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(71) Applicants and

(72) Inventors: **POLLINI, Mauro** [IT/IT]; Via del Mare, 56, I-72100 Brindisi (IT). **SANNINO, Alessandro** [IT/IT]; Via Gentile, 25, I-73100 Lecce (IT). **MAFFEZZOLI, Alfonso** [IT/IT]; Via Catalano, 5, I-73100 Lecce (IT). **LICCIULLI, Antonio** [IT/IT]; Via N. Sauro, 10, I-72023 Mesagne (IT).

(74) Agent: **LAFORGIA, Domenico**; Via Garruba, 3, I-70122 Bari (IT).

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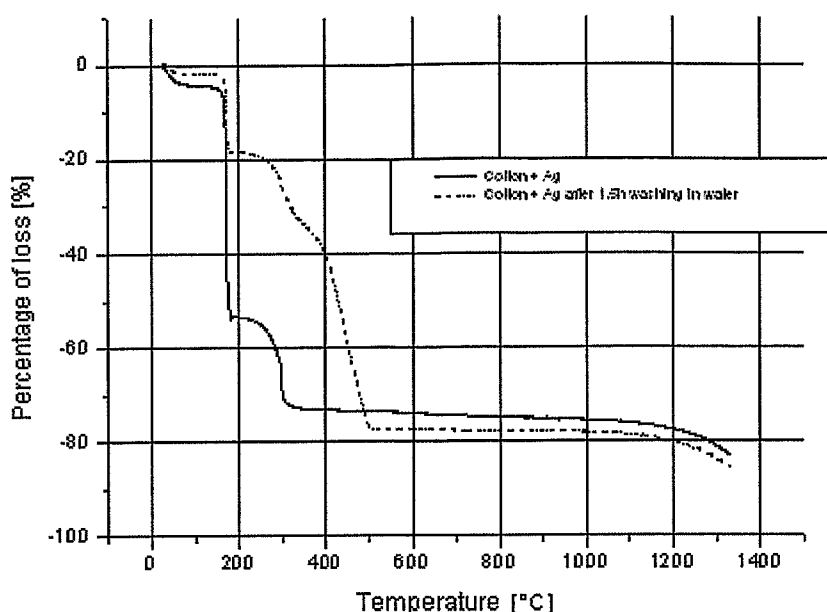
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(54) Title: ANTIBACTERIAL SURFACE TREATMENTS BASED ON SILVER CLUSTERS DEPOSITION



(57) Abstract: Process to obtain substances for antibacterial treatments, by surface impregnation of natural or synthetic material in an alcoholic solution with silver salt and, later, by their exposure to UV-rays until metal silver clusters appear on the material surface. The invention relates to the obtained antibacterial substances. The simple preparation of the antibacterial material makes the whole process easier both for required time and for costs: the needed devices are just a UV lamp and a Ultrasound bath.

**“Antibacterial surface treatments based on Silver
clusters deposition”**

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Technical field

The present invention relates to a process to obtain substances for antibacterial treatments obtained by silver (particle) deposition and to the antibacterial obtained substances.

Silver has been known as a purifying agent since the Egyptian age when it was employed to purify water to be stored for a long period of time. Modern medicine makes use of silver as an antibacterial agent in the treatment of burns or eye infections in new-born babies, see M. Potenza, G. Levinsons, AIM 59 (2004). Since the last century silver solutions have been used as an antibacterial agent to help treat infected wounds, and is used for the water purification system on the NASA space shuttle. The anti-inflammatory properties of silver have been proved by a reduced reddening of infected wounds edges. Other heavy metal, such as zinc, lead, gold, nickel, cadmium, copper and mercury are also known to have anti-bacterial properties, but some of them cannot be not used because of their toxicity or because of the high costs. Among heavy metals, only silver, zinc and copper can be used as antibacterial agents. Zinc is less

effective than the others; while copper, though highly effective against some mildews, when combined with silver has a synergic effect, however it cannot be used in contact with food. Silver ion is the most effective ion with the lowest toxicity. On this
5 subject, see: J. M. Schierholz, L. J. Lucas, A. Rump, G. Pulverer, *Journal of Hospital Infection* (1008) 40: 257-262; Gadd GM, Laurence OS, Briscoe PA, Trevors JT. *Silver accumulation in Pseudomonas stutzeri* AG 259. *Bio Metals* 1989; 2: 168-173; Wahlberg JE. *Percutaneous toxicity of metal compounds*. *Arch*
10 *Environ Health* 1989; 11: 201-203; Williams RL, Williams DF. *Albumin adsorption on metal surfaces*. *Biomat* 1988; 9: 206.

The material releases silver ions that attach themselves to the bacteria, incapacitating them and preventing them from growing or reproducing. Therefore, a silver-based antibacterial product
15 cannot be everlasting, because its silver quantity will decrease in time. When released by the material, silver ions act on the bacteria (see Y. Noue, Y. Kanzaki, *Environmental Bioinorganic Chemistry*, *Journal of inorganic Biochemistry* 377), according to a still unknown mechanism, which can be summarized in this
20 way: when silver is ingested by the bacterium, it destroys its cell walls, inhibits its reproduction and stops its metabolism, see M. Potenza, G. Levinsons, *AIM* 59 (2004). Silver has no toxic effect on living human cells. It has a very powerful antibacterial property, since a solution with only 1 ppm of pure elemental
25 silver has an effective bacterial killing action. Natural or

synthetic materials (e.g. fabric, woven and similar), with antibacterial properties have already been realized in several fields, such as clothing, medicine, filtering systems, transportation and others. They have different shapes and trade-
5 names but all of them are very expensive, because of the existing difficulties in their realization.

Disclosure of the invention

The invention is characterized by its simplicity and
10 inventiveness due to the fact that it uses no binders between the material and the silver. It relates to a process to obtain substances for antibacterial treatments obtained by impregnated natural or synthetic materials in an alcohol solution with silver salt and, afterward, by exposing it to UV-rays until the metal
15 silver clusters appear on the material surface. The invention also relates to the obtained antibacterial substances.

The simplicity of the antibacterial material preparation makes the whole process easier both for required time and for costs: the equipment needed to carry on the procedure comprises a UV
20 lamp and an ultrasounds bath.

These and other advantages will be pointed out in the detailed description of the invention that will refer to the figures of the tables 1/3, 2/3 and 3/3, each of them exemplifying and not restrictive.

Way of carrying out the invention

With reference to the above mentioned tables:

- Fig. 1 shows the results of a thermal-gravimetric analysis;
 - Fig. 2 is a S.E.M. representation (650 X) of the 100% cotton
5 fibers, impregnated with the silver;
 - Fig. 3 is a S.E.M. representation (4300 X) of the 100% cotton
fibers, impregnated with silver;
 - Fig. 4 shows a growth test of Escherichia coli JM101
AMERSHAM on a 100% cotton sample;
 - 10 • Fig. 5 shows a growth test of Escherichia coli JM101
AMERSHAM on a cotton sample, impregnated with silver;
 - Fig. 6 shows a growth test of Escherichia coli JM101
AMERSHAM on a cotton sample, impregnated with
kanamicina antibiotic;
- 15 The first step of the procedure is the preparation of the silver
solution; the alcohol solvent (for example, methanol) is mixed to
silver salts (for example, silver nitrate AgNO_3). Other silver
salts, such as silver chloride or silver acetate, can be used as
well. The weight ratio of the solvent to the solute is strictly
20 dependent on the silver quantity to be deposited on the material.
A typical example is a solution at 5%_{wt} of silver nitrate in
methanol. The best dissolution of silver salt in alcohol can be
achieved when the solution is exposed to ultrasound rays for few
minutes, until completely homogenous. Moreover, according to
25 laboratory tests, the solution can be stored for a long time in dark

keeping conditions, without losing its effectiveness. This helps the industrialization process, because the solution would be ready to use whenever a material is to be impregnated. However, the long-stored solution should be newly exposed to the ultrasound rays, when the weight percentage of the silver in the solution is high (like 5% is).

The silver impregnation protocol of fibre, woven or, in general, the material is the following:

1. immersion of the material in the solution
- 10 2. exposure of the material to UV rays
3. drying of the material

The exposure of the material to UV allows the chemical reduction of the silver cations and the formation of the nearly metal clusters well bound to the material. As the same time the material changes its colour, for example from white to dark brown. To form and fix the metal silver clusters to the material a radiation power range between 20 W/m² and 10000 W/m² is needed with an exposure time between 5 sec and 30 minutes, and a wave length between 285 and 400 nm. In a preferred procedure, the distance of the lamp from the sample surface is 10 cm, corresponding to a power of 500 W/m² and an exposure time between 1 and 2 minutes. In Fig. 1 the results of a thermal-gravimetric analysis have been shown for a comparison between a not washed 100% cotton sample and a washed (1,5 h) 100% cotton sample. On both, silver has been deposited, starting from

a 5%_{wt} silver nitrate solution. TGA curves show a fix residual equal to 21.51%_{wt} in the first case and 18.74%_{wt} in second case (washed fibre). These percentage do not include the cotton fix residual, which is 3.6%. In Fig. 2 and 3, images from the scan
5 electronic microscope (SEM) are shown: they are related to 100% cotton fibres on which silver has been deposited. Above all in Fig. 3 (4300 X), the metallic clusters are perfectly visible.

The antibacterial effectiveness has been checked (but not exclusively) with *Escherichia coli* JM101 AMERSHAM
10 bacterial cultivation. The test has been carried out on several samples, even those treated with antibiotic. The testing slabs have been previously filled by agar, that is an excellent medium for growing soil bacteria. Once the agar became solid, 1 ml bacterial suspension has been injected into each slab and
15 distributed on the whole agar surface. Then the fibre samples have been introduced and the slabs have been put in an oven at 37°C for 24 h. The results in Figs. 4-6 show a remarkable antibacterial property of the fibre, which were treated according to the present invention: their performance is equal or even
20 better than the one of fibres, which were impregnated with the kanamycin antibiotic. The bacterial growth inhibition areas have to be evaluated by measuring the area surrounding the sample, in which no bacterial proliferation can be seen. From Fig. 4, you can observe that the 100% cotton does not show any
25 antibacterial behaviour. In Fig. 5, which is related to fibres

impregnated with silver, according to the present invention, the antibacterial behaviour is shown: a well defined area around the sample, without bacterial proliferation, can be noted. Same antibacterial behaviour is shown in Fig. 6, which is related to a cotton sample, impregnated with kanamicina antibiotic.

A slight different process consists in the fact that the deposit of the silver solution on the material can be realized by spraying the solution by an airbrush. The following step, the exposure to the UV rays, does not change.

Example

An example of carrying out the process is the described below.

a) solution preparation

For 100g solution with 5%_{wt} of silver nitrate, you would need 95.24g methanol and 4.76g AgNO₃.

Dilute the silver salt in the methanol, by dipping the becker in an ultrasounds bath for five minutes.

b) impregnation

Shortly dip the fibers inside the becker, containing the solution; then expose them to the UV rays for approximately two minutes; the silver clusters will appear together with a color change in the fibers, which, if white, will become dark brown.

Claims

- 1) Process to obtain substances for antibacterial treatments obtained by impregnated natural or synthetic materials in an alcohol solution with silver salt and, afterward, by exposing it to UV-rays until the metal silver clusters appear on the material surface.
- 2) Process according to the claim 1, wherein said material is fabric or woven, said alcohol is methanol and said salt is silver nitrate.
- 3) Process according to the claim 2, wherein said exposure to UV-rays is characterized by the following ranges: wave length $285 \div 400$ nm, power $20 \div 10000$ W/m² and exposure time 5s and 30 min.
- 4) Antibacterial natural fabric characterized by the fact that it is obtained by its surface impregnation in a methanol solution with silver nitrate (any percentage) and, later, by exposing said natural or synthetic material to UV-rays until metal silver clusters appear on the material surface.
- 5) Antibacterial natural fabric according to the claim 4, wherein said fabric is made of cotton.
- 6) Antibacterial natural fabric according to the claim 4 or 5, wherein said exposure to UV-rays is characterized by the following ranges: wave length $285 \div 400$ nm, power $20 \div 10000$ W/m² and exposure time 5s and 30 min.

- 7) Antibacterial polymeric fabric characterized by the fact that it is obtained by its surface impregnation in a methanol solution with silver nitrate (any percentage) and, later, by exposure of said natural or synthetic material to UV-rays until metal silver clusters appear on the material surface.
- 8) Antibacterial polymeric fabric according to the claim 7, wherein said exposure to UV-rays is characterized by the following ranges: wave length $285 \div 400$ nm, power $20 \div 10000$ W/m² and exposure time 5s and 30 min.
- 9) Antibacterial natural woven characterized by the fact that is obtained by its surface impregnation in a methanol solution with silver nitrate (any percentage) and, afterward, by exposure of said natural or synthetic material to UV-rays until metal silver clusters appear on the material surface.
- 10) Antibacterial natural woven according to the claim 9, wherein said exposure to UV-rays is characterized by the following ranges: wave length $285 \div 400$ nm, power $20 \div 10000$ W/m² and exposure time 5s and 30 min.
- 11) Antibacterial polymeric woven characterized by the fact that is obtained by its surface impregnation in a methanol solution with silver nitrate (any percentage) and, later, by exposure of said natural or synthetic material to UV-rays until metal silver clusters appear on the material surface.
- 12) Antibacterial polymeric woven according to the claim 11, wherein said exposure to UV-rays is characterized by the

following ranges: wave length $285 \div 400$ nm, power $20 \div 10000$ W/m² and exposure time 5s and 30 min.

13) Antibacterial woven/nonwoven fabric characterized by the fact that is obtained by its surface impregnation in a methanol solution with silver nitrate (any percentage) and, later, by exposure of said natural or synthetic material to UV-rays until metal silver clusters appear on the material surface.

14) Antibacterial woven/non woven fabric according to the claim 13, wherein said exposure to UV-rays is characterized by the following ranges: wave length $285 \div 400$ nm, power $20 \div 10000$ W/m² and exposure time 5s and 30 min.

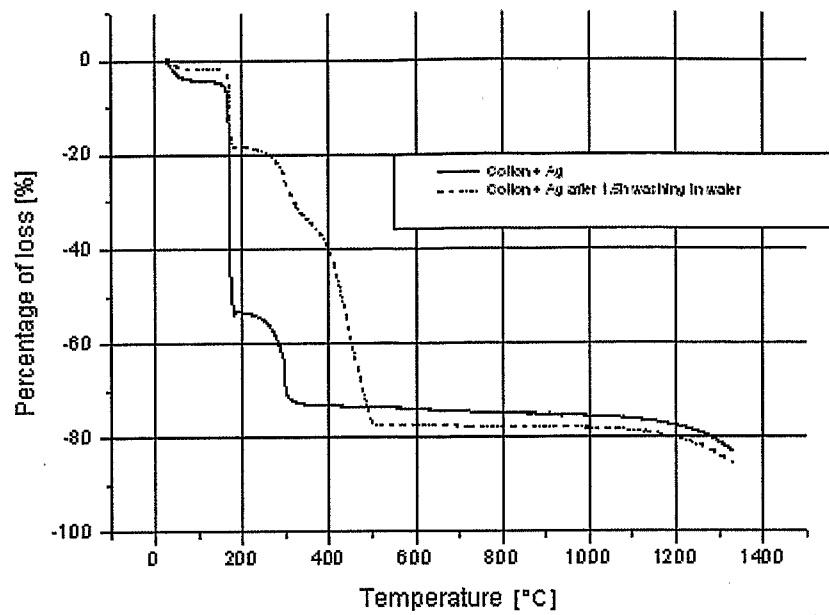


Fig. 1

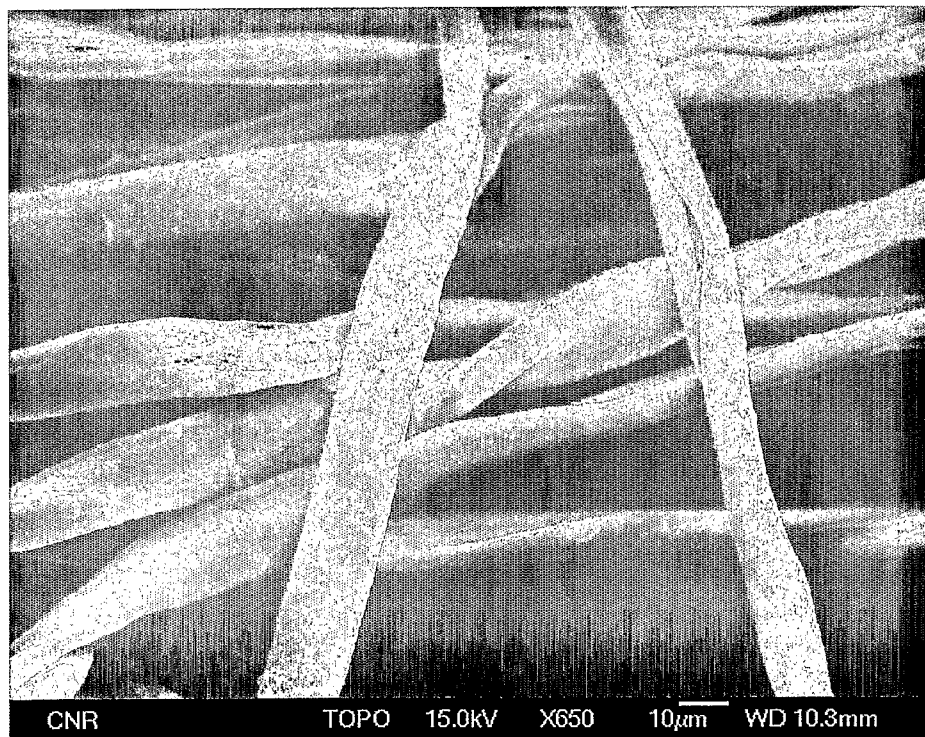


Fig. 2

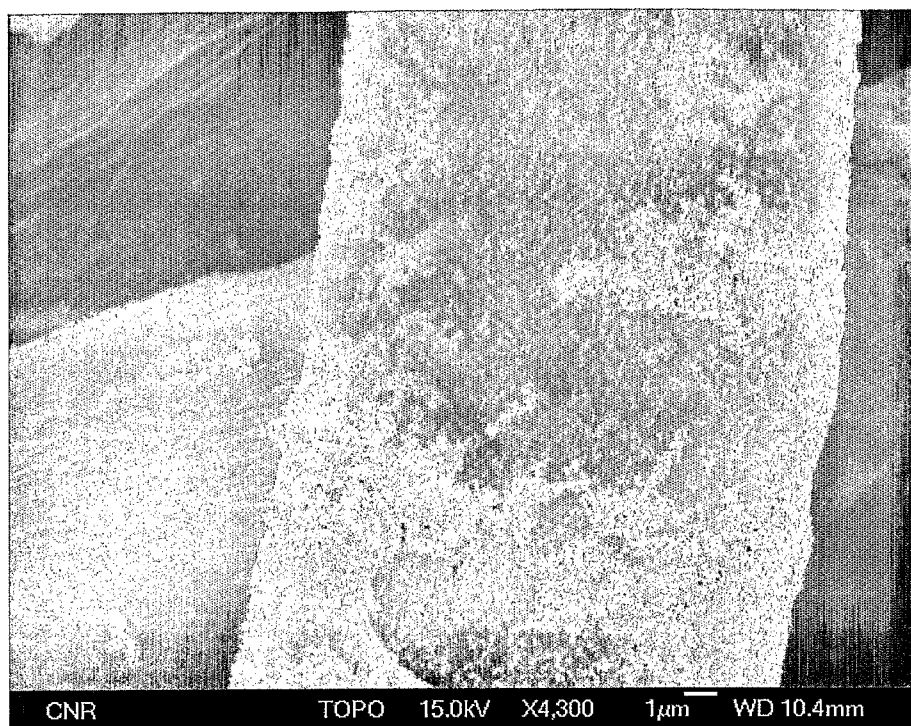


Fig. 3



Fig. 4

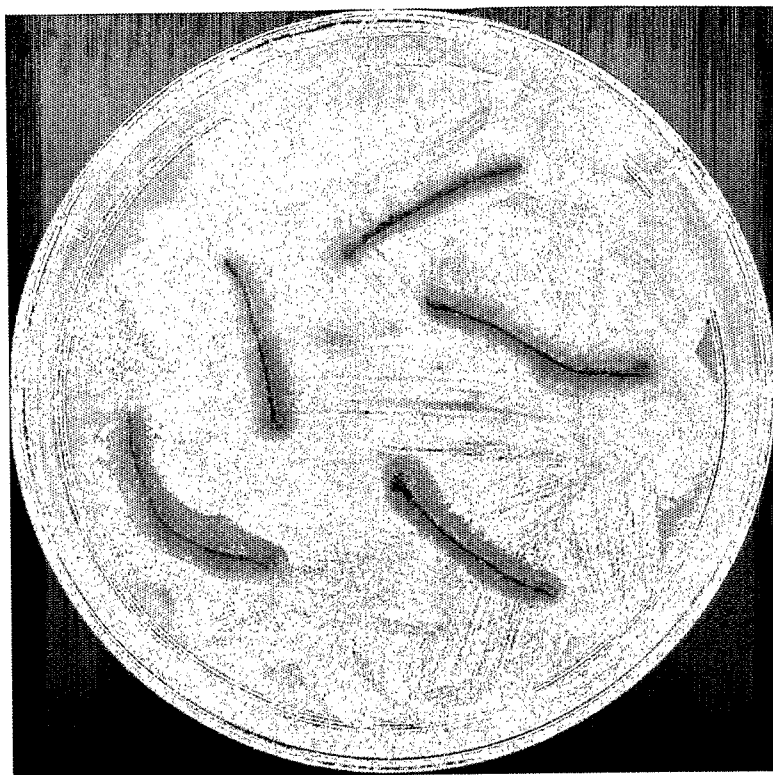


Fig. 5

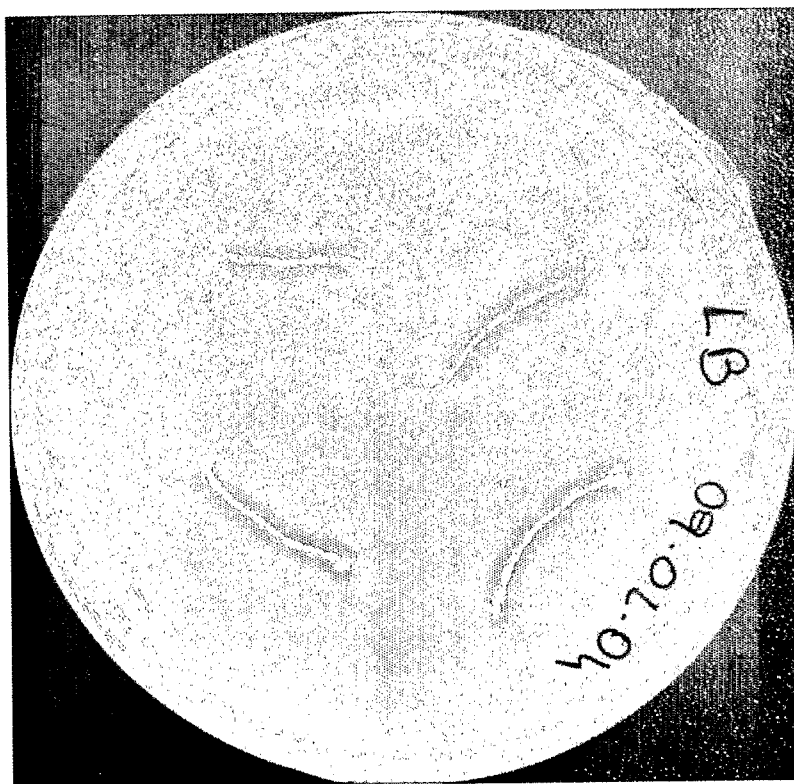


Fig. 6