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(54) Title: PROCESS FOR PREPARING DISPERSIONS OF TIO<sub>2</sub> IN THE FORM OF NANOPARTICLES, AND DISPERSIONS OBTAINABLE WITH THIS PROCESS AND FUNCTIONALIZATION OF SURFACES BY APPLICATION OF TIO<sub>2</sub> DISPERSIONS

(57) Abstract: A description is given of a process for preparing nanoparticulate dispersions of TiO<sub>2</sub> in the crystalline anatase form and the dispersions obtained with said process, useful for preparing photocatalytic coatings on surfaces and the photocatalytic decontamination of gas and liquids.



WO 2006/061367 A1

PROCESS FOR PREPARING DISPERSIONS OF  $\text{TiO}_2$  IN THE FORM OF NANOPARTICLES, AND DISPERSIONS OBTAINABLE WITH THIS PROCESS AND FUCTIONALIZATION OF SURFACES BY APPLICATION OF  $\text{TiO}_2$  DISPERSIONS

5 **Field of the invention**

The present invention relates to the field of processes for preparing compounds in the form of nanometric particles, and in particular regards a process for preparing dispersions of  $\text{TiO}_2$  in the form of nanoparticles.

**State of the art**

10 Titanium dioxide is used as a white pigment of good covering power in particular in paint and in the production of paper and synthetic rubber. More recent applications of titanium dioxide are those that exploit its photocatalytic activity, i.e. its capacity to generate, by the action of ultra-violet light, radical species able to catalyse the oxidative degradation of noxious or toxic substances such as benzene, dioxane and  
15 other organic pollutants, and also of unpleasant and infectious substances such as moulds and bacteria. These applications extend from the fight against pollutants in the environmental field, to the field of cleaning and sterilizing.

For said applications titanium dioxide is used as a coating on surfaces to be treated, so as to maximize the photocatalytic effect. The crystalline form of titanium dioxide,  
20 namely anatase, is preferred for this type of application because, in addition to being chemically stable and easily available, it also has a greater photocatalytic activity than the other two crystalline forms, rutile and brookite.

On the other hand, the overlap of the titanium dioxide absorption spectrum with the solar spectrum is not very great even in its anatase form, indicating a low  
25 photocatalytic efficiency. Various attempts have therefore been made to modify  $\text{TiO}_2$ , for example by doping it with other metals or preparing the compound in question in the form of nanoparticles; in this manner, the surface area and therefore photocatalytic efficiency are vastly increased.

Various processes for preparing anatase  $\text{TiO}_2$  are known, even in nanoparticulate  
30 form, but as far as the applicant is aware all these processes lead to powdered  $\text{TiO}_2$  being obtained.

A process for preparing a suspension of nanoparticles in high boiling point alcohol is the polyol process described for example in C. Feldmann "Polyol mediated synthesis of nanoscale functional materials" which allows the obtaining of suspensions very stable for a long time but, contrary to the presently claimed process, it uses mineral acid as inhibitor of polycondensation (see also in this connection WO 99/62822).

To be usable for preparing photocatalytic coatings this powdery material must be dispersed in a suitable solvent and possibly formulated with additives to improve coating adhesion. However, this causes the titanium dioxide particles to coagulate, making it impossible to maintain the activity and photocatalytic efficiency of the particulate material. Moreover, over time the TiO<sub>2</sub> particles in these dispersions tend to sink to the bottom of the containers in which they are stored, giving rise to stability problems during storage.

The need is therefore felt for providing a process which enables stable nanoparticulate dispersions of titanium dioxide in the anatase form to be prepared.

### **Summary of the invention**

The applicant has now devised a process by which nanoparticulate TiO<sub>2</sub> in the anatase form and already dispersed in suitable solvents is obtained, it being directly usable for preparing photocatalytic coatings. The dispersions obtained with the process of the invention have not led to particle coagulation phenomena even after prolonged storage, allowing coatings to be prepared that maintain the photocatalytic activity of the particulate material by virtue of dispersion homogeneity.

The present invention therefore provides a process for preparing nanoparticulate dispersions of anatase TiO<sub>2</sub> in a mixture of water and a suitable complexing solvent, comprising the following steps:

- i) reacting a titanium alkoxide with a suitable complexing solvent;
- ii) distilling the solution derived from step i) until a small volume results;
- iii) adding water to the solution derived from step ii) together with said complexing solvent and one or more polycondensation inhibitors, then heating the reaction mixture under reflux, to obtain the desired nanoparticulate dispersion.

Another process to obtain nanoparticle suspensions of titanium dioxide, TiO<sub>2</sub>, is the aqueous hydrolysis of titanium alkoxides such as titanium methoxide, ethoxide,

normal-propoxide, isopropoxide, normal-butoxide, and isobutoxide. The titanium isopropoxide is preferred for the same reasons previously described.

Titanium isopropoxide is added to a hot water solution containing mineral acid (such as hydrochloridric or nitric acid) and a non-ionic surfactant (such as Triton X-100).

5 The hydrolysis process is maintaining to reflux for 24 hours.

The invention also provides nanoparticulate dispersions of anatase  $\text{TiO}_2$  in a mixture of water and a suitable complexing solvent, obtainable with the aforesaid process, and their use for preparing photocatalytic surface coatings for antibacterial action, photocatalytic decontamination of gas and liquids, and for preparing cosmetic  
10 formulations which protect the skin against sunlight.

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

#### BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows the diffractogram attained from XRD analysis of the product obtained  
15 in example 1, after drying it at  $200^\circ\text{C}$  for 12 hours.

Figure 2 shows a TEM photo of  $\text{TiO}_2$  nanoparticles (90000x).

Figure 3 shows the diffractogram attained from XRD analysis of the product obtained in example 8.

#### Detailed description of the invention

20 With the process of the invention, the formation of  $\text{TiO}_2$  in anatase form takes place directly in the water/complexing solvent mixture used in step i), obtaining at the end of the process a dispersion of  $\text{TiO}_2$  particles between 3 and 20 nm in size. Particle size measurement was undertaken with different techniques well known to the expert of the art, such as XRD (X-ray diffraction), FEG-SEM (Field Emission Gun – Scanning  
25 Electron Microscopy), TEM (Transmission Electron Microscopy) and DLS (Dynamic Light Scattering). These dispersions, in contrast to those prepared by dispersing nanometric powers in solvent mixtures, exhibit neither agglomerate formation nor coagulation and precipitation phenomena, even after prolonged storage of the dispersion.

30 The advantages of dispersions of this type are evident, and related to the uniformity and photocatalytic effectiveness of the coatings which can be prepared therewith.

The polydispersion index of the dispersions obtainable with the process of the invention, measured by the DLS (Dynamic Light Scattering) technique, is less than 0.3, hence differentiating the dispersions of the invention from those obtainable with the traditional method of preparing the nanoparticulate powder and then dispersing it  
5 in solvent. A typical TEM image of our nanoparticles dispersion is shown in Fig.2.

The titanium alkoxide used as the starting product in the present process can be chosen for example from the group consisting of titanium methoxide, ethoxide, normal-propoxide, isopropoxide, normal-butoxide, and isobutoxide.

Among these products, titanium isopropoxide is the preferred starting compound in  
10 the present process for various reasons. Among the titanium compounds that can be used it is the least expensive and the one which has the best reactivity under the conditions of the present process; moreover, its use leads to isopropyl alcohol being obtained as by-product of step ii), a product easily recoverable from the process of the invention and valued for its wide usage in the detergent industry.

15 The complexing solvents typically used in the present process are ethylenglycol, diethylenglycol and polyethylene glycols, having molecular weights for example of between 200 and 600. Longer chain polyethylene glycols of molecular weight up to 10,000 can also be used. In this case, at the end of the process and after cooling, instead of a  $\text{TiO}_2$  dispersion in a liquid, nanoparticles of  $\text{TiO}_2$  are obtained dispersed  
20 in a solid matrix. The final product preserves the nanometric dimensions of  $\text{TiO}_2$  and the low polydispersion index observed for liquid dispersions. The preferred complexing solvent is diethylene glycol.

Excellent results have been obtained by conducting reaction step i) using titanium isopropoxide and diethylene glycol in a 1:3 molar ratio.

25 Within the scope of the present invention, the term "polycondensation inhibitor" means typically a mixture comprising at least one mineral acid and one organic acid, where the mineral acid can be chosen for example from the group consisting of hydrochloric acid, nitric acid, sulfuric acid, perchloric acid, hydrobromic acid, and hydroiodic acid, and the organic acid is preferably acetic acid.

30 In accordance with a particularly preferred embodiment of the present process, the polycondensation inhibitor is a mixture of hydrochloric acid and acetic acid.

The quantity of polycondensation inhibitor added is such that the quantity of the mineral acid is between 0.1 and 10% by volume on the total volume of the reaction mixture, while the quantity of the organic acid is between 1 and 20% by volume on the total volume of the reaction mixture.

5 The water/complexing solvent mixture used in accordance with the invention also enables the dispersion to be used directly for preparing photocatalytic coatings practically for any type of application, even for applications in the cosmetic or textile fields for coating products destined for contact with the skin.

Where they are used for preparing coatings, the present dispersions can possibly be  
10 formulated with additives and diluents commonly used in the field of surface coatings such as adhesion improving agents or solvents like water or ethanol to obtain the desired dilution.

Where they are instead used to decontaminate liquid or gaseous products, the present dispersions are respectively adsorbed on a silica gel support, or on another  
15 suitable inorganic support with good adhesion characteristics such as glass, ceramic, porous ceramics, fibres, textiles and so on, which is then immersed in the liquid or placed, as such or diluted, into containers through which the gas to be purified is bubbled.

The supports onto which a surface coating prepared with the present dispersions can  
20 be applied are very varied, ranging from fibre fabrics, either on the roll or made-up, to ceramic products, to glass, metal or mirror supports and the like.

Photocatalytic activity of the surface coating in accordance with the invention is exhibited after exposing the coating itself to light at a suitable wavelength, typically less than 388 nm, to produce a surface with antibacterial, bacteriostatic and super-  
25 hydrophilic properties following exposure to UV light. The TiO<sub>2</sub> coated supports demonstrate a complete absence of water repellance, known as super-hydrophilicity, thus rendering the TiO<sub>2</sub> treated surfaces self-cleaning.

Moreover, given the very small TiO<sub>2</sub> particle size, the present dispersions are almost transparent, thus leaving unchanged the appearance of the surface to which they are  
30 applied. Their transparency also makes them suitable for use in the cosmetic field for preparing high protection UV sun filters.

A further advantage of the present dispersions is their behaviour at high temperatures. In this respect, applying the surface coating onto ceramic supports requires high temperature treatment of the support onto which the dispersion has been applied, the present dispersions maintaining unchanged the appearance, the  
5 crystalline form of anatase and the nanoparticulate nature of the coating prior to heating.

In accordance with a particular embodiment of the present process, doping of the Ti can be achieved with a metal chosen from the transition metal group and in particular Ag, Cu or Ce by the addition of one of their salts to step i) or alternatively to step iii) of  
10 the present process. In this manner, the process will result in the formation of an Ag, Cu or Ce doped TiO<sub>2</sub> dispersion, able to exhibit its catalytic activity even without UV light irradiation.

Some illustrative and non-limiting examples of the invention are given hereinafter.

#### EXAMPLE 1

15 Preparation of nanoparticulate dispersion of anatase TiO<sub>2</sub> in water/diethylene glycol starting from Ti isopropoxide

5.53 litres of diethylene glycol are fed into a 20 litre flask to which are added 5.54 litres of titanium isopropoxide. The reaction mixture is maintained under agitation for 5 minutes, then heated to 120°C distilling off the isopropyl alcohol which forms, until a  
20 small volume results. 11.1 litres of diethylene glycol, 125 ml of 32-33% w/w hydrochloric acid, 2.07 litres of glacial acetic acid and 125 ml of deionised water are added. The temperature is brought to 180°C and the mixture maintained under reflux for 2 hours.

The product thus obtained was characterised as follows.

25 Firstly, the concentration of TiO<sub>2</sub> in the final product was measured using the technique of inductively coupled plasma atomic emission (ICP) in accordance with standard methodology. From this analysis the quantity of TiO<sub>2</sub> in the dispersion was found to be equal to 5.7% by weight on the total weight of the dispersion.

A sample of the dispersion obtained as aforescribed was oven dried at 200°C for  
30 12 hours until the solvent was completely evaporated. The powder thus obtained was then analysed by XRD using a Philips X'Pert PRO diffractometer, in order to

understand its crystalline structure: as can be seen in figure 1, the position and the intensity of the peak shown by the diffractogram are typical of anatase.

From the diffractogram of figure 1, and in particular from the width of the principal peak, the average dimensions of the TiO<sub>2</sub> particles were calculated by applying Sherrer's formula, to find an average diameter value equal to 4.5 nm.

This value was also confirmed from transmission electron microscope observation on a sample of the dispersion obtained as aforescribed, after being diluted 1:100 with ethanol.

#### EXAMPLE 2

##### 10 Preparation of nanoparticulate dispersion of anatase TiO<sub>2</sub> in water/diethylene glycol starting from Ti ethoxide

5.53 litres of diethylene glycol were loaded into a 20 litre flask to which were added 3.76 litres of titanium ethoxide. The reaction mixture is maintained under agitation for 5 minutes, then heated to 130°C distilling away the ethanol that forms. 11.1 litres of diethylene glycol, 125 ml of 32-33% w/w hydrochloric acid, 2.07 litres of glacial acetic acid and 125 ml of deionised water are added. The temperature is brought to 180°C and the mixture maintained under reflux for 2 hours.

This product was characterised in the same manner as that given in example 1 to obtain the same crystalline phase and particles of similar dimensions. In addition the product obtained was used to carry out the same tests described above in examples 2, 3 and 4 with similar results to those obtained for the product prepared as in example 1.

#### EXAMPLE 3

##### 25 Preparation of nanoparticulate dispersion of anatase TiO<sub>2</sub> in water starting from Ti isopropoxide

18.720 Kg of water solution obtained mixing water with 100gr of hydrochloridric acid and 80gr of a 1% w/w solution of Triton X-100 in water are fed into 20 litre flask. The reaction mixture is heated to 50°C. 1.280 Kg of titanium isopropoxide are added. The reaction mixture is mantained under reflux to 50°C for 24 hours. The product thus obtained was characterised as follows.

30 Firstly, the concentration of TiO<sub>2</sub> in the final product was measured using the

technique of inductively coupled plasma atomic emission (ICP) in accordance with standard methodology. From this analysis the quantity of TiO<sub>2</sub> in the dispersion was found to be equal to 1.8% by weight on the total weight of the dispersion.

A sample of the dispersion obtained as aforescribed was oven dried at 100°C for 12 hours until the solvent was completely evaporated. The powder thus obtained was then analysed by XRD using a Philips X'Pert PRO diffractometer, in order to understand its crystalline structure.

#### EXAMPLE 4

##### Application of nanoparticulate dispersion of TiO<sub>2</sub> in water/diethylene glycol onto fabric

25 ml of deionised water were added to 75 ml of the dispersion prepared as aforescribed in example 1 and the dispersion thus diluted was placed in a bowl. A 20 cm x 60 cm strip of cotton fabric was immersed in the bowl for 10 seconds, then removed and passed between two rollers of silicone material to remove excess solvents. The fabric was then oven dried, washed in a washing machine, dried again and the UV ray protection factor (UPF) offered by the coated fabric was measured with the standard spectrophotometric methods for this type of measurement, a UPF of 35.40 being found.

#### EXAMPLE 5

##### Application of nanoparticulate dispersion of TiO<sub>2</sub> in water/diethylene glycol onto wool

25 ml of deionised water were added to 75 ml of the dispersion prepared as aforescribed in example 1 and the dispersion thus diluted was placed in a bowl. A 20 cm x 60 cm strip of wool fabric was immersed in the bowl for 10 seconds, then removed and passed between two rollers of silicone material to remove excess solvents. The fabric was then oven dried, washed in a washing machine and dried again. Onto this wool fabric was tested antibacterial properties in observance of rule AATCC TM 100:99. In the following table are reported the results of tests.

	Percentage of put down of microbial strain
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Sample	Staphylococcus aureus	Bacillus subtilis	Aspergillus niger
Pure wood	0	0	77.60
Wood treated with Titanium Dioxide	>99.94	99.60	99.47

## EXAMPLE 6

Application of nanoparticulate dispersion of TiO<sub>2</sub> in water/diethylene glycol onto a Cotton wire

5 25 ml of deionised water were added to 75 ml of the dispersion prepared as  
 aforescribed in example 1 and the dispersion thus diluted was placed in a bowl.  
 A cotton wire was immersed in the bowl, dried in a oven and rolled onto a spool.  
 With this wire was obtained a knitted fabric and was tested the UV ray protection  
 factor (UPF) offered by the coated fabric. This properties was measured with the  
 10 standard spectrophotometric methods and a UPF of 30.20 being found.

## EXAMPLE 7

Application of nanoparticulate dispersion of TiO<sub>2</sub> in water/diethylene glycol onto ceramic surfaces – studies of adherence and resistance to high temperatures

The nanoparticulate dispersion prepared as aforescribed in example 1 was used  
 15 to create a photocatalytic coating on an unglazed gres support, adding 5% by weight  
 of a low melting frit, to facilitate adherence of the titanium dioxide to the support. The  
 frit used had a relatively low hemisphere temperature, equal to 700°C, and the  
 following chemical composition:

SiO <sub>2</sub> 48.32 %	CaO 6.95 %
20 Al <sub>2</sub> O <sub>3</sub> 2.22 %	MgO 1.94 %
K <sub>2</sub> O 0.049 %	Li <sub>2</sub> O 13.9 %
Na <sub>2</sub> O 0.06 %	ZnO 4.05 %
B <sub>2</sub> O <sub>3</sub> 22.55 %	

The dispersion of example 1 was applied by dip-coating to the support, which was  
 25 subjected to thermic cycles at both 700°C and 600°C. After the firing treatment the  
 support maintained its original appearance and demonstrated good adhesion

between coating and substrate.

The behaviour of the present coating at high temperatures was studied by high temperature powder diffractometry (XRD-HT). It was thus observed that the phase transition from anatase to rutile begins at only about 800°C, arriving at completion at about 900°C. By applying Sherrer's formula, the nanocrystal dimensions at the various temperatures was also calculated.

Table 1 below gives the  $2\theta$  angle at which the measurement was taken, the width of the peak at half height which when inserted in Sherrer's formula serves to calculate the crystallite dimensions, the crystallite dimensions and the temperature relative to the preceding dimensions.

Table 1

Crystalline phase	$2\theta$ angle	FHWD	dimensions (nm)	T (°C)
anatase	25.04	1.3354	60.9	300
anatase	25.11	1.2553	64.8	400
anatase	25.10	1.1532	70.6	500
anatase	25.05	0.9405	86.5	600
anatase	25.05	0.4045	201.2	700
anatase	25.03	0.2614	311.3	800
anatase	25.02	0.1935	420.5	900
rutile	27.10	0.1401	583.3	900
rutile	27.08	0.137	596.4	1000

The same method was used to evaluate increase in crystallite size at a constantly maintained frit firing temperature but at differing times, and in this case good coating adherence was found even for prolonged firing times, the crystallite size increasing over time but to an acceptable extent such as not to reduce the photocatalytic effectiveness of the coating.

To verify the adherence of the coating to the substrate the entire sample was subjected to ultrasound cycles in ethanol and in acetone for different times (5 and 60 minutes) and to repeated washings with cloths of different abrasiveness (sponging).

After every ultrasound cycle an XRD analysis was carried out to verify any reduction in the amount of anatase present in the coating, finding however that the treatments carried out have not influenced either the crystalline form of TiO<sub>2</sub> or adherence of the coating to the support.

5 EXAMPLE 8

Application of nanoparticulate dispersion of TiO<sub>2</sub> in water/diethylene glycol onto ceramic surfaces – Photocatalytic effect

Two samples of the same gres, glazed in white, were “stained” with the same quantity of a solution containing 10 ppm of methylene blue. Only one of the two samples had  
10 previously been coated with the dispersion of the invention as described in example 4.

The two samples were then exposed to light from a UV lamp for various periods of time: 10, 30, 60, 90 and 120 minutes. While on the untreated sample no change in the methylene blue stain was observed, a progressive disappearance of the blue  
15 stain was observed for the sample covered with the dispersions of the invention. The same experiment was repeated with a indelible marker stain, only observing disappearance of the stain on the coated sample after 45 minutes’ exposure to UV light.

The two above experiments were repeated in sunlight instead of with a UV lamp, and  
20 the same results were obtained.

EXAMPLE 9

Application of nanoparticulate dispersion of TiO<sub>2</sub> in water/diethylene glycol onto glass.

The dispersion of example 1 was applied by dip-coating or spray to the support,  
25 which was subjected to thermic cycles for 30 minutes at 200°C and for 30 minutes at 500°C. After the firing treatment the support maintained its original appearance and demonstrated good adhesion between coating and substrate.

This sample was “stained” with a solution containing 10 ppm of methylene blue. The sample was then exposed to light from a UV lamp and a progressive disappearance  
30 of the blue stain was observed. This experiments was repeated in sunlight instead of with a UV lamp, and the same result was obtained.

## EXAMPLE 10

Application of nanoparticulate dispersion of TiO<sub>2</sub> in water/diethylene glycol onto glass-ceramic surface.

The dispersion of example 1 was applied by dip-coating or spray to the support, which was subjected to thermic cycles for 30 minutes at 200°C and for 30 minutes at 700°C. After the firing treatment the support maintained its original appearance and demonstrated good adhesion between coating and substrate.

This sample was "stained" with a solution containing 10 ppm of methylene blue. The sample was then exposed to light from a UV lamp and a progressive disappearance of the blue stain was observed. This experiments was repeated in sunlight instead of with a UV lamp, and the same result was obtained.

## EXAMPLE 11

Application of nanoparticulate dispersion of TiO<sub>2</sub> in water/diethylene glycol onto various surface (glass, glass-ceramic, glaze, body gres).

At the dispersion of example 1 was added 0.01 to 10% of surfactant as for example a non ionic surfactant (such as Triton X-100) to improve the spreading onto the surface. This solution was applied by dip-coating or spray to the support, which was subjected to thermic cycles for 30 minutes at 200°C and for 30 minutes at 500°C for glass or 700°C for glass-ceramics, glaze and body gres. After the firing treatment the support maintained its original appearance and demonstrated good adhesion between coating and substrate.

This sample was "stained" with a solution containing 10 ppm of methylene blue. The sample was then exposed to light from a UV lamp and a progressive disappearance of the blue stain was observed. This experiments was repeated in sunlight instead of with a UV lamp, and the same result was obtained.

## EXAMPLE 12

Application of nanoparticulate dispersion of TiO<sub>2</sub> in water onto ceramic composite obtained with inorganic material and a polyester resin.

50 ml of deionised water were added to 50 ml of the dispersion prepared as aforescribed in example 1 bis and the dispersion thus diluted was placed in a spray gun. This sample was sprayed onto surface of composite material and after

was kept at 100°C for 1 hour.

This sample was “stained” with a solution containing 10 ppm of methylene blue. The sample was then exposed to light from a UV lamp and a progressive disappearance of the blue stain was observed. This experiments was repeated in sunlight instead of  
5 with a UV lamp, and the same result was obtained.

**CLAIMS**

1. Process for preparing nanoparticulate dispersions of anatase TiO<sub>2</sub> in a mixture of water and a suitable complexing solvent comprising the following steps:
  - i) reacting a titanium alkoxide with a suitable complexing solvent;
  - 5 ii) distilling the solution derived from step i) until a small volume results;
  - iii) adding, under acidic conditions, water to the solution derived from step ii) together with said complexing solvent and one or more polycondensation inhibitors, then heating the reaction mixture under reflux to obtain the desired nanoparticulate dispersion.
- 10 2. Process as claimed in claim 1, wherein said complexing solvent is a polyethylene glycol.
3. Process as claimed in claim 2, wherein said complexing solvent is diethylene glycol.
4. Process as claimed in claim 1, wherein said titanium alkoxide is chosen from the  
15 group consisting of titanium methoxide, ethoxide, normal-propoxide, isopropoxide, normal-butoxide, and isobutoxide.
5. Process as claimed in claim 4, wherein said titanium alkoxide is titanium isopropoxide.
6. Process as claimed in claim 1, wherein said polycondensation inhibitor is a  
20 mixture comprising at least one mineral acid and one organic acid.
7. Process as claimed in claims 1 and 6, wherein the quantity of polycondensation inhibitor added in step iii) is such that the quantity of the mineral acid is between 0.1 and 10% by volume on the total volume of the reaction mixture, while the quantity of the organic acid is between 1 and 20% by volume on the total volume of the reaction  
25 mixture.
8. Process as claimed in claim 6, wherein said mineral acid is chosen from the group consisting of hydrochloric acid, nitric acid, sulfuric acid, perchloric acid, hydrobromic acid, and hydriodic acid, said organic acid being acetic acid.
9. Process as claimed in claim 6, wherein said polycondensation inhibitor is a  
30 mixture of hydrochloric acid and acetic acid.
10. Process as claimed in claim 1, wherein the molar ratio of said titanium alkoxide

to said complexing solvent is 1:3.

11. Process as claimed in claim 1, also comprising the addition of a salt of metals of the first or second transition group to step i) or alternatively to step iii).

12. Process as claimed in claim 11, wherein said first or second transition group  
5 metals are chosen from Ag, Cu and Ce.

13. Nanoparticulate dispersions of anatase  $\text{TiO}_2$  in a mixture of water and a suitable complexing solvent, obtainable with the process as defined in claims 1-12.

14. Dispersions as claimed in claim 13, wherein said complexing solvent is a polyethylene glycol.

10 15. Dispersions as claimed in claim 14, wherein said complexing solvent is diethylene glycol.

16. Use of nanoparticulate dispersions of  $\text{TiO}_2$  as defined in claims 13-15 for preparing photocatalytic coatings on surfaces which require said treatment.

15 17 Use as claimed in claim 16 wherein said photocatalytic coatings comprise a surfactant.

18. Use according to Claim 18 wherein said surfactant is a non ionic surfactant.

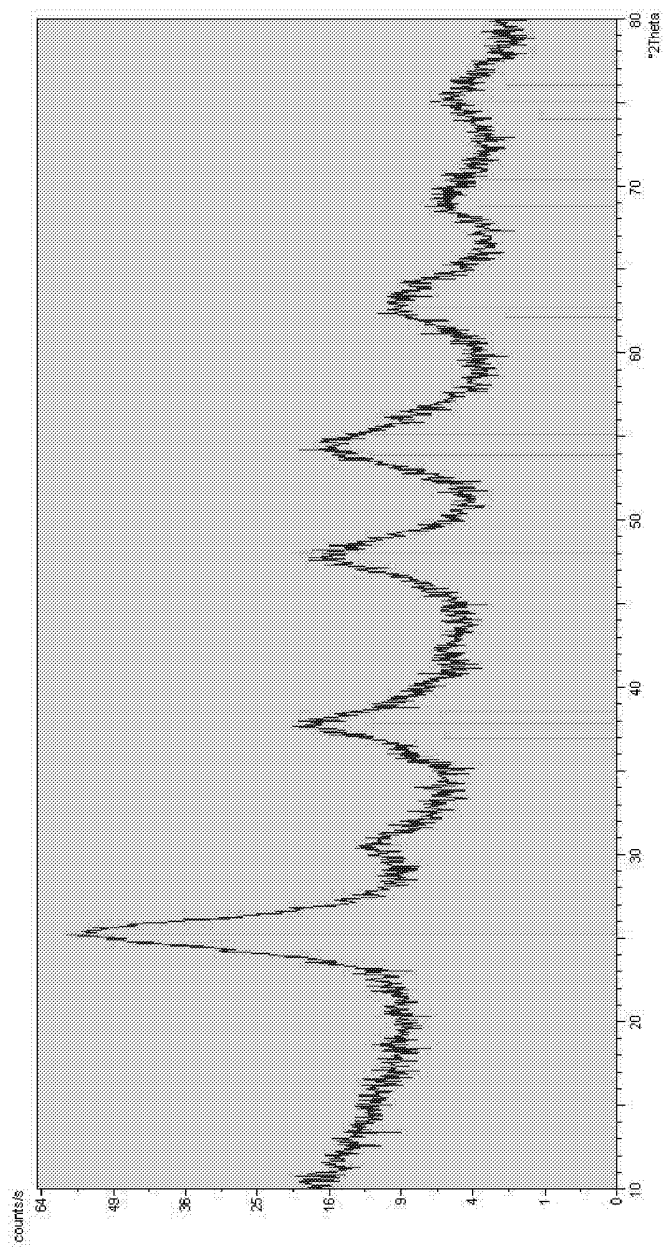
19. Use according to claim 18 wherein such non ionic surfactant is Triton x 100.

20. Use as claimed in claims 16 - 19 , wherein said surfaces are chosen from the surfaces of textile, metallic, ceramic products, and glazes.

20 21. Use of nanoparticulate dispersions of  $\text{TiO}_2$  as defined in claims 13-15 for photocatalytic decontamination of gas and liquids.

22. Use of nanoparticulate dispersions of  $\text{TiO}_2$  as defined in claims 13-15 for preparing cosmetic formulations with high protection of the skin against the sun.

Figure 1



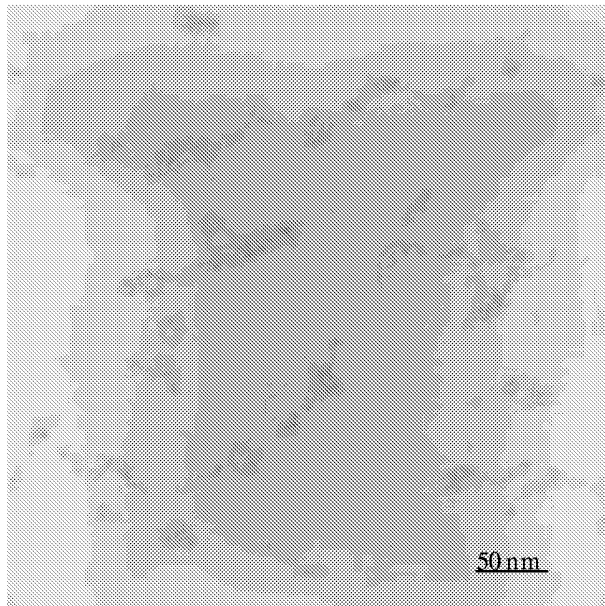
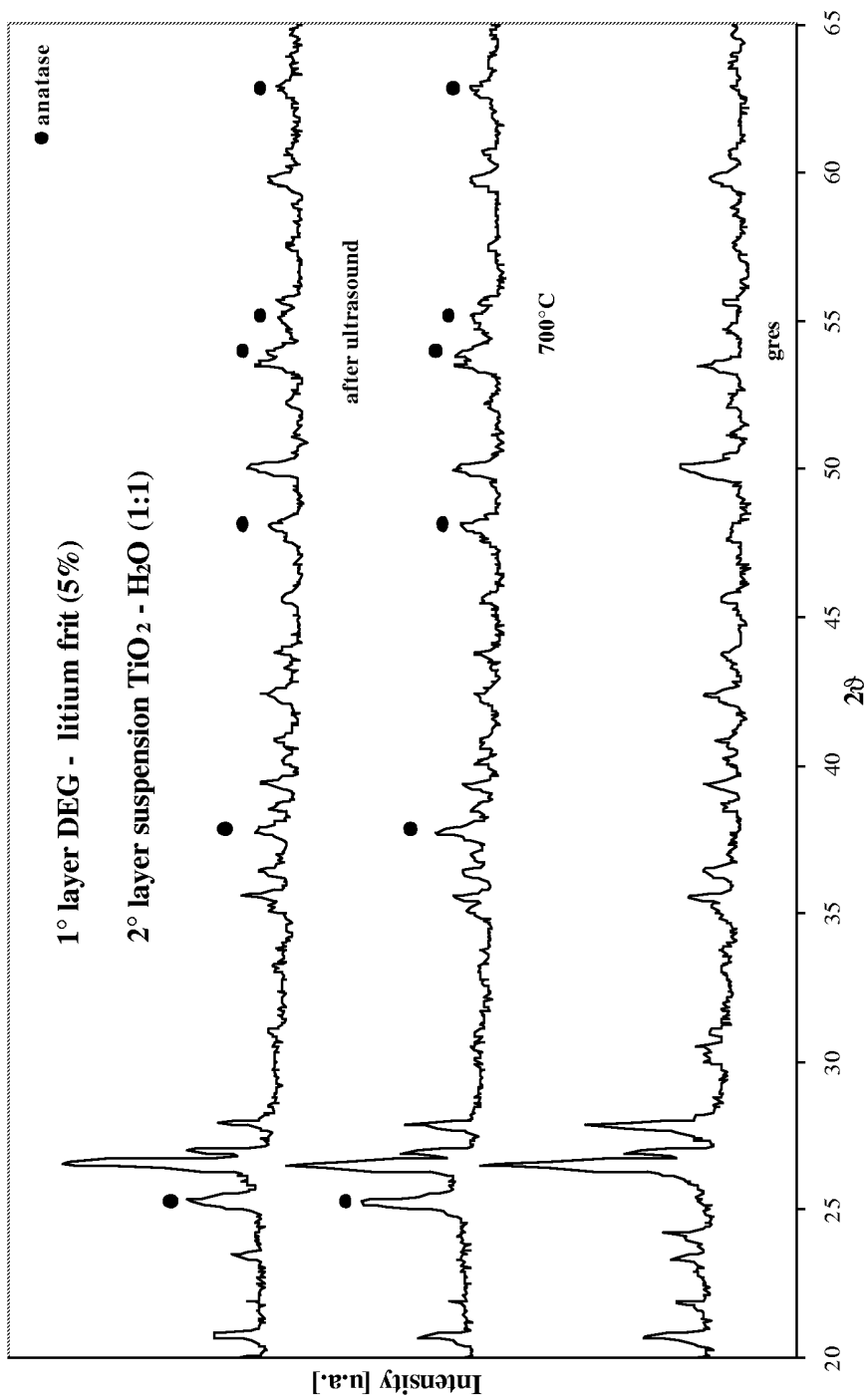


Figure 2

Fig.3



## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2005/056478

A. CLASSIFICATION OF SUBJECT MATTER C01G23/053 B01J35/00 B01D53/86 C03C17/25		
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 B01J B01D C03C		
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, CHEM ABS Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	C. FELDMANN: "Polyol-Mediated Synthesis of Nanoscale Functional Materials" ADVANCED FUNCTIONAL MATERIALS, vol. 13, no. 2, 2003, pages 101-107, XP002342330	1-12
X	paragraphs 'INTRODUCTION!', 'SYNTHESIS!', 'CATALYSIS!', 'EXPERIMENTAL!' -----	13-22
Y	EP 0 770 579 A (ASAHI GLASS COMPANY LTD) 2 May 1997 (1997-05-02) page 3, line 13 - line 18 -----	1-12
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 02, 29 February 2000 (2000-02-29) & JP 11 322338 A (NOEVIR CO LTD), 24 November 1999 (1999-11-24) abstract -----	1-10
	-/--	
<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	"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	
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Date of the actual completion of the international search  7 March 2006	Date of mailing of the international search report  17/03/2006	
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  Siebel, E	

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2005/056478

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 99/62822 A (MINNESOTA MINING AND MANUFACTURING COMPANY) 9 December 1999 (1999-12-09) page 5, line 23 - page 6, line 14 -----	1-10
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WO 9962822	A	09-12-1999	JP	11343118 A		14-12-1999
JP 2003119024	A	23-04-2003	NONE			