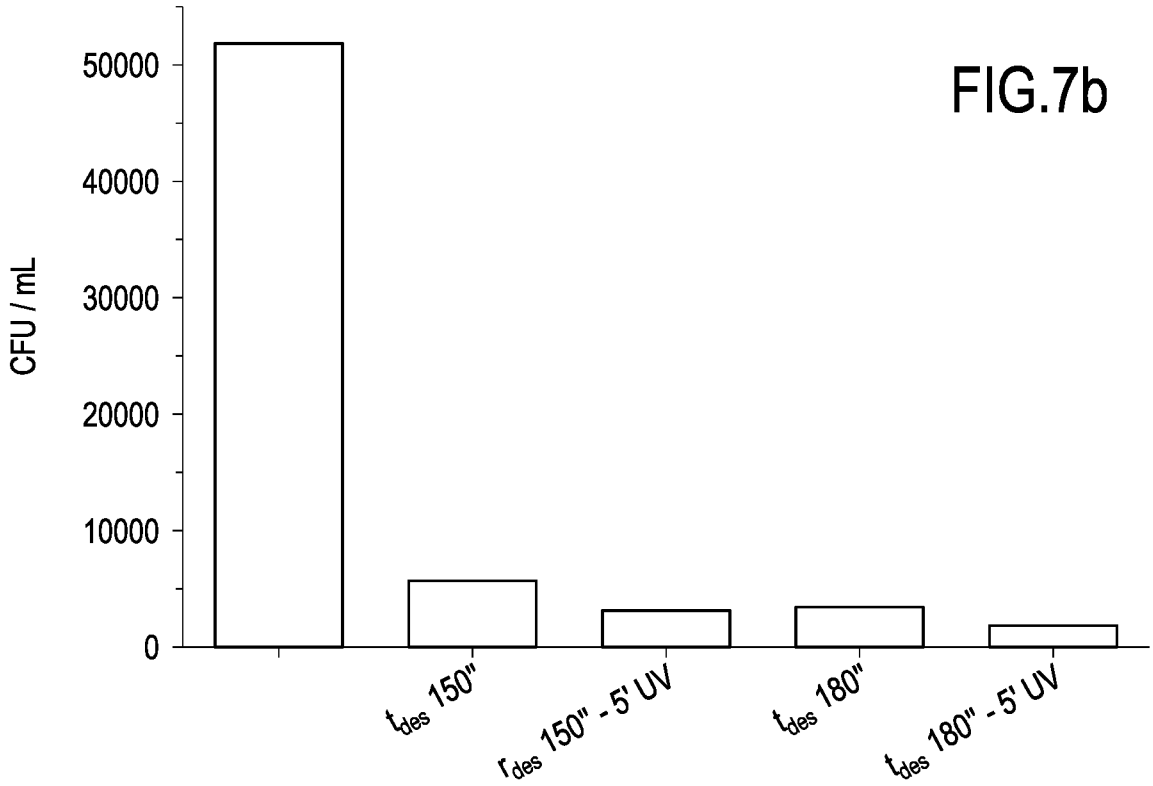

50000
40000
30000
20000
10000
0
CFU / mL
$t_{des}$ 150"
$r_{des}$ 150" - 5' UV
$t_{des}$ 180"
$t_{des}$ 180" - 5' UV

FIG.7b


50000
40000
30000
20000
10000
0
CFU / mL
$t_{des}$ 150"
$r_{des}$ 150" - 5' UV
$t_{des}$ 180"
$t_{des}$ 180" - 5' UV

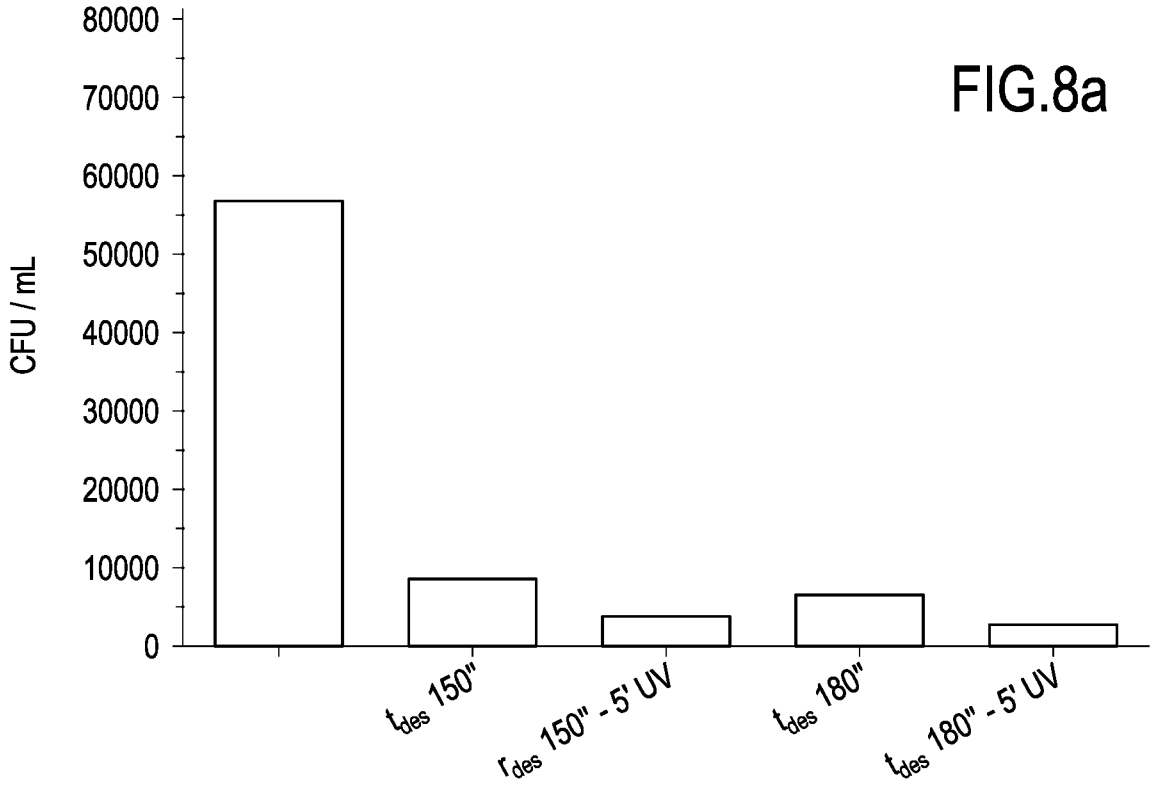

80000
70000
60000
50000
40000
30000
20000
10000
0
CFU / mL
$t_{des}$ 150"
$r_{des}$ 150" - 5' UV
$t_{des}$ 180"
$t_{des}$ 180" - 5' UV

FIG.8a

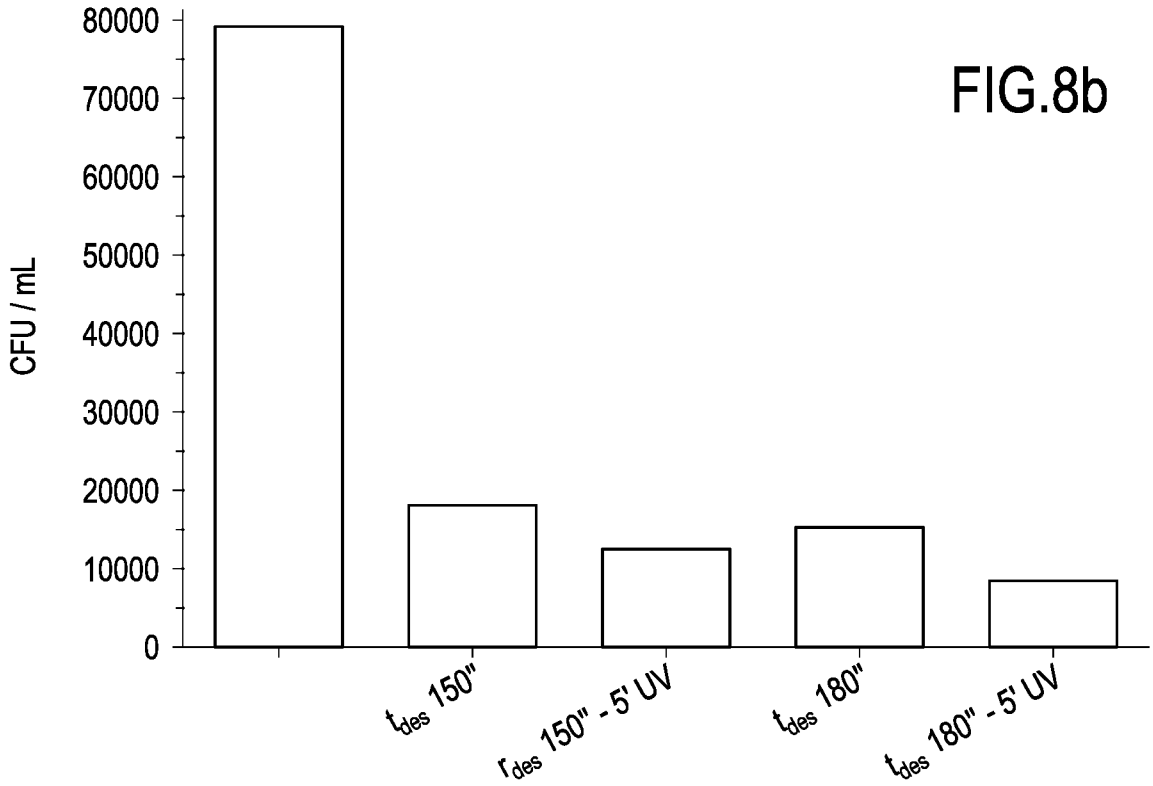

80000
70000
60000
50000
40000
30000
20000
10000
0
CFU / mL
$t_{des}$ 150"
$r_{des}$ 150" - 5' UV
$t_{des}$ 180"
$t_{des}$ 180" - 5' UV

FIG.8b

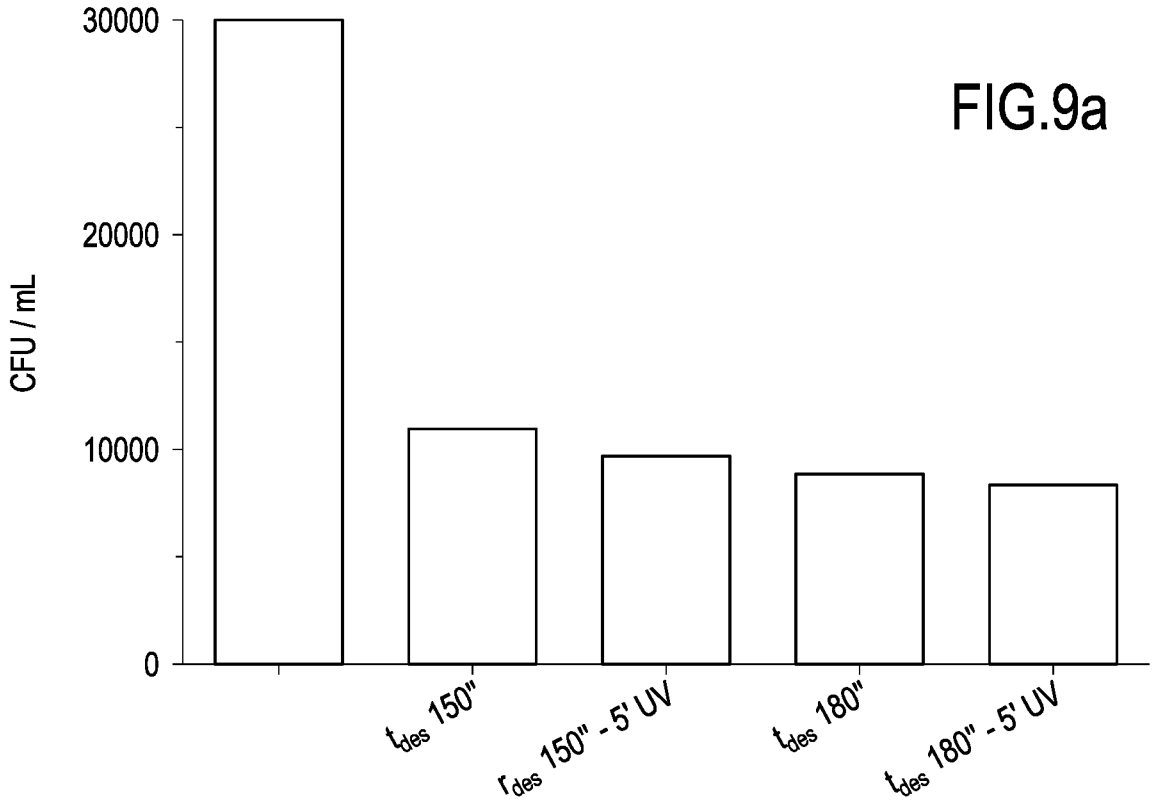

30000
20000
10000
0
CFU / mL
$t_{des}$ 150"
$r_{des}$ 150" - 5' UV
$t_{des}$ 180"
$t_{des}$ 180" - 5' UV

FIG.9a

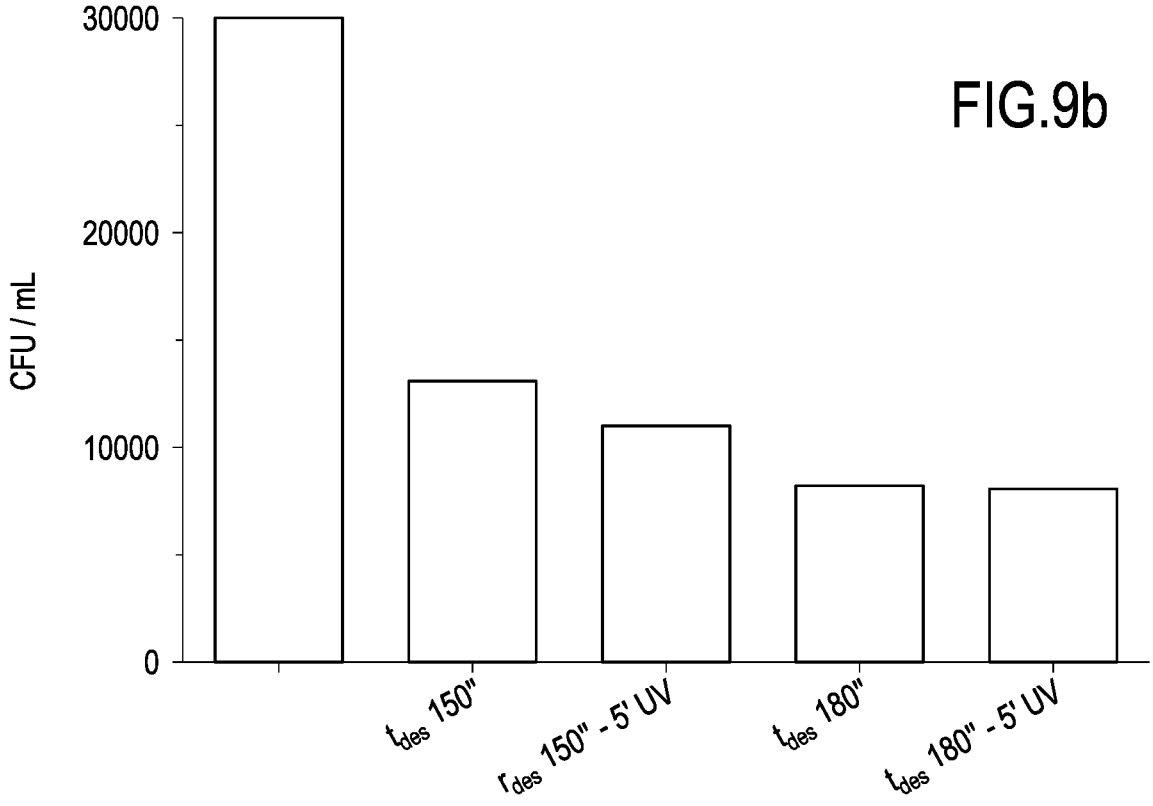

30000
20000
10000
0
CFU / mL
$t_{des}$ 150"
$r_{des}$ 150" - 5' UV
$t_{des}$ 180"
$t_{des}$ 180" - 5' UV

FIG.9b

FIG.10a

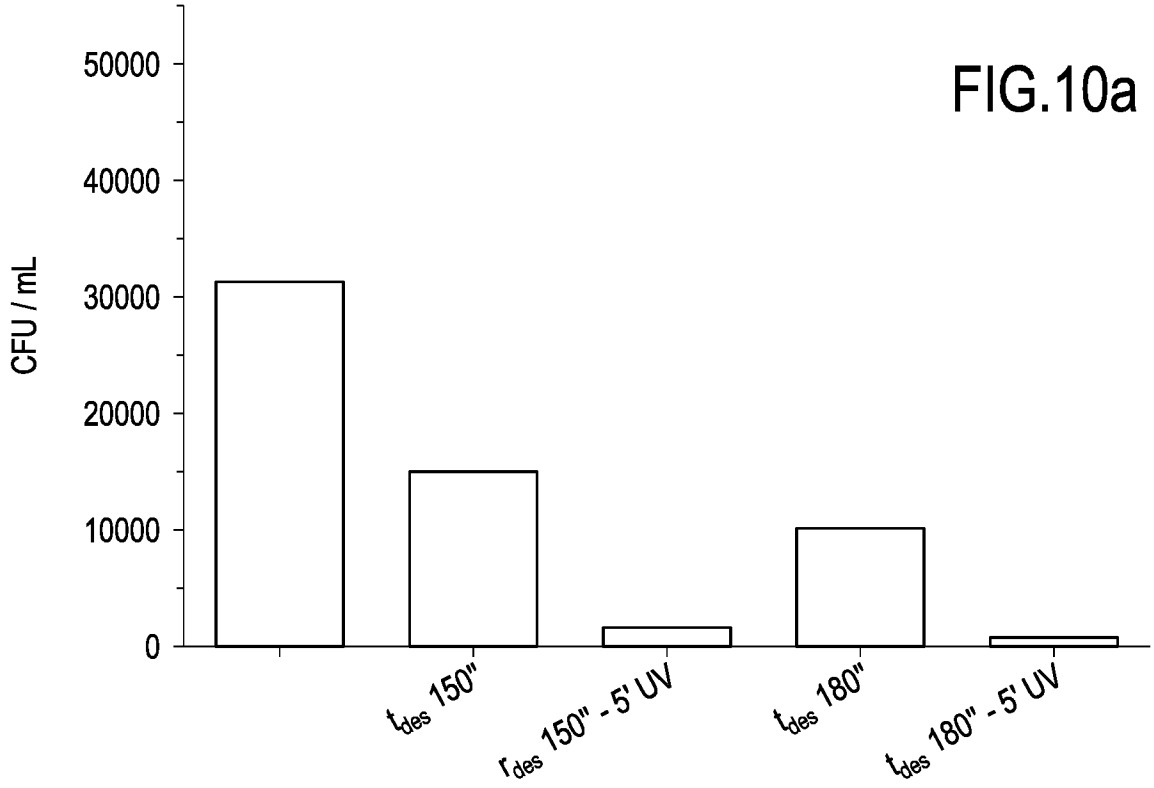
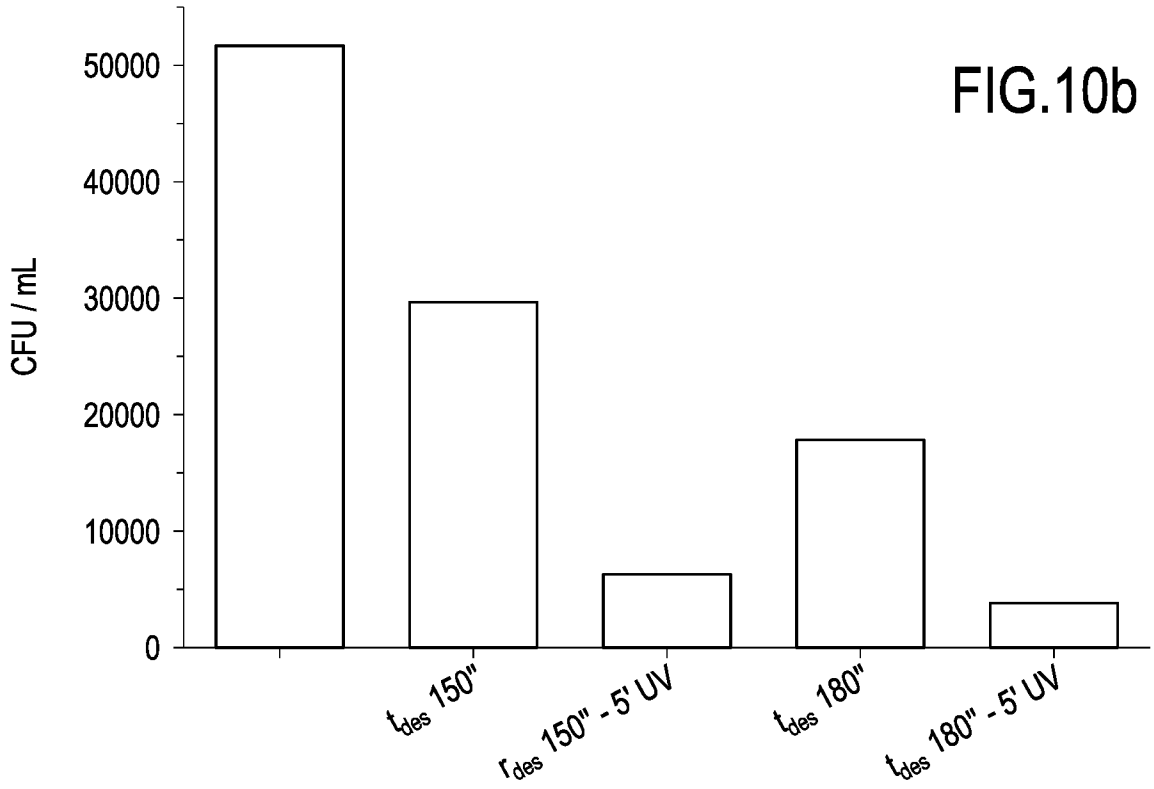



FIG.10b



# INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/055113

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61L31/08
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)
A61B A61L

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, CHEM ABS Data, BIOSIS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 11 October 2018 | 31/10/2018 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Sierra Gonzalez, M |

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# INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2018/055113

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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