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(54) **PHOTOCATALYTIC AND INFRARED-EMITTING CERAMIC POWDER APPLICABLE TO TEXTILE FIBRES AND METHOD FOR PRODUCING SAID POWDER**

(57) The invention relates to a photocatalytic and infrared-emitting ceramic powder applicable to textile fibers, and to a method for producing said powder, said powder consisting of a micrometric or nanometric mixture of variable amounts of alumina, silica, zircon and titanium oxide, in proportions between 1 and 80%, and with a particle size less than 20 microns, preferably less than 5 microns. The production method comprises dry grinding or wet grinding systems provided with jet grinders or attrition grinders.

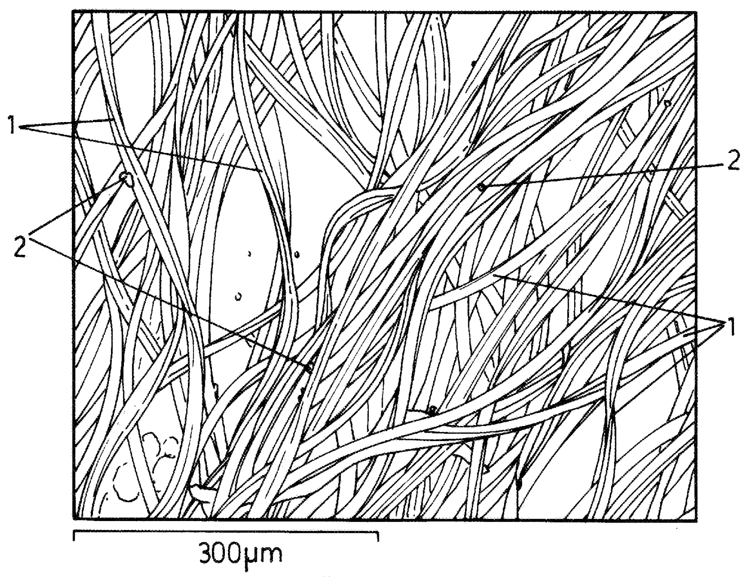

FIG.1

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Description

Object of the Invention

[0001] As expressed by the title of the present specification, the invention relates to a photocatalytic and infrared-emitting ceramic powder applicable to textile fibers and to the method for producing said powder.

[0002] The object of the invention more particularly relates to a composition which, consisting of a mixture of alumina, silica, zircon and titanium oxide, makes up a micrometric or nanometric ceramic powder with photocatalytic capability when it is excited by light and for emitting in the far infrared region when heated, being susceptible to being incorporated in natural or synthetic textile fibers and therefore in fabrics to provide them with additional properties, for example bactericidal properties.

[0003] In parallel, a second aspect of the invention relates to the method for producing said ceramic powder from the mixture of the elements making it up and which can be found in variable amounts.

Field of Application of the Invention

[0004] The field of application of the present invention is simultaneously comprised within the chemical sector and the textile sector, primarily concerning the industry dedicated to producing natural or synthetic textile fibers and which can in turn be woven for producing fabrics, alone or mixed with others.

Background of the Invention

[0005] Patent document JP63274660, filed in 1988, relates to a ceramic mixture designed to improve the efficiency of driers and heaters. Said powder consisted of a mixture of mineral oxides such as alumina, silica, titania and zircon, and was doped with small amounts of colloidal sized platinum and palladium particles. This powder could be consolidated and formed using a conventional calcium aluminate cement.

[0006] After 1990 a series of patents emerged which, using powder mixtures such as the one described in the mentioned patent, incorporate these particles in natural and artificial fabrics to improve some properties thereof, such as comfort, thermal insulation, infrared emission, and some biological properties, such as muscle performance.

[0007] Patent document EP0462275B1 (1990), relating to a "Powder which radiates feeble-energy infrared rays, synthetic fiber containing the same, and textile products produced therefrom" can be mentioned among said patents. The patent describes a powder mixture of alumina and pure titanium, sometimes with other components such as silicon carbide, with finely divided metallic platinum and/or palladium additives. According to said patent, said mixture would show infrared activity. It also claims synthetic fibers loaded with this powder, and the textiles produced with them.

[0008] Patent document JP19920213557/US199403004307 (1995), relating to a "Far infrared radiant composite fiber containing metal", claims fabrics produced with synthetic fibers including platinum and at least one metal oxide of the metals aluminum, silicon and titanium, with the property of emitting infrared radiation when contacted with the human body.

[0009] Another case to cite is patent document EP 1291405B1 (2006), relating to a "Composition for far infrared irradiation with excellent antistatic property and fiber and textile product both containing the same". It claims a composition with antistatic properties, bactericidal properties and infrared radioactive properties, containing in all the possible proportions: a) alumina; b) at least one of the oxides TiO_2 and SiO_2; c) at least one element or compound of the following: platinum, a platinum compound, palladium, a palladium compound, iridium, an iridium compound, rhodium, or a rhodium compound; d) at least one of the following components: silver or a silver compound. The claims also include producing fibers, fabrics, and packaging material containing such compositions.

[0010] Finally, patent document US415532P/ES2341765 (2010): "Method for enhancing muscle performance" has a single claim for a method for enhancing muscle performance, consisting of wearing a given type of textile material, and not a method for producing same, or a specific mineral composition. The mentioned compositions are generic compositions (titanium dioxide, alumina, silicon oxides), and are covered by the earlier patents mentioned above.

[0011] However, at least the applicant is unaware of a powder having photocatalytic activity, susceptible to being loaded in textile fibers and fabrics, capable of eliminating contaminants, odor-causing molecules, nitrogen oxides, etc., having been described.

[0012] On the other hand, it is known that a number of applications of the photocatalytic properties of titanium oxide TiO_2 have emerged in the last 10 years. When titanium dioxide is exposed to light containing UV rays, air-purifying properties, self-cleaning properties and antimicrobial properties can be spontaneously and simultaneously generated on the surface of the material containing it.

[0013] That is because titanium dioxide is a photocatalytic material having an electronic structure made up of two bands, the valence band (full of electrons) and the conduction band (no electrons). The energy difference between the conduction band and the valence band is referred to as the forbidden band, and when a photon with energy exceeding said band comes into direct contact with this photocatalytic material, an electron (e-) of the valence band moves to the conduction band, thereby leaving an electron vacancy (h+). Some of the photoexcited, electron-vacant pairs are diffused towards the surface of the photocatalytic material, where they are retained to participate in chemical reactions with oxygen and water molecules present in the environment.

[0014] The electron vacancies (h+) can react with adsorbed donor molecules such as water molecules to produce hydroxyl radicals (highly reactive).

[0015] Acting as an electron acceptor, the oxygen present in air can react with electrons to form superoxide radical anions (0_2-). The hydroxyl radicals (oxidizers) and the superoxide radical anions (reducers) generated on the surface of TiO_2 have demonstrated enormous capability of degrading different types of microorganisms, almost all types of organic contaminants and other inorganic compounds such as NOx and SO_2 (Maury, A. et al.; Mat. Construcción, 60(298), 33-50. 2010).

[0016] Generally, the fast rate of degradation of the compounds is a function of light absorption, transport of the photogenerated charges (e- and h+) to the surface, recombination of e- and h+, reaction of e- and h+, on the surface of the photocatalyst, mass transfer of the reactants and the characteristics of the particles, in relation to both structural characteristics and morphological characteristics.

[0017] Titanium dioxide can crystallize into three types of crystalline structures which are: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Of these three crystalline forms of TiO_2, rutile is the most stable, because anatase and brookite are transformed into rutile under heating. Brookite has no significant photocatalytic activity when it is used with visible light. Rutile, in turn, has the smallest forbidden band, 3.0 eV (equivalent to 413 nm in wavelength), whereas anatase has the largest forbidden band, 3.2 eV (388 nm). Both forbidden bands are close to the border wavelength between the long UV wavelength (315- 400) and visible light (400-700). When long UV wavelengths coming only from visible light were used, a considerable reduction in the photocatalytic activity of TiO_2 was observed. Therefore, many efforts were made to reduce the magnitude of the forbidden band and to allow the photocatalytic effect of TiO_2 to be produced with visible light. Highlighted among these strategies is the use of metal doping (iron and wolfram) and non-metal doping (carbon, nitrogen and sulfur) in TiO_2 (Milani, R.; et al.; SASBE 3rd International Conference Proceedings. 2009).

[0018] Despite the described background documents, relating to the present invention, no patent or invention having the technical, structural and constitutive features of the ceramic powder herein proposed as claimed has been found.

Brief Description of the Invention

[0019] The invention relates to a micrometric or nanometric ceramic powder having photocatalytic activity when it is excited by light and which is made up of a mixture of alumina, silica, zircon and titanium oxide in variable amounts. Furthermore, a secondary property of this ceramic powder is the capability of emitting electromagnetic radiation in the far infrared region when it is heated.

[0020] The percentages of the different components are in proportions ranging between 1 and 80%, 100% being the sum total thereof.

[0021] The method for producing said powder comprises the mixture of ceramic powder which is ground to sizes less than 20 microns, in any of the conventional dry or wet industrial or laboratory grinding devices.

[0022] The powder mixture is then incorporated to natural or synthetic textile fibers, either in mass or in the form of a surface coating, by conventional methods in the textile industry.

[0023] Fibers loaded with the ceramic powders are woven by hand or in mechanical weaving machines for producing fabrics, cords, nets, etc.

Description of the Drawings

[0024]

Figure 1 shows the representation of a microscopic view of fibers loaded with the ceramic powder of the invention.

Figure 2 shows a graph of the x-ray fluorescence spectrum of a sample of the ceramic powder object of the invention, where its main chemical components are observed.

Detailed Description of the Invention

[0025] Specifically, as previously described the invention relates to a ceramic powder susceptible to being used as a filler in natural or artificial textile fibers made up of a mixture of two types of minerals: a first type, consisting of alumina (Al_2O_3), silica (quartz, SiO_2), and zircon (SiO_4Zr), the main feature of which is its stability and refractoriness, and according to the mentioned literature, its capability of emitting in the far infrared region when these compounds are heated. The other fundamental component is titanium oxide, TiO_2, in the form of anatase or rutile, with a strong photocatalytic capability, as explained in the background of this invention. This photocatalytic activity has bactericidal, anticontaminant and anti-odor effects.

[0026] The invention also describes the method for preparing the mixture of components and the use thereof in loading fibers and fabrics.

[0027] More specifically, the components of the ceramic powder are as follows:

Silica, silicon oxide, and more specifically SiO_2.-Quartz, alpha-SiO_2, which is a low-temperature silica polymorph, is used. It is one of the most abundant minerals in the earth's crust and is obtained with very high purities for the glass industry, ceramic industry, refractory industry, etc.

[0028] Its properties are: hardness: 7; specific weight:

2.65 g/cc; streak: white; fracture: conchoidal; no exfoliation; rhombohedral system; vitreous luster; hexagonal shape; belongs to the family of silicates (tectosilicates); pyroelectric and piezoelectric.

[0029] Alumina, corundum - Its chemical formula is alpha- Al_2O_3. It is very stable and melts at a very high temperature (2020°C). It has great chemical inertia. Its monocrystalline form is the sapphire. It is the main raw material in advanced ceramics and refractories.

[0030] Properties: hardness: 9; specific weight: 4.0 g/cc; streak: white; fracture: conchoidal; no exfoliation; trigonal system; vitreous luster; hexagonal shape, in tablets or prisms.

[0031] Zircon, zirconium silicate, specifically SiO_4Zr.- This is a refractory compound with a very high melting point (2400°C). It contains small amounts of hafnium and is sometimes weakly radioactive. It is used in refractories, advanced ceramics, as precious stone, in insulating fibers, etc.

[0032] Properties: hardness: 7.5; specific weight: 4.07 g/cc; streak: white; fracture: conchoidal; no exfoliation; tetragonal system; vitreous luster; tablet or prismatic form; belongs to the family of silicates; fluorescent under ultraviolet light.

[0033] The mixture of these components has the capability of emitting radiation in the far infrared region when heated at a low temperature. This property is inherent to the composition and structure of the components, and is sufficiently described in the literature.

[0034] Titania, titanium oxide, specifically TiO_2.- It is presented in three polymorphic forms: brookite, anatase and rutile. Anatase and rutile have photocatalytic activity. They are used in paints, coatings, enamels, etc.

[0035] Properties of the anatase form: hardness: 5.5; specific weight: 3.9 g/cc; streak: white; fracture: subconchoidal; crystalline system: tetragonal; shape: bipyramidal masses; special properties: photocatalytic activity.

[0036] Properties of the rutile form: hardness: 6.5; specific weight: 4.25 g/cc; streak: white; fracture: conchoidal; crystalline system: tetragonal; shape: short prisms, needles, twin crystals; special properties: photocatalytic activity.

[0037] It should be pointed out that micrometric or nanometric ceramic powder is understood in the present invention as a mixture of the mentioned mineral components in variable proportions, and for producing same, said components are subjected to a mixing and subsequent grinding process assuring the final fineness of the mixture.

[0038] It is important to point out that the particle size of the final powder must be less than 20 microns, and preferably less than 5 microns, with an important fraction below the micron. This size is achieved by using grinding systems well proven in the industry, fundamentally jet grinders or attrition grinders. In any case, the effectiveness of the powder will be greater the larger the specific surface and therefore, the smaller the particle size thereof.

[0039] Likewise, in the present invention loading the textile fibers is understood as the process by means of which the ceramic powder is added or incorporated to the mass or to the surface of the fibers, which can be done in two different processes:

a) mass incorporation of the powder into the polymer during the spinning process by mixing suitable amounts thereof to the polymer pellet; or

b) coating the surface of the fibers with the mineral powder, working under hot conditions or by means of a suitable solvent, i.e., by means of a sizing process designed for this purpose.

[0040] The percentage of ceramic powder added to the fiber must be enough so that its effect is noticeable, i.e., the concentration of active elements must be enough to produce infrared emission and the photocatalytic effect sought, but this concentration cannot be so high so as to modify the fiber lightness and flexibility properties and the capability thereof of being woven.

[0041] As a result, the percentage of ceramic powder added to the fiber must be comprised between 0.5 and 5% by weight, except for special applications, in which the percentage can be higher.

[0042] Examples of the method for preparing the proposed ceramic powder according to the invention are provided below.

Example 1

[0043] This example relates to the preparation of the ceramic powder starting from raw materials existing on the market, and using standard ceramic processing laboratory equipment. The method object of the example is as follows:

- 100 grams of micronized alumina powder (purity > 98%) are weighed and transferred to a container made of an inert material, such as porcelain, glass, stainless steel, etc.
- 100 grams of quartz powder having a purity greater than 99% are weighed and added to the alumina in the container.
- 50 grams of zircon having commercial purity are then weighed and again added to the mixture.
- The powder is stirred with a spatula, and 250 milliliters of ethyl alcohol or methyl alcohol are added. It is stirred until a plastic mass is formed, which is transferred to an attrition grinder, adding 150 milliliters of distilled water. The mixture is ground in the presence of 30% stabilized zircon balls 2 mm in diameter.
- After 20 minutes of grinding, the zircon balls are separated by sieving, and the suspension of the ceramic powder is dried at a temperature less than 50°C.
- Finally, the dry powder is sieved through a sieve having a mesh opening of 75 microns and packaged for use.

Example 2

[0044] Like in Example 1, this example relates to the preparation of the ceramic powder starting from raw materials existing on the market and using standard ceramic processing laboratory equipment. The method object of Example 2 is as follows:

- 200 grams of commercial kaolinite of formula Al_2O_3, $2SiO_2$,$2H_2O$ are weighed and transferred to a container made of an inert material, such as porcelain, glass, stainless steel, etc.
- 100 grams of zircon having commercial purity are then weighed and added to the kaolinite powder.

[0045] The powder is stirred with a spatula and 300 milliliters of ethyl alcohol or methyl alcohol are added. It is stirred until a plastic mass is formed, which is transferred to an attrition grinder, adding 200 milliliters of distilled water. The mixture is ground in the presence of 30% stabilized zircon balls 2 mm in diameter.

- After 20 minutes of grinding, the zircon balls are separated by sieving, and the suspension of the ceramic powder is dried at a temperature less than 50°C.
- Finally, the dry powder is sieved through a sieve having a mesh opening of 75 microns and packaged for use.

[0046] As previously indicated, the powder mixture is intended for being incorporated to natural or synthetic textile fibers, either in mass or in the form of a surface coating, by conventional methods in the textile industry.

[0047] Figure 1 shows the representation of a micrograph of a synthetic polymer thread loaded with the ceramic powder of the invention, fibers (1) having diameters of 10.22 ± 1.36 microns and having a fairly smooth surface, as well as filler particles (2) of the ceramic powder on some points of its surface being able to be seen therein.

[0048] Figure 2 shows a graph of the x-ray fluorescence spectrum of a sample of the ceramic powder object of the invention, where its main chemical components, i.e., oxygen, silicon, aluminum, zirconium and titanium, are shown.

[0049] Having sufficiently described the nature of the present invention as well as the manner of putting it into practice, it is not considered necessary to further describe the invention so that any person skilled in the art can understand the scope thereof and the advantages derived from it, it being hereby stated that the invention can be carried out to practice within its essential features in other embodiments differing in detail from the one indicated by way of example, and such embodiments will be likewise covered by the protection which is sought provided that the fundamental principle thereof is not altered, changed or modified.

Claims

1. A photocatalytic and infrared-emitting ceramic powder applicable to textile fibers which, having photocatalytic capability when it is excited by light and for emitting in the far infrared region when heated, is **characterized by** consisting of a micrometric or nanometric mixture of variable amounts of alumina, silica, zircon and titanium oxide.

2. The photocatalytic and infrared-emitting ceramic powder applicable to textile fibers according to claim 1, **characterized in that** the percentages of alumina, silica, zircon and titanium oxide are in proportions ranging between 1 and 80%, 100% being the sum total thereof.

3. The photocatalytic and infrared-emitting ceramic powder applicable to textile fibers according to claim 1 or 2, **characterized in that** the particle size of the final powder is less than 20 microns.

4. The photocatalytic and infrared-emitting ceramic powder applicable to textile fibers according to claim 2, **characterized in that** the particle size of the final powder is less than 5 microns.

5. A method for producing ceramic powder according to the ceramic powder described in any of claims 1-4, **characterized in that** it comprises dry grinding or wet grinding systems provided with jet grinders or attrition grinders.

6. The method for producing ceramic powder according to claim 5, **characterized in that** it comprises the following steps:

- weighing the components and transferring them to a container made of an inert material, such as porcelain, glass, stainless steel, etc.;
- stirring with a spatula and adding ethyl alcohol or methyl alcohol, stirring until forming a plastic mass, which is transferred to a grinder, adding distilled water, grinding the mixture in the presence of 30% stabilized zircon balls 2 mm in diameter;
- after 20 minutes of grinding, separating the zircon balls by sieving, and drying the suspension of the ceramic powder at a temperature less than 50°C;
- finally, sieving the dry powder through a sieve having a mesh opening of 75 microns and packaging for use.

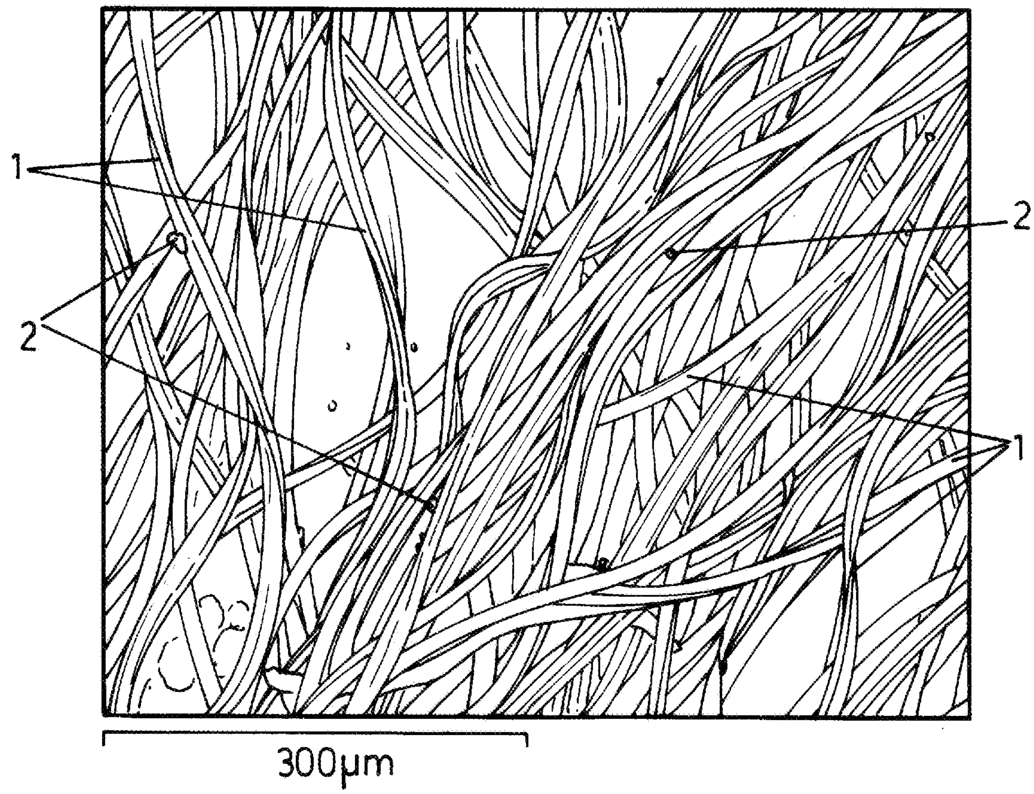

FIG.1

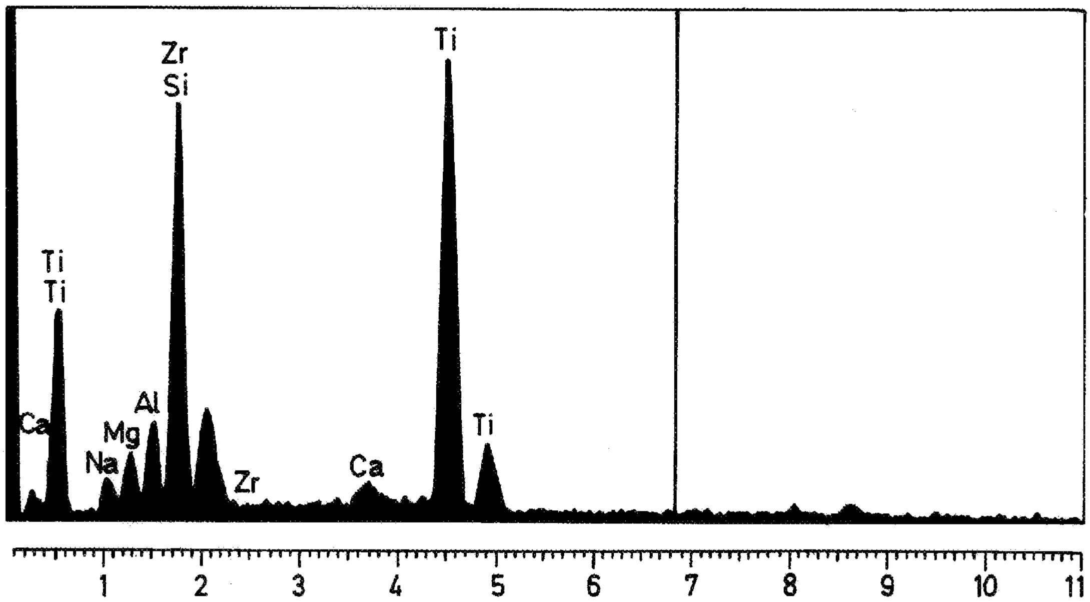

FIG.2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ES2014/070082

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)
D01F, D06M

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)

EPODOC, INVENES, WPI

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	US 4999243 A (MAEDA NOBUSHIGE) 12/03/1991, column 2, line 1 - column 3, line 65.	1-6
A	PARTHASARATHI, V. AND THILAGAVATHI, G. "Synthesis and Characterization of Titanium Dioxide Nanoparticles and their applications to textiles for microbe resistance". Journal of Textile and Apparel, Technology and Management. Volume 6, Issue 2, 2009.	1
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance.
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure use, exhibition, or other means.
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other documents , such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27/04/2014	**(29/04/2014)**
Name and mailing address of the ISA/ OFICINA ESPAÑOLA DE PATENTES Y MARCAS Paseo de la Castellana, 75 - 28071 Madrid (España) Facsimile No.: 91 349 53 04	Authorized officer B. Aragón Urueña Telephone No. 91 3493277

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/ES2014/070082

CLASSIFICATION OF SUBJECT MATTER

D01F1/10 (2006.01)
D06M11/79 (2006.01)
D06M11/46 (2006.01)

Form PCT/ISA/210 (extra sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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