

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
9 August 2007 (09.08.2007)

PCT

(10) International Publication Number
WO 2007/088151 A1

- (51) **International Patent Classification:**
COIG 23/053 (2006.01) *C03C 17/25* (2006.01)
BOLJ 35/00 (2006.01) *C09C 1/36* (2006.01)
- (21) **International Application Number:**
PCT/EP2007/050826
- (22) **International Filing Date:** 29 January 2007 (29.01.2007)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
FI2006A000030 1 February 2006 (01.02.2006) IT
- (71) **Applicant (for all designated States except US):** COL-
OROBIA ITALIA S.p.A. [IT/IT]; Via Pietramarina 53,
1-50053 Sovigliana Vinci (IT).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** **BALDI, Giovanni**
[IT/IT]; Via Tizzavoli, 4, 1-50025 Montespertoli (IT).
BITOSSI, Marco [IT/IT]; Via Bottinaccio 14, 1-50056
Montelupo Fiorentino (IT). **BARZANTI, Andrea** [IT/IT];
Via San Giuseppe 8, 1-50056 Montelupo Fiorentino (IT).
- (74) **Agents:** **GERVASI, Gemma** et al.; Corso Di Porta Vittoria
9, 1-20122 Milan (IT).
- (81) **Designated States (unless otherwise indicated, for every
kind of national protection available):** AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS,
JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS,
LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY,
MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS,
RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW

- (84) **Designated States (unless otherwise indicated, for every
kind of regional protection available):** ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European (AT, BE, BG, CH, CY, CZ, DE, **DK**, EE, ES, FI,
FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT,
RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,
GN, GQ, GW, ML, **MR**, NE, SN, TD, TG).

Declaration under Rule 4.17:

— of inventorship (Rule 4.17(iv))

Published:

- with international search report
— before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.



WO 2007/088151 A1

(54) **Title:** METHOD FOR THE PREPARATION OF AQUEOUS DISPERSIONS OF TIO₂ IN THE FORM OF NANOPARTI-
CLES, AND DISPERSIONS OBTAINABLE WITH THIS METHOD

(57) **Abstract:** The invention relates to a method for the preparation of aqueous dispersions of TiO₂ in the crystalline form anatase, as well as the dispersions obtained with said method, useful for the preparation of photocatalytic coatings for surfaces, and for the photocatalytic decontamination of gases and liquids.

Method for the preparation of aqueous dispersions of TiO₂ in the form of nanoparticles, and dispersions obtainable with this method

FIELD OF THE INVENTION

5 The present invention relates to the field of methods for the preparation of compounds in the form of nanometric particles, and in particular, to a method relating to a way for preparing TiO₂ dispersions in the form of nanoparticles.

PRIOR ART.

10 Titanium dioxide is a white pigment with a very strong covering capacity used in particular in paints, and in the production of paper and synthetic rubber. Among the most recent applications of Titanium dioxide is the attempt to use its photocatalytic activities to best advantage, in other words, through the action of ultraviolet light, to use this capacity to generate radical species able to catalyse the oxidising degradation of harmful or toxic substances, such as benzene, dioxin,
15 and other organic pollutants, but also unpleasant and sickness-provoking substances such as mould and bacteria. These applications are therefore used in wide environmental fields ranging from combating pollutants to detergents and sterilising products.

For these applications, Titanium dioxide is used as a coating on the surfaces to be
20 treated in order to maximise the photocatalytic effect. The crystalline form of Titanium dioxide called "anatase" is the most popular for this type of application because, as well as being chemically stable and easily available, it also possesses a photocatalytic activity that is higher than the other two crystalline forms, rutile and brookite.

25 On the other hand, the superposition of the Titanium dioxide absorption spectrum, even in anatase form, on the solar spectrum, is not very large, and this results in low photocatalytic efficiency levels. For this reason various attempts have been made to modify TiO₂, for example, by doping it with other metals, or by preparing the compound in question in the form of nanoparticles; in fact this increases the
30 surface area enormously and thus, also the photocatalytic efficiency.

Several methods exist for preparing TiO₂ anatase, including in nanoparticle form, that provide TiO₂ in powder form. In order to be suitable for the preparation of

photocatalytic coatings, this powder must be dispersed in an appropriate solvent and formulated with other possible additives to improve coating adhesion, but this causes the coagulation of the Titanium dioxide particles making it impossible to maintain the photocatalytic efficiency and activity of the particulate material.

5 Moreover, over a period of time, the TiO_2 particles in these dispersions tend to settle in the bottom of the containers where they are stored creating stability problems during storage.

Furthermore, the patent application n° FI2004A252 (by the same Applicant) describes a method that allows the preparation of stable nanoparticle dispersions
10 of Titanium dioxide in anatase form where

water and suitable complexing solvents are used as the solvents

SUMMARY OF THE INVENTION.

Recently the Applicant created a method for obtaining nanoparticles of Titanium dioxide in anatase form already dispersed in water only, and directly usable for the
15 preparation of photocatalytic coatings. The dispersions obtained with the method according to the invention did not provoke particle coagulation even after prolonged storage, thus allowing the preparation of coatings which maintain the photocatalytic activity of the particulate material thanks to dispersion homogeneity.

20 Therefore the aim of the present invention is a method for the preparation of nanoparticle dispersions of Titanium dioxide in anatase form in water, wherein a Titanium alkoxide is made to react under heat in water in the presence of mineral acid and a non-ionic surfactant and where necessary, the solution is finally reduced to a small volume. A further aim of the invention is the use of the
25 nanoparticle dispersions of Titanium dioxide in anatase form in water, obtained using this method, as well as their use for the preparation of photocatalytic surface coatings, for the photocatalytic decontamination of gases and liquids, and for the preparation of formula for cosmetics that provide a protective action against sun rays for the human skin .

30 The characteristics and advantages of the invention will be illustrated in detail in the following description.

BRIEF DESCRIPTION OF THE APPENDED FIGURE

Figure 1 shows a diffractogram of the dried product powder, where the y-axis shows the radiation intensity while the x-axis shows the amplitude of the radiation incidence angle. This analysis demonstrates how crystalline titanium dioxide in anatase form is obtained using this method.

DETAILED DESCRIPTION OF THE INVENTION.

The method of the present invention is able to produce TiO_2 in anatase form directly in water, and to obtain a dispersion of TiO_2 particles at the end of the process with a size between 30-50 nm. Particle measurement was performed using various methods well known to those skilled in the art, such as XRD (X-Ray Diffraction), FEG-SEM (Field Emission Gun - Scanning Electron Microscopy), TEM (Transmission Electron Microscopy) and DLS (Dynamic Light Scattering). Unlike those prepared dispersing nanometric powders in the solvent mixtures or in water, these dispersions show no signs of conglomeration or coagulation and solid precipitation, even after prolonged periods of the dispersion product storage.

The advantages to be gained with dispersions of this type are obvious and associated with the photocatalytic efficiency and uniformity of the coatings that can be prepared with said dispersions. The dispersion index obtainable with the method according to the present invention, measured with DLS (Dynamic Light Scattering) techniques, is lower than 0.3, and thus the dispersion according to the invention differs from those obtained using prior methods composed of the preparation of nanoparticle powder, subsequently dispersed in solvent.

The titanium alkoxide used as the starting product in this method can be chosen from the group composed of titanium methoxide, ethoxide, normal-propoxide, isopropoxide, normal-butoxide, and isobutoxide.

Particularly preferable is Titanium isopropoxide since it is cheaper and reacts better under the conditions used in the present method.

The non-ionic surfactants are surface-active agents composed of an apolar part and a polar function, non-ionisable ether, ester, ether-ester; particularly preferable is Triton X-100 (TX-100)

The term mineral acid according to the invention refers, for example, to an acid chosen from the group composed of: hydrochloric acid, nitric acid, sulphuric acid,

perchloric acid, hydrobromic acid and hydrogen iodide; preferably halogen acids are used, and in particular hydrochloric acid.

The alcoholate molar ratio of titanium alkoxide /mineral acid is between 0.005 and 15, and preferably between 5 and 6.

- 5 The reaction temperature ranges between 15°C and 95°C, preferably between 45°C and 55°C.

Reaction times range between 12 h and 72 h, and preferably 24 h.

Where necessary, when used for coating preparations, the present dispersions can possibly be formulated using additives and diluents commonly employed in
10 the field of surface coatings, such as adhesion improved agents or solvents such as water or ethanol for example, in order to obtain the required dilution level.

On the other hand, when used to decontaminate liquid or gaseous products, the present dispersions are adsorbed respectively on a silica gel support, or on some other suitable inorganic support with adsorbent characteristics, that is then immersed
15 in the liquid, or placed in its current state or diluted, in containers in which the gas to be purified is bubbled through for washing.

The supports on which surface coatings prepared with the present dispersion can be applied are widely varied, from woven fibre products in rolls or already made up into garments, to ceramic products, as well as supports in glass, metal, mirror, and
20 similar materials.

The photocatalytic activity of the surface coating according to the present invention is explained as a result of the exposure of the coating in question to light with a suitable wave length, typically less than 388 nm, which produces a surface with bacteria-proof, bacteriostatic and super-hydrophilic properties after its
25 exposure to UV light. In fact, supports coated with TiO₂ show a total lack of water repellent capacity, so-called super-hydrophilic capacity, that makes surfaces treated with TiO₂ self-cleaning.

Moreover, given the extremely small size of the TiO₂ particles, the present dispersions are practically transparent, leaving the appearance of the surface on
30 which they are applied, totally unchanged. This transparency also makes the product suitable for use in cosmetic fields for the preparation of sun filters with high UV ray protection levels.

A further advantage of the present dispersions, is their behaviour at high temperatures. In fact, the application of the surface coating on ceramic supports requires high temperature processing of the support on which the dispersion is applied and the present dispersions maintain exactly the same appearance,
5 crystalline form of anatase and nanoparticle nature of the coating as before the heating process.

According to a particular embodiment of the present method, the Ti can be doped with a metal selected from the transition metal series, and in particular Ag, Cu and Ce by means of the addition of a salt of one of these metals to the starting
10 solution. In this way, the method will lead to the forming of a dispersion of TiO_2 doped with Ag, Cu or Ce, which are able to perform their catalytic activities even without UV light rays.

Below are certain examples of the invention provided as illustrations but to be considered by no means limiting.

15 Example 5 grams of concentrated HCl, 7.5 grms of TX-1 00, and water up to a total weight of 750 grams are placed in a 2 Litre reactor heated by means of diathermal oil circulating in the external jacket. The temperature is raised to 50°C. At this point 50 grams of $Ti[OCH(CH_3)_2]_4$ (TIP) are added very rapidly and a white flock precipitate can be seen immediately.

20 After 7 hours a very stable transparent sol is formed.

Characterisation

The characterisation occurs by determining the concentration of the Titanium dioxide present in the solution (ICP technique) and by determining the size of the particles (DLS technique).

25 Concentration: 1.5 % in weight of TiO_2

Size: 36.67 nm with a polydispersivity index of =0.282

Example 2

5 grams of concentrated HCl, 7.5 grams of TX-1 00, and water up to a total weight of 750 grams are placed in a 2 Litre reactor heated by means of diathermal oil
30 circulating in the external jacket. The temperature is raised to 50°C. At this point 50 grams of TIP are added very rapidly and a white flock precipitate can be seen immediately.

6

After 24 hours a very stable transparent sol is formed.

Characterisation

Concentration: 1.45 % in weight of TiO_2

Size: 30.26 nm with a polydispersivity index of =0.216

Example 3

500 cc of the product obtained through hydrolysis synthesis is placed in the rotavapor and concentrated. The bath is heated to 40°C and an oil-powered vacuum pump creates a vacuum in the bath.

10 110 cc of solution are obtained.

Characterisation

CONCENTRATION: 6.69 % IN WEIGHT OF TiO_2

SIZE: 26.72 nm with a polydispersivity index of =0.269

15 Example 4

5 grams of concentrated HCl, 1.0 gram of TX-100, and water up to a total weight of 936 grams are placed in a 2 Litre reactor heated by means of diathermal oil circulating in the external jacket. The temperature is raised to 50°C.

20 At this point 64 grams of TIP are added very rapidly and a white flock precipitate can be seen immediately.

After 24 hours a very stable transparent sol is formed.

Characterisation

Concentration: 1.8 % in weight of TiO_2

Size: 49.62 nm with a polydispersivity index of =0.246

Example 5

5 grams of concentrated HCl, and water up to a total weight of 936 grams are placed in a 2 Litre reactor heated by means of diathermal oil circulating in the external jacket. The temperature is raised to 50°C. At this point 64 grams of TIP

30 are added very rapidly and a white flock precipitate can be seen immediately.

After 24 hours a very stable transparent sol is formed.

Characterisation

Concentration: 1.8 % in weight of TiO_2

Size: 52.71 nm with a polydispersivity index of =0.286

Example 6

Application of nanoparticle dispersion of TiO₂ in water on fabric

The suspension obtained as described in the examples 1 - 5 can be used for treating fabrics and make them absorbent to ultraviolet radiation which is harmful to the skin, thus reducing the risk of developing skin cancer.

- 5 15 Kg of a 0.5M solution of sodium acetate and 0.5 Kg of Pimasil (siloxane resin) are added to 13Kg of the product prepared in water and concentrated to 6%. The compound obtained is applied to a fabric using a padding technique followed by rameuse drying. The fabric thus obtained has an UPF value comparable to 20 times the value of a non-treated fabric of the same type.

10 Example 7

Application of nanoparticle dispersion of TiO₂ in water on ceramic or glass surfaces.

- 15 The suspension obtained as described in the examples 1-5 can be applied to ceramic or glass surfaces (using airbrush or dip-coating techniques) in the current concentration or diluted (with water or alcohol) The surface obtained maintains its initial characteristics because the applied layer is completely transparent. The surface assumes all the functions with photocatalytic characteristics: self-cleaning, bacteria-proof, degrading capacity for organic pollutants.

CLAIMS

1. Method for the preparation of nanoparticle dispersions of TiO_2 in anatase form, wherein a titanium alkoxide is made to react under heat in water in the presence of mineral acids and a non-ionic surfactant, the solution thus obtained is possibly
5 reduced to a small volume if necessary.
2. Method according to claim 1, wherein said Titanium alkoxide is chosen from a group composed of titanium methoxide, ethoxide, normal-propoxide, iso-propoxide, normal-butoxide, and isobutoxide.
3. Method according to claim 2, wherein said Titanium alkoxide is Titanium iso-
10 propoxide.
4. Method according to claims 1 - 3 wherein said mineral acid is a halogen acid
5. Method according to claim 4 wherein said halogen acid is HCl.
6. Method according to claims 1 - 5 wherein said non-ionic surfactants possess the polar function of an ether or ester type.
- 15 7. Method according to claim 6 wherein said non-ionic surfactant is Triton X-1 00 (TX-1 00).
8. Method according to claims 1 - 7 wherein the titanium alkoxide/ halogen acid molar ratio is between 0.005 and 15.
9. Method according to claim 8 wherein the titanium alkoxide/ halogen acid molar
20 ratio is between 5 and 6.
10. Method according to claims 1 - 9 wherein the reaction temperature is between 15°C and 95°C , and the reaction times are between 12 and 72 hours.
11. Method according to claim 10 wherein the reaction temperature is between 45°C and 55°C , and the reaction time is 24 hours.
- 25 12. Method according to claims 1 - 11 wherein a metal salt Ag, or Cu or Ce, is added to the solution containing the titanium alkoxide, the mineral acid, and the surfactant.
13. Nanoparticle dispersions of TiO_2 in anatase form in water, obtainable using the method as defined in claims 1-11.
- 30 14. Nanoparticle dispersions of TiO_2 in water, wherein the Ti is doped with a metal selected from the series of transition metals obtainable using the method according to claim 12.

15. Dispersions according to claim 14 wherein said transition metal is selected from the group composed of :Ag, Cu and Ce.

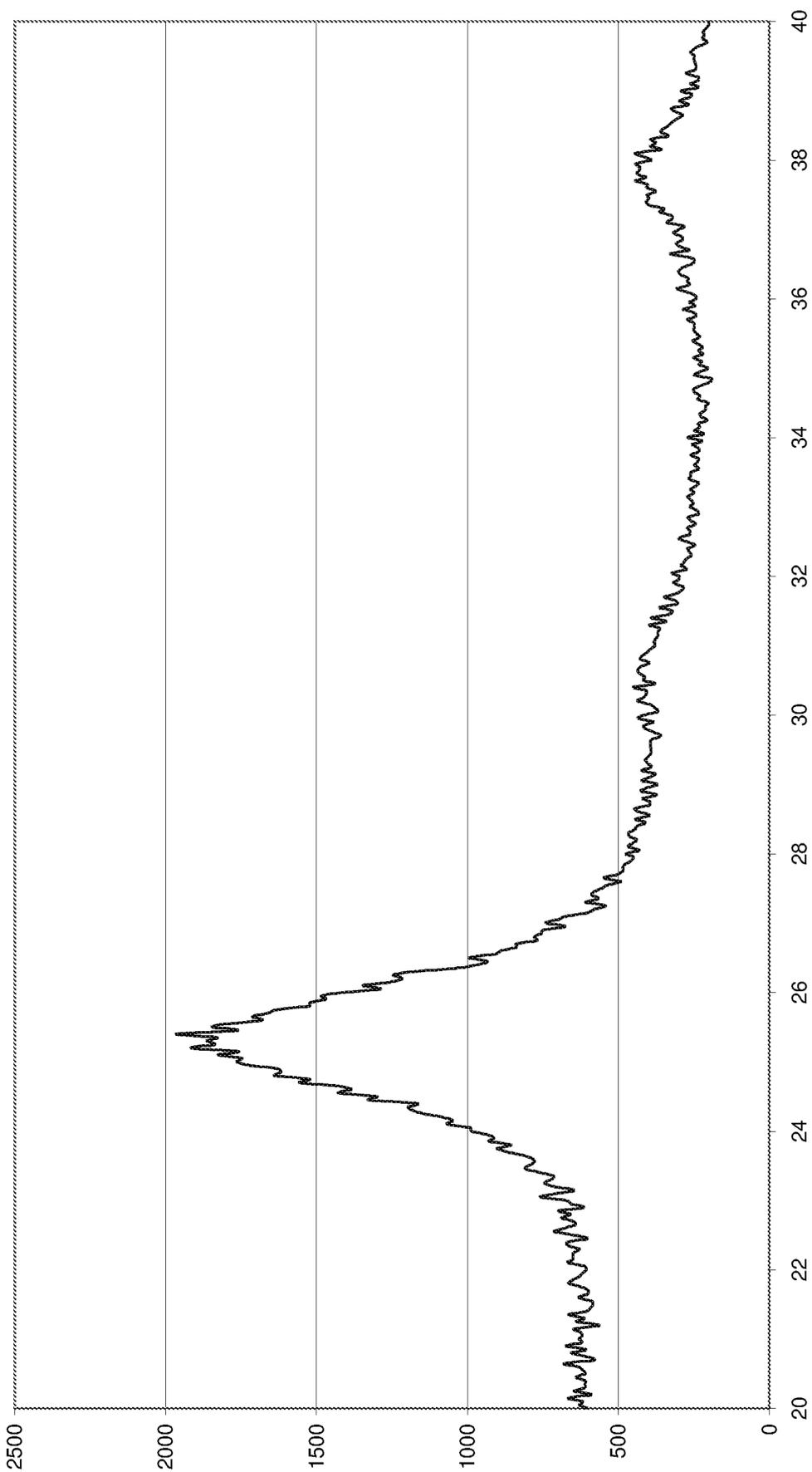
16. Use of nanoparticle dispersions of TiO_2 according to claims 13 - 15, for the preparation of photocatalytic coatings on surfaces that require said treatment.

5 17. Use according to claim 16, wherein said surfaces are selected among the surfaces of textile fabric, metal, ceramic and enamelled products.

18. Use of nanoparticle dispersions of TiO_2 according to claims 13 - 15, for photocatalytic decontamination of gases and liquids.

10 19. Use of nanoparticle dispersions of TiO_2 according to claims 13 - 15, for the preparation of cosmetics with a protective action for the human skin against sun rays.

FIGURE 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/050826

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C01G23/053	B01J35/00
	C03C17/25	C09C1/36
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)		
BOIJ COIG C03C C09C		
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 practical, search terms used)		
EPO-Internal , WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
Y	FELDMANN c : "Polyol -Mediated Synthesis of Nanoscale Functional Materials" ADVANCED FUNCTIONAL MATERIALS, WILEY VCH, WIENHEIM, DE, vol. 13, no. 2, February 2003 (2003-02), pages 101-107, XP002342330 ISSN: 1616-301X	1-12,14, 15,18
X	[Synthesis], [Color pigments], [Conclusions], [Experimental] ----- -/--	13,16, 17,19
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> 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	"I" 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	
"E" earlier document but published on or after the international filing date	"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	
"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)	"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 such documents, such combination being obvious to a person skilled in the art	
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
8 June 2007	15/06/2007	
Name and mailing address of the ISA/ European Patent Office, P B 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-2040 Tx 31 651 epo nl Fax (+31-70) 340-3016	Authorized officer CORRIAS, M	

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/050826

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	M .ADDAMO, V . AUGUGLI ARO, A .DI PAOLA, E . GARCIA LOPEZ, V . LODDO, G . MACR , R . MOLINARI, L . PALMISANO, M . SCHIAVELLO: "Preparation, characterization and photoactivity of polycrystalline nanostructured TiO ₂ catalysts" JOURNAL OF PHYSICAL CHEMISTRY, vol. 108, 2 November 2004 (2004-11-02), pages 3303-3310, XP002383061 [Introduction], [Experimental section] -----	1-12,14, 15,18
X	US 6 905 814 B1 (AUBAY ERIC ET AL) 14 June 2005 (2005-06-14) column 1, line 10 - column 2, line 35; examples 1-7 -----	13,16,17
A	WO 99/62822 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 9 December 1999 (1999-12-09) page 5, line 23 - page 7, line 24; examples 1-3 -----	1-19
P, X	WO 2006/061367 A (COLOROBIA ITALIANA SPA [IT]; BALDI GIOVANNI [IT]; BITOSI MARCO [IT];) 15 June 2006 (2006-06-15) page 2, line 16 - page 3, line 10 the whole document -----	1-19

INTERNATIONAL SEARCH REPORT

information on patent family members

International application No

PCT/EP2007/050826

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6905814	B1	14-06-2005	AU 2677300 A 04-09-2000
			EP 1151068 A1 07-11-2001
			WO 0049119 A1 24-08-2000
			FR 2789591 A1 18-08-2000
WO 9962822	A	09-12-1999	JP 11343118 A 14-12-1999
WO 2006061367	A	15-06-2006	NONE