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(54) Title: PHOTOCATALYTIC PARTICLES AND PROCESS FOR THE PRODUCTION THEREOF

(57) Abstract: Method for the production of a treated article having photocatalytic activity; the method comprises an application step, during which composite particles are applied on a surface of a base product comprising ceramic; each composite particle comprises a respective microparticle of TiO₂ and a plurality of respective silver-based nanoparticles supported by the relative microparticle of TiO₂; the silver-based nanoparticles are 3% to 12% by weight with respect to the overall weight of the microparticles of TiO₂ and of the silver-based nanoparticles; the treated article shows surprisingly high photocatalytic properties even if irradiated only in the visible light range.



WO 2016/157155 A1

"PHOTOCATALYTIC PARTICLES AND PROCESS FOR THE PRODUCTION THEREOF"

TECHNICAL FIELD

5 The present invention relates to a method to produce a treated article and a treated article.

The present invention also relates to composite particles and a process for the production of composite particles.

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BACKGROUND TO THE INVENTION

In the field of ceramic materials it is known to coat objects with TiO_2 so that said objects can express photocatalytic properties. The coating is usually produced using particles of titanium dioxide with nanometric dimensions in order to obtain materials that can be easily cleaned and are able to partially purify the air of organic and inorganic pollutants (for example NO_x and SO_x). Often, to obtain good adhesion of the TiO_2 on the surface of the objects, organic polymers are used.

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The known methods for coating ceramic objects with titanium dioxide and the articles thus obtained have various drawbacks, including the following.

25 The use of nanometric particles is harmful to health. The catalytic effects are relatively low and are often non-reproducible.

The solidity of the adhesion of the layer of TiO_2 to the objects is not stable in time.

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The international patent application having publication number WO2010146410 (filed by the same applicant) proposes the use of micrometric particles of TiO_2 for the surface treatment of tiles. The laboratory tests have confirmed that the tiles obtained in this way have a photocatalytic efficiency such

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that under radiation with UV-A light they:

- are photocatalytic by degradation of methylene blue in aqueous phase (ISO 10678:2010);
- are antibacterial also for MRSA bacteria (antibiotic-resistant) (ISO 27447:2009);
- are able to degrade NO_x;
- are able to degrade VOC (ethanol, toluene, acetone, acetaldehyde, formaldehyde);
- are self-cleaning according to the ISO 27448-1:2009 standard;
- have photodegradation activity which takes place also in the aqueous phase. The tests performed both on powders and tiles have shown their efficiency in degradation of organic dyes, acetylsalicylic acid (aspirin), phenol and paracetamol.

It is pointed out, however, that the TiO₂ is photoexcited between 315 and 400 nm (with maximum at 380 nm) in the UV-A range (the theoretical datum of 380 nm is typical of the single crystals).

The tiles treated with TiO₂ are therefore not able to act in the absence of light and are relatively ineffective also when installed in closed environments lit by normal LED lights (which typically emit with wavelengths beyond 400 nm and therefore only in the visible and not in the ultraviolet range).

The object of the present invention is to provide a method for the production of a treated article, a treated article, composite particles and a process for the production of composite particles which overcome, at least partially, the drawbacks of the known art and are, at the same time, easy and inexpensive to produce and/or use.

SUMMARY

According to the present invention composite particles and a

process for the production of composite particles are provided as claimed in the following independent claims and, preferably, in any one of the claims depending directly or indirectly on the independent claims.

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BRIEF DESCRIPTION OF THE FIGURE

The invention is described below with reference to the attached figure, which illustrates a non-limiting embodiment example thereof, in which:

- 10 - figure 1 illustrates photographs taken by TEM of microparticles of TiO_2 supporting silver-based nanoparticles according to the present invention.

DETAILED DISCLOSURE

- 15 In accordance with a first aspect of the present invention, composite particles are provided, each of which comprises (in particular, consists of) a microparticle of TiO_2 and a plurality of silver-based nanoparticles (typically, with mean diameter ranging from 1 to 100 nm) supported by the
20 microparticle of TiO_2 . More precisely, the microparticle of TiO_2 has a respective outer surface; the silver-based nanoparticles are bound to said outer surface and exposed towards the outside.

- 25 In particular, the composite particles have a mean diameter ranging from 0.1 μm to 1 μm (more precisely, 0.5 μm). According to some embodiments, the composite particles have a mean diameter up to 0.2 μm (more precisely, up to 0.13 μm).

- 30 In particular, the silver-based nanoparticles comprise (more precisely, are selected from the group consisting of): nanoparticles of silver, of silver oxide and a combination thereof. According to some embodiments, the silver-based nanoparticles comprise silver oxide; more precisely, the
35 silver-based nanoparticles comprise (more precisely, are selected from the group consisting of): nanoparticles of

silver oxide and of silver, nanoparticles of silver oxide (and a combination thereof). Advantageously, the silver-based nanoparticles comprise (more precisely are) nanoparticles of a combination of silver and silver oxide.

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The composite particles with nanoparticles described above have experimentally shown a surprisingly high activity.

In some cases, the silver-based nanoparticles comprise (more
10 precisely are) silver nanoparticles.

Advantageously, the composite particles comprise from 3% (in particular, from 5%) to 50% (in particular, 30%) by weight of the silver-based nanoparticles with respect to the sum of the
15 weights of the silver-based nanoparticles and the microparticles of TiO_2 . In some cases, the composite particles comprise from 3% (in particular, from 5%) to 12% (in particular, 10%) by weight of the silver-based nanoparticles with respect to the sum of the weights of the silver-based
20 nanoparticles and the microparticles of TiO_2 .

The percentage by weight of the silver-based nanoparticles, with respect to the sum of the weights of the silver-based nanoparticles and the microparticles of TiO_2 , can be measured
25 by means of ICP/OES (inductively coupled plasma optical emission spectrometry) (more precisely, with a Perkin Elmer Optima 8300 instrument).

In particular, the microparticles of TiO_2 have a mean diameter
30 ranging from 0.1 μm to 1 μm (more precisely, 0.5 μm). In some cases, the microparticles of TiO_2 have a mean diameter up to 0.2 μm (more precisely, up to 0.13 μm).

According to some embodiments, the silver-based nanoparticles
35 have a mean diameter ranging from 1 nm to 30 nm (in particular, 20 nm; in some cases, 10 nm).

Unless specified to the contrary, in this text the mean diameter of the microparticles of TiO_2 and the composite particles is measured by means of X-ray diffraction (XRD).

5 More precisely, the calculation of the mean diameter of the microparticles of TiO_2 is performed by means of the Scherrer equation: $t = 0.9\lambda / (\beta_{hkl} \times \cos\theta_{hkl})$, in which t is the dimension of the crystallites (corresponding to the particle), λ is the wavelength of the X rays of the radiation for $\text{CuK}\beta$, β_{hkl} is the full width at half maximum (FWHM) at the (hkl) peak and θ_{hkl} is the angle of diffraction. In particular, the measurements are performed using a PW3050/60 X'Pert PRO MPD diffractometer by PAN analytical working Bragg-Brentano, and using as source the high-power ceramic tube PW3373/10 LFF with a Cu anode equipped with Ni filter to attenuate $\text{K}\beta$. The dispersed photons were collected by a RTMS (Real Time Multiple Strip) X'accelerator-detector. The measurement can be verified by means of TEM (as indicated below in relation to the silver-based nanoparticles).

20 Unless specified to the contrary, in this text the mean diameter of the silver-based nanoparticles is measured by means of TEM. More precisely, the calculation of the mean diameter is performed by measuring the largest dimension of one hundred particles (taken at random) and obtaining the mean. In particular, a JEOL 3010-UHR instrument is used (acceleration potential: 300 kV; filament LaB_6).

Advantageously, at least 98% (in particular, at least 99.5%) by weight of the microparticles of TiO_2 with respect to the overall weight of the microparticles of TiO_2 are of anatase. In some specific cases, the microparticles of TiO_2 are of anatase.

35 According to some embodiments, the composite particles have a surface area (measured by means of BET) ranging from 5 m^2/g

to 30 m²/g.

In particular, the surface area can be determined by means of conventional methods of N₂ absorption (BET - Brunauer-Emmett-Teller). More precisely, the determination is performed at 77 K using a sorptometer (Costech Mod. 1042).

As better demonstrated by the examples given below, the composite particles according to the present invention have proved to be surprisingly active.

According to some embodiments, the composite particles are obtainable (in particular, obtained) by means of a process in accordance with a second aspect of the present invention (defined below).

In accordance with a second aspect of the present invention, a process is provided for the production of composite particles (in particular, composite particles according to the first aspect of the present invention).

The process comprises a loading step, during which silver-based nanoparticles are obtained (and) bound to outer surfaces of microparticles of TiO₂ so as to obtain said composite particles.

According to some embodiments, the loading step comprises in turn a mixing sub-step, during which a solution containing silver ions and the microparticles of TiO₂ is kept under stirring so as to obtain an intermediate mixture. More precisely, the mixing sub-step lasts at least 12 hours (in particular, 18 hours to 30 hours) and the solution (containing silver ions and the microparticles of TiO₂) is kept at a temperature ranging from 30°C to 50°C.

Advantageously, the solution has from 3% to 12% by weight of

the silver ions with respect to the sum of the weights of the silver ions and microparticles of TiO_2 .

According to some embodiments, the loading step also comprises
5 a heating sub-step, which is (at least partially) subsequent to the mixing sub-step. In some cases, during the heating sub-step, the intermediate mixture is kept at a temperature higher than 300°C for at least 30 minutes. More precisely, during the heating sub-step, said intermediate mixture is kept
10 at a temperature ranging from 350°C (in particular, approximately from 390°C) to 600°C (in particular, approximately to 500°C) for a time ranging from 40 minutes to 150 minutes.

15 Advantageously, the loading step comprises a drying sub-step to reduce the water content of the (more precisely, to dry the) intermediate mixture, providing heat to said intermediate mixture. The drying sub-step is (at least partially) subsequent to the mixing sub-step. In particular, the drying
20 sub-step is (at least partially) previous to the heating sub-step. In some cases, during the drying sub-step, the intermediate mixture is kept at a temperature lower than 150°C (in particular, lower than 120°C ; more in particular, lower than 110°C). Advantageously, during the drying sub-step,
25 the intermediate mixture is kept at a temperature higher than 40°C (in particular, higher than 80°C ; more in particular, higher than 85°C). More precisely, during the drying sub-step, the intermediate mixture is kept at the temperatures indicated above for at least 10 hours (in particular, at least 20
30 hours). In particular, during the drying sub-step, the intermediate mixture is kept at the temperatures indicated above up to 35 hours (in particular, up to 30 hours).

According to some embodiments, the loading step also comprises
35 a dissolution sub-step (which is at least partially previous to the mixing sub-step e), during which a silver salt (in

particular, AgNO_3) is dissolved in a (polar) solvent. In particular, said solvent comprises (more precisely, is) water. In some cases the dissolution sub-step and the mixing sub-step are (at least partially) overlapping.

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Typically, the solution containing silver ions and the microparticles of TiO_2 is water (based). According to specific embodiments, the solution consists of water, the microparticles of TiO_2 and the silver salt (substantially dissolved).

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In particular, during the loading step a silver colloid is not present.

15 Advantageously, the microparticles of TiO_2 and the silver-based nanoparticles are as defined according to the first aspect of the present invention.

According to some embodiments, the process (in particular, the loading step) is carried out in the absence of a reducing agent, for example ammonia, hydrazine, hydrogen, ascorbic acid, NaBH_4 (and a combination thereof).

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In particular, the mixing sub-step, the drying sub-step and the heating sub-step are carried out in the absence of a reducing agent, for example ammonia, hydrazine, hydrogen, ascorbic acid, NaBH_4 (and a combination thereof).

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This is one of the ways (particularly advantageous) of obtaining silver-based nanoparticles containing silver oxide.

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According to some embodiments, the process (in particular, the loading step) is carried out in the absence of an emulsifier (more precisely, surface-active agent), for example CTAB, polyvinylpyrrolidone. In particular, in some cases, the loading step is carried out in the absence of an organic

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compound.

More precisely, the drying sub-step and the heating sub-step are carried out in the absence of an emulsifier (more
5 precisely, surface-active agent), for example CTAB, polyvinylpyrrolidone. In particular, the drying sub-step and the heating sub-step are carried out in the absence of an organic compound.

10 It has been experimentally observed that in this way production of the composite particles is surprisingly improved.

In the present text, when it is affirmed that a process or a
15 step are carried out in the absence of a compound (for example an emulsifier and/or an organic compound), it is understood that said process and/or step are carried out without any (one or more) said compound and therefore also without a plurality of said compounds.

20 Advantageously, the process comprises a sonication step (which is at least partially previous to the loading step e), during which the microparticles of TiO_2 undergo sonication in a liquid, in particular water.

25 According to some embodiments, the microparticles of TiO_2 are dispersed in water and sonicated at 20 kHz (in particular, with an ULTRASONIC transistor instrument).

30 Advantageously, the process comprises a wetting step (which is at least partially previous to the loading step e), during which the microparticles of TiO_2 are wetted with an organic solvent (in particular acetone). In this way it is possible to clean and free the pores of the microparticles of TiO_2 .

35 Advantageously, the solution containing silver ions and the

microparticles of TiO_2 comprises a dispersing agent. In particular, the dispersing agent is based on polyacrylic acid and sodium (approximately 15% by weight with respect to the overall weight of the dispersing agent). The dispersing agent
5 can, for example, be Reotan L produced by Lamberti S.p.A..

Due to the dispersing agent, an improved and stable suspension of the microparticles of TiO_2 is obtained.

10 In accordance with a third aspect of the present invention, a method is provided for the production of a treated article, said method comprising an application step, during which composite particles (in particular, the composite particles as per the first aspect of the present invention) are applied on
15 a surface of a base product (comprising ceramic; more precisely, consisting of ceramic). According to some embodiments, the base product is a tile.

In particular, each composite particle comprises (more
20 precisely, consists of) a respective microparticle of TiO_2 and a plurality of respective silver-based nanoparticles supported by the relative microparticle of TiO_2 .

According to some embodiments, the composite particles are
25 spray-applied on the surface of the base product.

Advantageously, the silver-based nanoparticles range from 3% to 12% by weight with respect to the overall weight of the microparticles of TiO_2 and the silver-based nanoparticles.

30 Advantageously, the microparticles of TiO_2 and the silver-based nanoparticles are defined as indicated according to the first aspect of the present invention.

35 Preferably, the method also comprises a baking step, which is at least partially subsequent to the application step and

during which the base product on which the composite particles have been applied is treated at a temperature up to 780°C; more precisely, from 400°C (in particular, from 500°C) to 780°C (in particular, to 750°C; more precisely, to 700°C). In particular, during the baking step the base product (on which the composite particles have been applied) is treated at a temperature ranging from 600°C (in particular, from 630°C) to 690°C (in particular, to 680°C).

According to some embodiments, the base product on which the composite particles have been applied is treated with a heating cycle which entails raising the temperature from an initial temperature lower than 40°C (more precisely, from approximately 20°C to approximately 30°C) to a higher temperature ranging from 400°C (in particular, from 500°C) to 750°C (in particular, to 700°C; more in particular, to 690°C) in a time of at least 30 minutes (in particular, from 30 minutes to 60 minutes; more precisely, from approximately 35 minutes to approximately 50 minutes). Once said temperature has been reached, the base product on which the composite particles have been applied is cooled in a time of at least 30 minutes (in particular, 30 minutes to 60 minutes; more precisely, approximately 35 minutes to approximately 50 minutes) to return approximately to a temperature lower than 40°C (more precisely, from approximately 20°C to approximately 30°C).

Advantageously, during the application step, at least 0.1 g (more precisely, at least 0.6 g) of composite particles are applied per square metre of said surface of the base product. In particular, during the application step, up to 5 g (more precisely, up to 3 g; even more precisely, up to 1.3 g) of composite particles are applied per square metre of said surface of the base product.

According to some embodiments, the composite particles are

applied in a suspension comprising 70% to 90% by volume of water with respect to the overall volume of the suspension. Advantageously, the suspension comprises from 5% (in particular, from 7%; more in particular, from 10%) to 20% by volume of a dispersing agent with respect to the overall volume of the suspension. In particular, the dispersing agent is substantially liquid. More precisely, the dispersing agent is suspension (aqueous).

In some cases, the cited suspension comprises up to 5% (more precisely, up to 3%; even more precisely, up to 2%) by weight of composite particles with respect to the overall weight of the suspension. In particular, the cited suspension comprises at least 0.4% (more precisely, at least 1%; even more precisely, at least 1.5%) by weight of composite particles with respect to the overall weight of the suspension.

In particular, the dispersing agent comprises silica (in suspension) and sodium ion (more precisely, a sodium salt; even more precisely, dissolved in water).

According to some embodiments, the dispersing agent comprises 25% to 35% by weight of sodium ion with respect to the overall weight of the dispersing agent. In some cases, the dispersing agent comprises 40% to 50% by weight, with respect to the overall weight of the dispersing agent, of sodium ion. Advantageously, the dispersing agent comprises 7% to 16% by weight, with respect to the overall weight of the dispersing agent, of silica (in particular quartz). In some cases, the dispersing agent comprises 8% to 15% by weight, with respect to the overall weight of the dispersing agent, of a polysaccharide with high molecular weight.

According to specific embodiments, the dispersing agent comprises (more precisely, is) xanthan gum.

Advantageously, the method comprises a process according to the second aspect of the present invention. More precisely, the method comprises a loading step, during which the silver-based nanoparticles are obtained (and) bound to the outer surfaces so as to obtain said composite particles and which comprises in turn a mixing sub-step and a heating sub-step, which is at least partially subsequent to the mixing sub-step.

Advantageously, during the mixing sub-step a solution containing silver ions and the microparticles of TiO_2 is kept under stirring (in particular, at a temperature from 30°C to 50°C). During the heating sub-step, said solution is kept at a temperature higher than 300°C (in particular, 350°C to 600°C) for at least 30 minutes (in particular, 40 minutes to 80 minutes).

In accordance with a fourth aspect of the present invention, a treated article is provided, obtainable (in particular, obtained) by means of the method as per the third aspect of the present invention. More precisely, the article has a base product comprising ceramic (more precisely, consisting of ceramic).

In particular, the article comprises (a plurality of) composite particles on the (more precisely, bound to the) surface of the article. More precisely, the composite particles are bound to the surface (of the base product).

According to some embodiments, the article has at least 0.1 g (more precisely, 0.6 g) of composite particles per square metre of the cited surface. In particular, the article has up to 5 g (more precisely, up to 3 g; even more precisely, up to 1.3 g) of composite particles per square metre of said surface (of the base product).

More precisely, the composite particles are defined as

indicated according to the first aspect of the present invention.

In accordance with a fifth aspect of the present invention,
5 the use of an article is provided according to the fourth aspect of the present invention for photodegradation. In accordance with a sixth aspect of the present invention, the use of an article is provided according to the fourth aspect of the present invention as an antibacterial.

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In accordance with a seventh aspect of the present invention, the use of composite particles is provided according to the first aspect of the present invention for photocatalysis.

15 In accordance with an eighth aspect of the present invention, the use of composite particles is provided according to the first aspect of the present invention for photodegradation. In particular, the use of composite particles according to the first aspect of the present invention is provided for the
20 photodegradation of NO_x and/or VOC. More precisely, the use of composite particles is provided according to the first aspect of the present invention for the photodegradation of organic pollutants and/or odours (and/or NO_x and/or VOC).

25 In accordance with a ninth aspect of the present invention, the use of composite particles is provided according to the first aspect of the present invention as an antibacterial.

In accordance with a tenth aspect of the present invention,
30 the use of composite particles is provided according to the first aspect of the present invention for anti-pollution.

Further characteristics of the present invention will become evident from the following description of a merely
35 illustrative non-limiting example.

Example 1

This example discloses the procedure for the production of microparticles of TiO_2 supporting silver-based nanoparticles (treated particles).

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3 grams of TiO_2 powder (Kronos 1077 - microparticles of TiO_2 with mean diameter between 0.1 and 1 μm) were wetted with 10 ml of acetone to remove the surface dirt and free the pores of the oxide.

10

0.42 g of AgNO_3 (Fluka with 99% purity) were dissolved in 5 ml of water. The solution thus obtained was added to the TiO_2 powder and placed in a flask connected to a rotavapor. In the rotavapor the mixture of the powder and the solution was kept under gentle stirring for approximately 24 hours at approximately 40°C. Subsequently, the wet powder obtained was dried in a stove at approximately 90°C for approximately 24 hours and then calcined for approximately 2 hours at approximately 400-450°C.

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Figure 1 illustrates HR-TEM photographs of the treated particles obtained.

The powders were also characterised by means of the following techniques:

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- i) XRD for verification of the crystallographic phases
- ii) FTIR (Fourier transform infrared spectroscopy) for verification of the OH groups on the surface
- iii) XPS for verification of the OH groups on the surface
- iv) UV-vis for determination of the band gap with data processing according to the Kubelka-Moon model
- v) By means of ICP/OES with a Perkin Elmer Optima 8300 instrument, it was verified that the percentage of silver on the microparticles of titanium oxide was approximately 8% by weight.

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Example 2

This example reports unsuccessful attempts made before identifying the procedure described in example 1.

5 Before identifying the procedure as per example 1, various attempts were made that did not produce satisfactory results.

Initially, an attempt was made to use nanoparticles in a colloidal solution which was then brought into contact with
10 microparticles of TiO_2 .

For example a test was performed using the following combination of compounds: Ag colloidal + CTAB (Cetyl trimethylammonium bromide).

15

Silver nanoparticles were then prepared in situ using base combinations of the following type: AgNO_3 + CTAB or colloidal Ag + AgNO_3 + CTAB.

20 In these cases, the CTAB acted not only as a stabilizer of the colloid but probably also as an active component in reduction of the silver ion (as described, for example, in "Synthesis of CTAB-IPA reduced copper nanoparticles *Materials Chemistry and Physics*", Volume 91, Issue 2, Pages 507-512, Anjali A.
25 Athawale, Prachi P. Katre, Manmohan Kumar, Megha B. Majumdar; and "A simple way of preparing high-concentration and high-purity nano copper colloid for conductive ink in inkjet printing technology", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Volume 360, Issue 1, Pages 99-104,
30 Xiao-Feng Tang, Zhen-Guo Yang, Wei-Jiang Wang). The procedure used entails mixing at ambient temperature for approximately 24 hours and then treatment in a vacuum to evaporate the solvent used. The result was then treated in an oven at 100°C for approximately 20 hours.

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In this context, the following combinations were used, for

example:

- $\text{AgNO}_3 + \text{CTAB} + \text{CuSO}_4 + \text{NH}_3$ (both at ambient temperature and at high temperature)
- $\text{AgNO}_3 + \text{Glucose} + \text{CTAB} + \text{NH}_3$

5 Other reducing agents were also tested (like ascorbic acid) and other precursors (like AgCl), for example according to the combination:

- $\text{AgCl} + \text{NH}_4\text{OH} \rightarrow \text{Ag}(\text{NH}_3)_2 + \text{CTAB} + \text{reducing agent}$

The following combination was also tested:

- 10 • $\text{AgNO}_3 + \text{NH}_3 + \text{NaOH} + \text{NaCl}$

The combinations described above were first prepared by mixing together the different components (in order to obtain/stabilize suspensions of silver nanoparticles).

15

At this point, said combinations were placed in contact with microparticles of TiO_2 .

None of the above produced interesting results. In other words, the powders obtained (mainly white and not grey) showed much worse properties than the particles obtained in example 1.

Example 3

25 This example reports the procedure for the production of tiles using the treated particles obtained according to example 1.

The tiles were prepared as follows:

- Brushing and washing finished surface tiles with water to remove surface dirt

30 - Drying in a dryer

- Application on a tile surface, by means of airless sprayer, of a TiO_2 -based formulation (TiO_2 microparticles supporting silver-based nanoparticles obtained according to example 1), water and a commercial dispersing agent with the

35 following composition:

polysaccharide with high molecular weight 11.55 %

(xanthan gum)

quartz	11.55 %
sodium ion	30.50 %
chloride ion	46.40 %

5 100 litres of the formulation were obtained by mixing 85 l of water, 15 l of the dispersing agent and 2 kg of microparticles of TiO_2 supporting silver-based nanoparticles obtained according to example 1.

10 Approximately 0.8 g of formulation were spray-applied over one square metre of tiles.

The tiles thus obtained underwent the following successive treatments.

- 15 - Oven baking at 680°C with a cycle of approximately 80 min cold-cold (in particular, the cycle entails bringing the tiles from ambient temperature to 680°C in a time of 40 minutes; once this temperature has been reached, the tiles are cooled so as to again reach ambient temperature in a further 40
- 20 minutes);
- Washing with water and detergent and mechanical brushing to remove the TiO_2 not firmly adhered to the surface of the tiles;
- Drying under compressed air;
- 25 - Quality control;
- Storage.

The tiles were characterised by means of high resolution SEM-field emission.

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Example 4

This example reports experimental tests relative to the activity on VOC (Volatile Organic Compounds) of the treated particles obtained according to example 1.

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The experimental procedure reported in C.L. Bianchi, S. Gatto,

C. Pirola, A. Naldoni, A. Di Michele, G. Cerrato, V. Crocellà, V. Capucci, "Photocatalytic degradation of acetone, acetaldehyde and toluene in gas-phase: comparison between nano and micro-sized TiO₂", Applied Catalysis B: Env., 146 (2014)

5 123-130 was followed. The experimental parameters used were:

400 ppm of pure pollutant mixed in synthetic air

UV-A lamp at 30W/m²

Controlled humidity

Test duration: max 2 hours

10 VOC used: acetone, acetaldehyde, ethanol, toluene.

The results obtained are reported in the following tables 1 and 2, in which K_{tq} indicates simple TiO₂ powder (Kronos 1077) and K_{Ag} indicates the treated particles obtained according to example 1.

Table 1

UV	ACETONE		ACETALDEHYDE		ETHANOL	
Time (min)	K _{tq}	K _{Ag}	K _{tq}	K _{Ag}	K _{tq}	K _{Ag}
0	0	0	0	0	0	0
30	45	52	84	90	68	89
60	87	88	98	100	97	100
90	100	100	100	100	100	100
120	100	100	100	100	100	100

The table reports the degradation % values. It can be observed that the sample doped with Ag surprisingly shows a constantly higher photocatalytic efficiency with respect to the non-doped sample.

The toluene molecule was tested in the same conditions as those above, but with kinetics having an overall duration of 6 hours, given the complexity of the organic molecule to be degraded. The results (degradation % values) are reported in the following table:

Table 2

TOLUENE	K _{tq}	K _{Ag}
Time (min)		

0	0	0
60	18	42
120	26	56
180	32	65
240	38	70
300	42	80
360	46	85

Also in this case, even without reaching complete degradation, the doping with Ag surprisingly improves the photodegradation efficiency of the toluene.

5 Further tests were performed using the following experimental parameters:

400 ppm of pure pollutant mixed in synthetic air

Flat LED lamp at 4000 K (UV-A a 0W/m²)

Controlled humidity

10 Test duration: 4 hours

VOC used: acetone, acetaldehyde, ethanol, toluene

The results obtained (degradation % values) are reported in the following tables 3 and 4, in which K_{tq} indicates simple
15 TiO₂ powder (Kronos 1077) and K_{Ag} indicates the treated particles obtained according to example 1.

Table 3

LED	ACETONE		ACETALDEHYDE		ETHANOL	
Time (min)	K _{tq}	K _{Ag}	K _{tq}	K _{Ag}	K _{tq}	K _{Ag}
0	0	0	0	0	0	0
90	0	15	0	18	0	21
180	0	17	0	20	0	24
240	0	20	0	22	0	27

The sample K_{tq} does not show photocatalytic efficiency under LED illumination.

20

On the contrary, the Ag doped sample surprisingly shows a good activity if irradiated in the visible range also considering

the high concentration at which the powders are tested (much higher concentration with respect to a hypothetical ambient pollution with said molecules).

Table 4

TOLUENE	Ktq	K_Ag
Time (min)		
0	0	0
60	0	2
120	0	5
180	0	7
240	0	11
300	0	13
360	0	15

5 Also in the case of the toluene, the use of K_Ag provides a fairly good result, taking into account that the Ktq does not lead to any photodegradation, as already seen also with the other VOC.

10 In relation to the results obtained, it can be noted that the improvements obtained were not predictable. The known antibacterial activity of the Ag could not have predicted in any way the strong improvement in the photodegradation results observed experimentally.

15

Example 5

This example reports experimental tests relative to the activity on NO_x of the treated particles obtained according to example 1.

20

We followed the experimental procedure reported in vi. C.L. Bianchi, C. Pirola, F. Galli, G. Cerrato, S. Morandi, V. Capucci, "Pigmentary TiO₂: a challenge for its use as photocatalyst in NO_x air purification", Chemical Eng J, 261, (2015) 76-82. The experimental parameters used were:

25

1 ppm of pure pollutant mixed in synthetic air
UV-A lamp at 10W/m²

Controlled humidity

Test duration: 2 hours

5 The results obtained (degradation % values) are reported in the following table 5 in which Ktq indicates simple TiO₂ powder (Kronos 1077) and K_Ag indicates the treated particles obtained according to example 1.

Table 5

NOx	Ktq	K_Ag
Time (min)		
0	0	0
60	80	89
120	87	96

10 The presence of the Ag once again improves the performance also for degradation of the NOx.

Further tests were performed using the following experimental parameters:

1 ppm of pure pollutant mixed in synthetic air

Flat LED lamp at 4000K (UV-A at 0W/m²)

15 Controlled humidity

Test duration: 2 hours

20 The results obtained (degradation % values) are reported in the following table 6 in which Ktq indicates simple TiO₂ powder (Kronos 1077) and K_Ag indicates the treated particles obtained according to example 1.

Table 6

NOx	Ktq	K_Ag
Time (min)		
0	0	0
120	4	48

25 The difference in the photocatalytic efficiency when the samples are irradiated in the visible range is very impressive. After 2 hours the sample doped with Ag has degraded almost 50% of the pollutant present, while the Ktq sample shows a barely perceptible photocatalytic activity.

Also in these cases, it can be noted that the improvements obtained were not predictable. The known antibacterial activity of the Ag could not have predicted in any way the strong improvement in the photodegradation results experimentally observed.

Example 6

This example reports experimental tests relative to the activity of the treated tiles obtained according to example 3.

Unfortunately there are no laws and/or parameters to refer to for performing tests that allow accurate evaluation of the activity of ceramic materials in the visible range and, in experimental terms, it has been seen that it is not possible to use the same parameters as those used in examples 4 and 5 since an extremely low quantity of TiO_2 powder is present on the tiles, not comparable with that present in the reactors for the tests on the powders.

For this reason we are still at the stage of optimizing the parameters to be used for the tests, modifying those used for the tests on powders.

Two parameters in particular are subject to modification: initial quantity of NO_x (dropping from 1 ppm to 0.5 ppm) and test duration (2 to 6 hours).

In the same way for the tests with the VOC, the quantities of pollutants were reduced from 400 to 200 ppm.

It is observed that, in both the cases, both for the NO_x and for the VOC, the concentrations of the polluting molecules are such as to be always much higher than the values of the atmospheric pollution.

For the tests on the NO_x the following parameters were used:

0.5 ppm of pure pollutant mixed in synthetic air

Flat LED lamp at 4000K (UV-A at 0W/m²)

Controlled humidity

5 Test duration: 6 hours

The results obtained (degradation % values) are reported in the following table 7 in which K_{tq} indicates tiles on the surface of which simple TiO₂ powder (Kronos 1077) has been deposited and K_{Ag} indicates tiles on the surface of which the treated particles obtained according to example 3 have been deposited.

Table 7

NO _x	K _{tq}	K _{Ag}
Time (min)		
0	0	0
360	0	19

For the tests on the VOC the following parameters were used:

15 200 ppm of pure acetaldehyde mixed in synthetic air

Flat LED lamp at 4000K (UV-A at 0W/m²)

Controlled humidity

Test duration: 6 hours

20 The results obtained (degradation % values) are reported in the following table 8 in which K_{tq} indicates tiles on the surface of which simple TiO₂ powder (Kronos 1077) has been deposited and K_{Ag} indicates tiles on the surface of which the treated particles obtained according to example 3 have been deposited.

Table 8

NO _x	K _{tq}	K _{Ag}
Time (min)		
0	0	0
360	0	12

It is observed that also as regards the tiles, the results obtained are absolutely surprising, since it was not in any

way possible to hypothesise beforehand an improvement in the photodegradation properties following the addition of silver (so far known only for its antibacterial characteristics).

5 **Example 7**

This example reports experimental tests relative to the antibacterial activity of the particles obtained according to example 1.

10 According to the procedure established by the ISO 27447:2009 standard, the antibacterial activity is tested both with UV-A lamp and LED lamp.

According to the procedure established by the ISO 22196:2009
15 standard, the antibacterial activity is tested in the dark.
Also in this case the results are positive.

CLAIMS

1.- A process to produce composite particles; the process comprises a loading step, during which silver-based
5 nanoparticles are obtained bound to outer surfaces of microparticles of TiO_2 so as to obtain said composite particles; said loading step comprising, in turn, a mixing sub-step, a drying sub-step and a heating sub-step, which is at least partially subsequent to the drying sub-step; during
10 the mixing sub-step, a solution containing silver ions and the microparticles of TiO_2 is kept under stirring so as to obtain an intermediate mixture; during the drying sub-step, the water content of the intermediate mixture is reduced (in particular, the intermediate mixture is dried) by supplying heat to the
15 intermediate mixture itself; during the heating sub-step, said intermediate mixture is kept at a temperature higher than 300°C for at least 30 minutes; the silver-based nanoparticles being selected from the group consisting of: silver nanoparticles, silver oxide nanoparticles and a combination
20 thereof; the microparticles of TiO_2 having a mean diameter from $0.1\ \mu\text{m}$ to $1\ \mu\text{m}$.

2.- The process according to claim 1, wherein the silver-based nanoparticles comprise nanoparticles of a combination of
25 silver and silver oxide.

3.- The process according to claim 1 or 2, wherein the mixing sub-step lasts at least 18 hours at a temperature ranging from 30°C to 50°C ; during the drying sub-step the intermediate
30 mixture is kept at a temperature higher than 80°C (in particular, higher than 85°C) and lower than 150°C (in particular, lower than 110°C) for at least 10 hours (in particular, up to 35 hours); during the heating sub-step, said intermediate mixture is kept at a temperature from 350°C to
35 600°C for a time ranging from 40 minutes to 150 minutes; the solution has 3% to 12% by weight of the silver ions with

respect to the sum of the weights of the silver ions and the microparticles of TiO₂.

4.- The process according to one of the preceding claims,
5 wherein the microparticles of TiO₂ have a mean diameter from 0.1 µm to 0.5 µm (in particular, measured by means of XRD); at least 98% (in particular, at least 99.5%) by weight of the microparticles of TiO₂, with respect to the overall weight, are of anatase; the composite particles have a mean diameter
10 from 0.1 µm to 0.5 µm.

5.- The process according to one of the preceding claims and comprising a sonication step, which is at least partially prior to the loading step and during which the microparticles
15 of TiO₂ are sonicated in a liquid.

6.- The process according to one of the preceding claims and comprising a wetting step, which is at least partially prior to the loading step and during which the microparticles of
20 TiO₂ are wetted with an organic solvent.

7.- The process according to one of the preceding claims, wherein the mixing sub-step, the drying sub-step and the heating sub-step are carried out in the absence of a reducing
25 agent.

8.- The process according to one of the preceding claims, wherein the mixing sub-step and the drying sub-step are carried out in the absence of an emulsifying agent, in
30 particular an organic compound.

9.- The process according to one of the preceding claims, wherein the silver-based nanoparticles comprise silver nanoparticles.
35

10.- Composite particles, each of which comprises a respective

microparticle of TiO_2 and a plurality of respective silver-based nanoparticles supported by the relative microparticle of TiO_2 ; in particular, each microparticle of TiO_2 has a respective outer surface; the silver-based nanoparticles are bound to said outer surface and exposed towards the outside and are selected from the group consisting of: silver nanoparticles, silver oxide nanoparticles and a combination thereof; the microparticles of TiO_2 have a mean diameter ranging from $0.1\ \mu\text{m}$ to $1\ \mu\text{m}$.

10

11.- Particles according to claim 10, wherein the silver-based nanoparticles comprise nanoparticles of a combination of silver and silver oxide.

12.- Particles according to claim 10 or 11, which are obtained (or obtainable) with the process according to any one of the preceding claims.

13.- Particles according to one of claims from 10 to 12, comprising 3 to 12% by weight of the silver-based nanoparticles with respect to the sum of the weights of the silver-based nanoparticles and of the microparticles of TiO_2 .

14.- Particles according to one of claims from 10 to 13, wherein the microparticles of TiO_2 have a mean diameter from $0.1\ \mu\text{m}$ to $0.5\ \mu\text{m}$ (in particular, measured by means of XRD), the silver-based nanoparticles have a mean diameter from 1 nm to 20 nm (in particular, measured by means of TEM); the composite particles have a mean diameter from $0.1\ \mu\text{m}$ to $0.5\ \mu\text{m}$ (in particular, measured by means of XRD).

15.- Particles according to one of claims from 10 to 14, wherein at least 98% (in particular, at least 99.5%) by weight of the microparticles of TiO_2 , with respect to the overall weight of the microparticles of TiO_2 , are of anatase.

16.- Particles according to one of claims from 10 to 15, wherein the silver-based nanoparticles comprise, in particular are, nanoparticles of silver and silver oxide.

5 17.- A method for the production of a treated article; the method comprises an application step, during which composite particles according to one of claims from 9 to 13 are applied on a surface of a base product, in particular a ceramic tile; each composite particle comprises a respective microparticle
10 of TiO_2 and a plurality of respective silver-based nanoparticles supported by the relative microparticle of TiO_2 ; the silver-based nanoparticles are 3% to 12% by weight with respect to the overall weight of the microparticles of TiO_2 and of the silver-based nanoparticles.

15 18.- The method according to claim 17, wherein the microparticles of TiO_2 have a mean diameter from 0.1 μm to 0.5 μm (in particular, measured by means of XRD), the silver-based nanoparticles have a mean diameter from 1 nm to 20 nm (in
20 particular, measured by means of TEM); at least 98% (in particular, at least 99.5%) by weight of the microparticles of TiO_2 with respect to the overall weight of the microparticles of TiO_2 are of anatase; the composite particles have a mean diameter from 0.1 μm to 0.5 μm (in particular, measured by
25 means of XRD).

19.- The method according to claim 17 or 18, and comprising a baking step, which is at least partially subsequent to the application step and during which the base product on which
30 the composite particles have been applied is treated at a temperature from 400°C to 780°C.

20.- The method according to one of claims from 17 to 19, wherein said composite particles have a surface area (in
35 particular, measured by means of BET) from 5 m^2/g to 30 m^2/g .

21.- The method according to one of claims from 17 to 20, wherein, during the application step, from 0.6 g to 1.3 g of composite particles are applied per square metre of said surface of the base product.

5

22.- The method according to one of claims from 17 to 21, wherein the composite particles are applied in a suspension comprising from 70% to 90% by volume of water with respect to the overall volume of the suspension and, in particular, from
10 10% to 20% by volume of a dispersing agent with respect to the overall volume of the suspension, which in turn comprises from 25% to 35% by weight of sodium ion with respect to the overall weight of the dispersing agent, and from 7% to 16% by weight of silica with respect to the overall weight of the dispersing
15 agent (more precisely, quartz).

23.- The method according to one of claims from 17 to 22, wherein the microparticles of TiO_2 have respective outer surfaces; the method comprises a loading step, during which
20 the silver-based nanoparticles are obtained bound to the outer surfaces so as to obtain said composite particles; said step comprises in turn a mixing sub-step, a drying sub-step and a heating sub-step, at least partially subsequent to the drying step; during the mixing sub-step, a solution containing silver
25 ions and the microparticles of TiO_2 is kept under stirring (in particular, at a temperature from 30°C to 50°C) so as to obtain an intermediate mixture; during the drying sub-step, the intermediate mixture is kept at a temperature higher than 80°C (in particular, higher than 85°C) and lower than 150°C
30 (in particular, lower than 110°C); during the heating sub-step, said intermediate mixture is kept at a temperature higher than 300°C (in particular, from 350°C to 600°C).

24.- A method according to claim 23, wherein, during the
35 drying sub-step the intermediate mixture is kept at a temperature higher than 80°C (in particular, higher than 85°C)

and lower than 150°C (in particular, lower than 110°C) for at least 10 hours (in particular, up to 35 hours); during the heating sub-step, said intermediate mixture is kept at a temperature higher than 300°C (in particular, from 350°C to 5 600°C) for at least 30 minutes (in particular, from 40 minutes to 80 minutes).

25.- A treated article obtained (or obtainable) with a method according to one of claims from 17 to 24.

10

26.- An article according to claim 25, and comprising composite particles arranged on the surface of the article; in particular, the article has from 0.6 g to 1.3 g of composite particles per square metre of said surface.

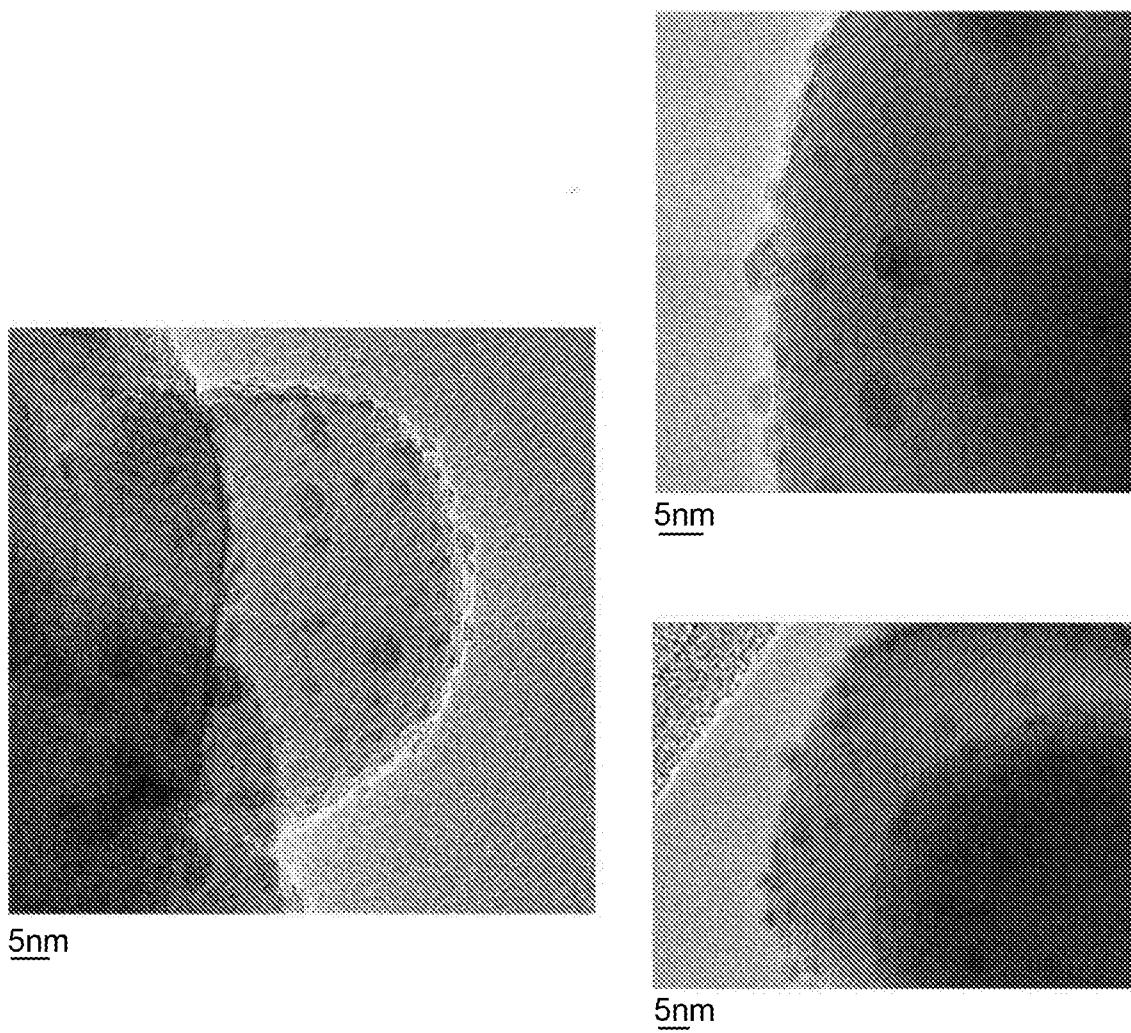


FIG.1

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2016/051886

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01G23/047 C01G23/08 C01G5/00
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)
C01G

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 102 764 649 B (UNIV SHAANXI SCIENCE & TECH) 11 June 2014 (2014-06-11)	1,10
Y	page 5, paragraph [0034] - page 6; example 3 page 4, paragraph [0011] page 5, paragraph [0023] -----	1-26
Y	JP H08 99812 A (KAWAZUMI GIJUTSU KENKYUSHO KK) 16 April 1996 (1996-04-16) page 4, paragraph [0018]; example 1 -----	1-26
Y	DE 101 31 173 A1 (ITN NANOVAION GMBH [DE]) 16 January 2003 (2003-01-16) column 4; example 2 ----- -/-	1-26



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2004/052998 A1 (ITN NANOVAION GMBH [DE]; NONNINGER RALPH [DE]; SCHICHTEL MARTIN [DE]) 24 June 2004 (2004-06-24) page 11; example 1 -----	1-26
Y	JP 2001 038222 A (DAIDO STEEL CO LTD) 13 February 2001 (2001-02-13) page 5, column 1, paragraph [0026] - page 5, column 2, paragraph [0027] -----	1-26
Y	KIM K D ET AL: "Formation and characterization of Ag-deposited TiO ₂ nanoparticles by chemical reduction method", SCRIPTA MATERIALIA, ELSEVIER, AMSTERDAM, NL, vol. 54, no. 2, 1 January 2006 (2006-01-01), pages 143-146, XP025027934, ISSN: 1359-6462, DOI: 10.1016/J.SCRIPTAMAT.2005.09.054 [retrieved on 2006-01-01] page 144, column 2, paragraph 3 page 145, column 2, last line -----	1-26
Y	DASTJERDI R ET AL: "A review on the application of inorganic nano-structured materials in the modification of textiles: Focus on anti-microbial properties", COLLOIDS AND SURFACES. B, BIOINTERFACES, ELSEVIER, AMSTERDAM, NL, vol. 79, no. 1, 1 August 2010 (2010-08-01), pages 5-18, XP027053807, ISSN: 0927-7765 [retrieved on 2010-05-18] page 7, column 1, paragraph 2.1.1.1 - page 7, column 2, paragraph 1 -----	1-26
Y	ZHANG YUN ET AL: "Study of Nano-Ag Particles Doped TiO ₂ Prepared by Photocatalysis", JOURNAL OF NANOSCIENCE AND NANOTECHNOLOGY, AMERICAN SCIENTIFIC PUBLISHERS, US, vol. 9, no. 6, 1 June 2009 (2009-06-01), pages 3904-3908, XP009187313, ISSN: 1533-4880 page 3906, column 2, paragraph 1 - page 3907, column 2, paragraph 2 -----	1-26

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2016/051886

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 102764649	B	11-06-2014	NONE
JP H0899812	A	16-04-1996	NONE
DE 10131173	A1	16-01-2003	NONE
WO 2004052998	A1	24-06-2004	AU 2002361032 A1 30-06-2004
			EP 1576060 A1 21-09-2005
			JP 2006508793 A 16-03-2006
			US 2006210636 A1 21-09-2006
			WO 2004052998 A1 24-06-2004
JP 2001038222	A	13-02-2001	NONE