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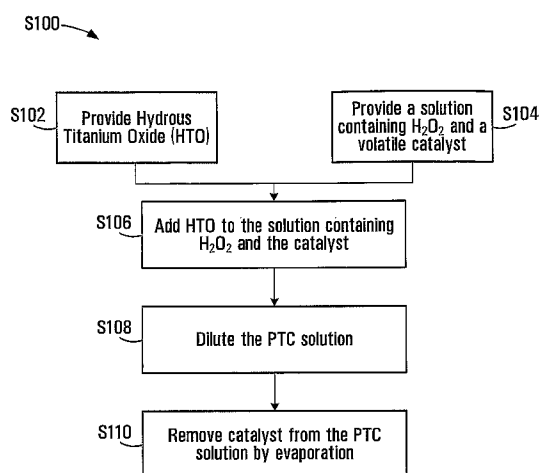


FIG. 3

(57) **Abstract:** A solution of titanium dioxide particles is prepared by reacting hydrous titanium oxide (HTO) and hydrogen peroxide (H₂O₂) in a solution, in the presence of a volatile base catalyst, to form a peroxo-titanium-complex (PTC). The solution is diluted by a factor of at least 2. A portion of the volatile catalyst is then removed by evaporation from the solution to form particles comprising titanium dioxide and PTC adsorbed to the particles, after which the solution has a pH of about 7 and is transparent. The particles in the solution may have a zeta potential of -60 to -80 mV, particle sizes from 10 nm to 25 nm, and a concentration higher than 4 w%, such as from 6 to 8 wt%.

SOLUTION OF PARTICLES CONTAINING TITANIUM DIOXIDE AND PEROXO-TITANIUM COMPLEX, AND ITS PREPARATION

FIELD OF THE INVENTION

[0001] The present invention relates to solutions of particles containing titanium dioxide and peroxo-titanium complexes, and their preparation.

BACKGROUND OF THE INVENTION

[0002] Titanium dioxide (TiO_2) particles having adsorbed peroxo-titanium complexes (PTC) in a particulate form are useful in a wide range of commercial and industrial applications, due to their desirable optical and chemical properties. A PTC contains a coordination complex that has a Ti(IV) ion and a peroxy ligand bonded to the Ti(IV) ion. The TiO_2 may be in different phases. For example, anatase TiO_2 can act as a photo-catalyst, and a coating containing anatase TiO_2 can have photo-activated self-cleaning properties. A conventional technique is to form and store such TiO_2 particles in a solution.

[0003] However, conventional processes for producing such a solution have some drawbacks, some of which are discussed in U.S. patent number 6,602,918 to Ichinose (hereinafter referred to as "Ichinose"), issued August 5, 2003. Ichinose discloses a process to address a common problem of other conventional processes – excessive heat is generated during formation of PTC and TiO_2 particles, as the chemical reactions in the formation process are very exothermic. The excessive heat causes condensation and precipitation, and thus reduced transparency of the resulting PTC solution. Ichinose discloses a three-step process to reduce condensation and precipitation. In the first step, a titanium-containing compound is reacted with hydrogen peroxide (H_2O_2) to form a peroxo complex in a solution, and a basic substance is subsequently added to the solution to form a peroxotitanium hydrate polymer, which precipitates in the solution. In the second step,

impurities and ionic substances are removed from the solution to separate them from the precipitate. For sufficient removal, repeated use of ion-exchange resins is required. In the third step, the precipitate is cooled and then reacted with H_2O_2 again to form the final product. It is believed that this process inhibits condensation for two reasons. First, the exothermic reactions of titanium-containing compounds with H_2O_2 take place in two stages, thus allowing better dispersion and removal of generated heat from the solution. Second, impurities and ionic substances in the reaction solution can promote condensation and their removal reduces condensation.

[0004] However, the Ichinose process has its drawbacks. The H_2O_2 consumption in this process is high. The process is time consuming. These factors, and the repeated addition and removal of ion-exchange resins, all contribute to increased production cost. In addition, the use of ion exchange resins also tends to introduce contaminants into the reaction solution, which reduces the stability of the particles produced. The concentration of the particles in the solution is less than 3%, which is also relatively low.

[0005] Further, in conventional techniques, TiO_2 in the particles is typically formed initially in the amorphous phase. Amorphous TiO_2 exhibits low photocatalytic activity. To increase photocatalytic activity, the particles need to be crystallized at high temperatures to form anatase TiO_2 . However, extensive heating can cause problems or can be inconvenient in many applications. In these cases, it is desirable to produce photocatalytic PTC materials, such as TiO_2 particles containing PTC or coatings, without extensive heating.

SUMMARY OF THE INVENTION

[0006] It has been found that a stable, transparent solution containing TiO_2 particles can be prepared as follows. Hydrous titanium oxide (HTO) and hydrogen peroxide (H_2O_2) are reacted in a solution, in the presence of a volatile base catalyst, such as an ammonium-generating base. Peroxo-titanium-complex (PTC) will form as a result of the reaction. The catalyst is

partially removed by evaporation, to form particles containing titanium dioxide and PTC adsorbed to the surfaces of the particles. To prevent overgrowth of the particles, the solution may be diluted by a factor of at least 2 and aged before the evaporation. In different embodiments, the pH may vary depending on the application. Evaporation of the catalyst may continue until the solution has a pH of about 7 and remains transparent. The PTC particles in the product solution may have nano-scale particle sizes, such as from 10 nm to 25 nm. The product solution may have a concentration of PTC particles of up to 8 wt% (weight percent). The PTC particles in the solution may have a zeta potential from -60 to -80 mV. The PTC particles in the diluted solution may be heated to form anatase TiO_2 , and then re-concentrated by evaporation. The resulting product solution may have a neutral pH. A neutral pH may be from 5.5 to 8.5, such as from 6.5 to 7.5.

[0007] The product solution, even with up to 8 wt% PTC concentration, can be stable over a long period of time, such as more than a year, without significant color change or precipitation. As the volatile catalyst can be removed by evaporation, without using complicated ion removal techniques such as ion-exchange resins, costs of production can be reduced.

[0008] Therefore, according a first aspect of the present invention, there is provided a method of preparing a solution comprising titanium dioxide particles. The method comprises reacting HTO and H_2O_2 in a solution, in the presence of a volatile base catalyst, to form a PTC; diluting the solution by a factor of at least 2, resulting in a diluted solution comprising PTC; and removing a portion of the volatile catalyst, by evaporation, from the diluted solution to form particles comprising titanium dioxide and PTC adsorbed to the particles, after which the diluted solution has a pH of about 7 and is transparent. A pH of about 7 may be from 5.5 to 8.5 or from 6.5 to 7.5. The particles in the solution may have a zeta potential of -60 to -80 mV. The particles may have particle sizes from 10 nm to 25 nm. The particles may have a concentration higher than 4 wt%, such as from 6 to 8 wt%. The solution may be agitated during reaction and removal of the catalyst. The catalyst may be a weak base. The weak base may be selected from

ammonium hydroxide and amine. The solution may comprise, before the reaction, from about 50 to about 600 ppm of the weak base. The method may comprise cooling the solution. The solution may be cooled to a temperature below about 5 °C before reaction. The solution may be cooled to a temperature of about 7 °C during the reaction. The solution may be diluted by a factor of 2 to 100, such as 6 to 15. The solution may be diluted by adding deionized water to the solution. The deionized water may have a temperature between 5 °C and room temperature. The particles may be heated to form anatase TiO₂. The particles may be heated to a temperature from about 90 to about 130 °C before or after the removal of the catalyst. The particles may be heated for about 30 minutes to about 10 hours. The particles may be heated in the diluted solution, or after being extracted from the diluted solution. The evaporation of the catalyst in the diluted solution may last for about 30 minutes to about 4 hours. The hydrous titanium oxide may be prepared by a process comprising mixing a Ti(IV) source and a basic substance in an aqueous solution to form a precipitate comprising hydrous titanium oxide, and recovering the precipitate. The basic substance is in an amount such that the aqueous solution has a pH from 6 to 7. The basic substance may be a volatile weak base. The basic substance may comprise ammonium hydroxide. The mixing may comprise dissolving the Ti(IV) source in acidified water to form a Ti solution; adding a dilute solution of the basic substance to the Ti solution; and subsequently adding a concentrated solution of the basic substance to the Ti solution. The dilute solution may comprise 0.1 to 5 wt% of the basic substance and the concentrated solution may comprise 15 to 30 wt% of the basic substance. The precipitate may be washed with deionized water. The Ti(IV) source may be a titanium salt selected from titanium tetrachloride (TiCl₄), titanium tetrafluoride (TiF₄), titanium sulphate (TiOSO₄), titanium tetranitrate (Ti(NO₃)₄), and alkoxy titanium (Ti(OR)₄). For example, the titanium salt may be TiCl₄.

[0009] In accordance with another aspect of the present invention, there is provided a solution prepared according to the method described in the preceding paragraph. The solution comprises titanium dioxide particles that comprise titanium dioxide and PTC adsorbed thereto. The particles in the

solution have a zeta potential of -60 to -80 mV. The particles may have particle sizes from 10 nm to 25 nm. The concentration of the particles in the solution may be higher than 4 wt%, such as from 6 to 8 wt%.

[0010] In accordance with another aspect of the present invention, there is provided a transparent solution comprising an aqueous solvent and titanium dioxide (TiO_2) particles dispersed in the solvent. The TiO_2 particles comprise titanium dioxide and peroxo-titanium complex (PTC) adsorbed to the titanium dioxide. The PTC comprises peroxo-ligands bonded to Ti(IV) . The TiO_2 particles have particle sizes from 10 nm to 25 nm and a zeta potential from -60 to -80 mV. The concentration of the TiO_2 particles in the solution is higher than 4 wt%, such as from 6 to 8 wt %. The solution has a pH of about 7. The TiO_2 particles may comprise amorphous or anatase TiO_2 , or both. The TiO_2 particles in the solution may exhibit photocatalytic activities in response to irradiation of light such as UV or visible light.

[0011] Other aspects and features of the present invention will become apparent to those of ordinary skill in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] In the figures, which illustrate, by way of example only, embodiments of the present invention,

[0013] **FIG. 1** shows a scheme for the chemical reaction between Ti(IV) and hydrogen peroxide;

[0014] **FIG. 2** shows exemplary peroxo-titanium complexes formed at different pH values;

[0015] **FIG. 3** is a flowchart for a process of preparing PTC particles in a solution, exemplary of an embodiment of the present invention;

[0016] FIG. 4 is a flowchart for preparing hydrous titanium oxide in the process of FIG. 3;

[0017] FIG. 5 is a line graph showing the relationship between the PTC stability and the dilution factors;

[0018] FIG. 6 is a graph showing the relationship between the pH and the aging time;

[0019] FIGS. 7 and 8 are data graphs showing the change in water contact angle during exposure to sunlight or xenon light, respectively;

[0020] FIG. 9 is a line graph showing X-ray Diffraction (XRD) spectra obtained from different samples of PTC particles;

[0021] FIGS. 10 and 11 are line graphs showing color change of tile surfaces coated with PTC particles during exposure to UV light or visible light, respectively; and

[0022] FIGS. 12 and 13 are transmission electron microscopy (TEM) images obtained from PTC particles before and after hydrothermal treatment, respectively.

DETAILED DESCRIPTION

[0023] In an exemplary embodiment of the present invention, hydrous titanium oxide (HTO) and hydrogen peroxide (H_2O_2) are reacted in a solution, such as an aqueous solution, and in the presence of a volatile base catalyst to form peroxo-titanium complexes (PTC). Without being limited to any particular theory, it is expected that the reactions in the solution may include the reaction (R1) shown in FIG. 1. Reaction R1 may be catalyzed by an alkaline, or base, catalyst such as ammonium hydroxide or amine. The reaction products of reaction R1 include PTC, such as the monomer shown in FIG. 2, which may subsequently form PTC polymers, and TiO_2 particles with PTC adsorbed to TiO_2 core (referred to herein as PTC particles).

[0024] PTC contains peroxo groups and can thus grow in size as a result of polymerization and condensation. The PTC particles may also contain various phases of TiO_2 which can form due to oxolation of the PTC. In an oxolation reaction, an oxo bridge is formed between two metal centers, such as the Ti(IV) ions in the present case. The formed PTC particles may be suspended in a solution. The polymerization and condensation of the PTC is influenced by the pH of the solution, as illustrated in **FIG. 2**. Monomer PTC will typically form first at lower pH, during the early stages of PCT formation. When the pH is increased, dimmers will initially form due to condensation. It is expected that trimers and tetramers, and other more complicated PTC polymers, can also form when the pH is further increased. This polymerization process can continue to form cross-linkage, thus facilitating the formation of Ti-O-Ti bonds. The increase in bridging and compaction of the PTC network eventually results in the formation of nano-sized particles, as illustrated in **FIG. 2**. It has been found that when formed in a concentrated solution, the particles tend to aggregate during formation, as the chance of interaction between the particles is high. In a diluted solution, however, aggregation is less likely due to reduced chance of interaction. As can be seen in **FIG. 2**, when the pH of the dilute solution increases to about 7, TiO_2 particles are formed with peroxo groups adsorbed to the TiO_2 cores. As such, the particles have high zeta potentials and thus good stability. That is, even if the solution is re-concentrated after the formation of the PTC particles, the particle sizes stay relatively stable. It has also been found that the pH of the dilute solution can be increased by removing the volatile catalyst through evaporation.

[0025] The volatile catalyst may be any suitable catalyst. In one embodiment, the catalyst is one that can generate an ammonium in the solution. The term "ammonium" may refer to a polyatomic cation in the form of NH_4^+ . Thus, ammonium may also refer to a protonated substituted amine, or a quaternary ammonium cation in the form of NR_4^+ . The catalyst may be a weak base such as ammonia or amine. In a different embodiment, the catalyst may be another suitable volatile weak base or alkaline. A weak base is a base that does not convert fully into hydroxide ions in water. Weak acids and

weak bases do not dissociate completely. The equilibrium constant (K_a) for a weak acid or weak base is small, usually less than about 1.

[0026] Strong bases, such as NaOH, that generate strong acids or cations, such as Na^+ or K^+ , are generally not suitable as the catalyst, because they can adversely affect the photocatalytic properties of the resulting product. For instance, Na^+ can cause re-combination of photogenerated electrons and holes, thus significantly reduce the photocatalytic reactivity if they are present in the final coating. In comparison, when a weak base such as ammonium or amine is used, it is not necessary to completely remove the weak base or its conjugate acid cation from the solution after the particles are formed. For example, the presence of ammonium or amine will not cause significant re-combination effect.

[0027] As illustrated in the exemplary procedure **S100** shown in **FIG. 3**, an appropriate amount of HTO may be prepared at **S102**, and a solution containing H_2O_2 and the volatile catalyst may be prepared at **S104**. The preparation of HTO and the solution will be described further below. The HTO is added to the solution containing H_2O_2 and the catalyst at **S106**. The solution is continuously agitated such as stirred to dissolve the HTO. The HTO may be added slowly to avoid excessive reaction heat being generated quickly and to allow the HTO to become completely dissolved. The pH of the PTC solution after the added HTO has been dissolved may be about 2 to 3.

[0028] The PTC solution is next diluted with deionized water at **S108**. It has been found that, surprisingly, dilution by a sufficient factor can reduce or limit polymerization and condensation thus limit the growth of the PTC particles in size. It is found that the product PTC solution is stable over a long period of time, such as over a year, when the solution is diluted by a factor of at least 2 before the partial removal of the catalyst, which will be described below. Even when the diluted solution is re-concentrated, the solution remains stable. The deionized water may have a temperature between 5 °C and the room temperature.

[0029] The PTC solution may be diluted by a factor of 2 to 100. In one embodiment, the dilution factor may be from 6 to 15. In another embodiment, the dilution factor may be from 7 to 100. A dilution factor of "n" means that the volume of added water is "n" times of the volume of the initial PTC solution. Dilution can slightly increase the pH of the solution, such as from around 2 to around 3.

[0030] At **S110**, a portion of the catalyst is removed from the diluted PTC solution, by evaporation, while the solution is agitated, such as stirred, until the solution becomes transparent and has a pH value about 7. In some embodiments, a pH of about 7 may include pH values from 5.5 to 8.5, or from 6.5 to 7.5. The pH value after the partial removal of the catalyst may be from 6 to 7. The solution may be aged to allow it to evaporate. Evaporation of the solution removes certain impurities, including any volatile substance introduced earlier, from the solution, thus facilitating the formation of a stable and transparent PTC solution. Volatile weak bases and acids such as Cl^- , F^- , SO_4^- , NO_3^- , and NH_4^+ , if present, may be gradually removed by evaporation. A solution is transparent when a naked eye can see an object or image through the solution. A solution may be considered transparent if it has a molar extinction coefficient higher than 1.5×10^6 at 400nm.

[0031] The solution may be stirred and aged until the solution shows a transparent orange color and the pH of the solution is higher than 6. The aging time may vary depending on the particular embodiment. In some cases, the aging time may last about 30 minutes to about 8 hours, such as from 30 minutes to 4 hours, at room temperature. The solution may also be stirred and evaporated for 3 to 5 hours. The pH of the PTC solution will increase automatically through a self-recovery process when the weak bases such as ammonium ions confined in the PTC structure are released gradually as the PTC decomposes. Aging may be carried out at room temperature (e.g. about 18-22 °C) or a lower temperature, such as between 4 °C and the room temperature. Agitation of the PTC solution can prevent aggregation of the PTC particles. It has been found that if the solution is aged without agitation, aggregation will occur in the PTC solution during aging. After sufficient

stirring and aging, the solution will become transparent, indicating that the PTC particles have become well stabilized.

[0032] It has been found that the pH of the PTC solution can affect the polymerization and the dispersion ability of the PTC particles, as well as the color of the solution.

[0033] At **S102** in the process of **S100**, the HTO may be prepared as illustrated in **FIG. 4**.

[0034] At **S112**, a Ti(IV) source is added into acidified water for hydrolysis. The acidified water may be formed by adding a small amount of acid such as diluted HCl (3.6%) to deionized water. The temperature of the Ti solution should be kept below 7°C, such as being cooled with ice water. Initially (before the reaction), the solution may be cooled to a temperature below about 5°C. It is noted that, in this description, when the solvent of any solution is not otherwise specified, the solvent may include water.

[0035] The Ti(IV) source may be any suitable titanium-containing substance that can provide Ti(IV) ions when dissolved in an aqueous solution. For example, a titanium salt such as titanium tetrachloride (TiCl₄), titanium tetrafluoride (TiF₄), titanium sulphate (TiOSO₄), or titanium tetranitrate (Ti(NO₃)₄), alkoxy titanium (Ti(OR)₄), or the like may be suitable. In one embodiment, the Ti(IV) source may have a concentration of less than 40 wt% in the Ti solution. The concentration of the Ti(IV) source in the solution may vary in different applications. The appropriate concentration may be readily determined by one skilled in the art for a given application. In some embodiments, the concentration of the Ti(IV) source should be sufficiently low such that no smoke will be released from the solution, and when the solution is cooled, such as upon mixing with cold deionized water, no significant precipitation occurs.

[0036] The Ti solution may be mixed with a base to neutralize the Ti salt and thus facilitate formation of the HTO precipitates.

[0037] In an exemplary embodiment, a suitable base is a volatile weak base. A volatile base may be advantageous in some embodiments because it can be later removed by evaporation. A weak base is used because its weak conjugate acid, such as ammonium, will have less or no adverse effects on the ultimate photocatalytic properties of the resulting solution or PTC particles, as discussed above. Further, when the weak base is volatile, it may be conveniently removed by evaporation.

[0038] An exemplary volatile weak base is ammonia, or ammonium hydroxide (NH_4OH). Other weak bases, such as R-NH_2 , may also be used. In the following description, it is assumed that NH_4OH is used as the volatile weak base.

[0039] In one embodiment, a solution of NH_4OH may be added to the Ti solution. A dilute solution of NH_4OH may be added first (at **S114**). A dilute solution of NH_4OH may have a NH_4OH concentration from 0.1 to 5 wt% (by weight), such as about 3 wt%. The solution may be agitated such as stirred while NH_4OH is added. The addition of NH_4OH in a diluted solution first can prevent formation of large HTO particles. As can be appreciated, larger particles may be more difficult to dissolve later.

[0040] Subsequently, a concentrated NH_4OH solution may be added (at **S116**), until the Ti solution has a value of pH from 6 to 7. The concentrated solution may have a NH_4OH concentration from 15 to 35 wt%, such as about 30 wt%. HTO will then form and precipitate in the solution.

[0041] The precipitate is washed, such as with deionized water to remove impurities (at **S118**). Impurities present in the solution may include dissolved ions such as Cl^- , F^- , SO_4^- , NO_3^- , and NH_4^+ . Water may be repeatedly added and removed until the solution containing the precipitate is sufficiently free of impurities and undesirable ions. However, unlike in some conventional processes, it is not necessary that the contaminating ions such as Cl^- and SO_4^- are completely removed at this stage. For example, washing may be performed until the electrical conductivity of the solution is reduced to an acceptable level, such as below 20 $\mu\text{S/m}$. As can be appreciated, the

electrical conductivity of the solution is dependent on the concentration of charged species such as ions in the solution, and thus it can be used to indicate the level of ion concentration in the solution. Added water may be removed, for example, using a suction-filtering technique, as can be understood by persons skilled in the art.

[0042] The washed precipitate may be collected by separating it from the solution (at **S120**). The collected precipitate contains hydrous titanium oxide, and may be in the form of a cake. The precipitate should not be completely dried as a dehydrated and solidified precipitate will have adverse effects on the final product.

[0043] At **S104** of process **S100** shown in **FIG. 3**, the solution containing H_2O_2 and the volatile catalyst may be prepared in any suitable manner. For example, a solution containing H_2O_2 and ammonium may be prepared by mixing a solution of H_2O_2 and an aqueous solution of ammonia, or ammonium hydroxide. The ammonium hydroxide may be replaced by an amine such as H_2NROH , where R may be C_2H_4 or another organic group. As discussed above, in different embodiments another volatile weak base may also be used instead of ammonia or amine as the catalyst. However, an alkali base such as NaOH is not suitable as discussed before.

[0044] The concentration of ammonium in the mixed solution should be in a suitable range. As explained below, if the concentration of ammonium is too high or too low, the resulting PTC particles will not be completely soluble in water and the resulting solution will remain translucent or the PTC will precipitate. It has been found that good results can be achieved if the concentration of NH_4OH or amine in the mixed solution is from about 50 to about 600 ppm. The mixed solution may be cooled to below 7 °C such as with ice or using a cooler. The H_2O_2 in the mixed solution may have an initial concentration higher than 10 wt%. The pH value of the mixed solution may be around 5.

[0045] In process **S100**, after aging the PTC solution may be optionally heated to crystallize TiO_2 to form crystallized (anatase) TiO_2 . For example,

the PTC solution may be subjected to hydrothermal treatment to heat the solution to a temperature from about 90 to about 130 °C. The hydrothermal treatment may last for about 30 minutes to about 10 hours. The hydrothermal treatment of the PTC solution may produce volatile cations such as ammonium in the solution, which are initially trapped in the PTC particles but released due to the heat treatment. The newly released volatile cations may be removed from the solution by further evaporation, such as using a rotary evaporation technique. As discussed above, evaporation can remove volatile substances such as ammonia. As a result, and depending on the removed substances, the pH value of the solution may change during evaporation. In one embodiment, after the hydrothermal treatment, evaporation can reduce the pH to a neutral level. As such, it is not necessary in the exemplary process to adjust the pH of the PTC solution by adding other basic or acidic substance or solution. After the hydrothermal treatment, the concentration of the particles in the solution may then be increased from 2 to 10 times and the re-concentrated solution can still remain stable.

[0046] The PTC may be crystallized to form anatase TiO_2 , either within the PTC solution or after they have been extracted from the solution. For example, the PTC solution may be deposited on a surface to form a coating which is then dried and heated to form anatase TiO_2 .

[0047] In general, particles containing anatase TiO_2 can exhibit high photocatalytic activities. For example, the PTC particles formed in the PTC solution can exhibit photocatalytic activities in response to irradiation of light, such as UV light. However, surprisingly and as will be further discussed below, it has been discovered that, even without crystallization through extensive heating, the PTC particles formed according to procedures **S100** can exhibit significant self-cleaning effect via super-hydrophilicity, although the self-cleaning effect may be weaker than in anatase TiO_2 . Thus, crystallization of the particles by heating is optional and may be omitted in applications where extensive heating is undesirable or inconvenient.

[0048] The PTC solution prepared as above can be stored for a relatively long period of time, such as from days to more than a year, without significant

condensation or gelation. It has been found that the particle sizes in the PTC solution are relatively small, such as less than 25 nm. The factors that can affect the particle sizes include zeta potentials on the particle surfaces and their concentration in the solution. The term "particle size" as used herein refers to the average diameter of the particles in a particulate. As the particles in a particulate may have non-spherical shapes and different sizes, the term "diameter" refers to the average or effective diameter. An effective diameter of a non-spherical particle is the diameter of a spherical particle that has the same volume as the non-spherical diameter. For example, some particles may have leaf-like shapes, in which case, the particles may have sizes of about 25 nm by about 10 nm, or less.

[0049] As discussed above, the pH value of the PTC solution may be adjusted by controlling the extent of evaporation, such as adjusting the strength and evaporation time. Evaporation also increases the concentration of PTC particles in the solution. A solution having a relatively high concentration of PTC particles, such as higher than 4 wt%, may be obtained. In some embodiments, the concentration may be as high as from 6 to 8 wt%.

[0050] Conveniently, the PTC solution can have a neutral pH value without using complicated and costly ion-exchange resins. Since the use of ion-exchange resins can introduce contamination into the solution, when they are not used, certain potential contamination is avoided. Less contamination can lead to improved stability of the PTC. The stability of the PTC solution may be measured by the zeta potential of the particles in the solution. The particles in a PTC solution prepared according the procedure **S100** can have a zeta potential from -60 to -80 mV. In comparison, the zeta potential of a PTC solution prepared according a conventional process is only about -40 mV, indicating significant contamination (less stability), which can result in reduced photocatalytic activity.

[0051] In some applications, the formed PTC solution may be used directly. In other applications, the PTC particles so formed, either in the anatase or amorphous phase, may be extracted from the PTC solution before use. The PTC solution may also be used to form coatings on surfaces, such

as exterior surfaces of buildings. The coatings may be easy to clean and may be self-cleaning as the PTC particles in the coating are photocatalytic. The coating may be formed using any suitable technique such as spin or spray coating.

[0052] In the exemplary procedure **S100**, it is not necessary to add H_2O_2 more than once and it is not necessary to add and remove ion-exchange resins. As a result, these procedures take less time to complete and are less expensive to perform, as compared to the Ichinose process discussed earlier. Further, as HTO and H_2O_2 are only brought together for a limited period of time, the time for potential recondensation is limited. As will be further discussed below, the PTC particles prepared according to these processes are relatively stable, even when the concentration of PTC particles is relatively high, such as higher than 4 wt% and up to 8 wt%.

[0053] The embodiments of the present invention are further illustrated with the following non-limiting examples.

[0054] EXAMPLES:

[0055] Example I:

[0056] Hydrous titanium oxide was prepared as follows. Initially, 5 litres of deionized water was provided in a container. The water was ice-cooled and had a temperature from 5 to 7 °C. 33 ml of a solution containing 36.6 wt% of TiCl_4 was added to the container. The TiCl_4 solution was obtained from Sumitomo™ Co. 200 ml of a dilute NH_4OH solution containing 3.0% of NH_4OH was added to the container. The content of the container is mixed by stirring. A concentrated solution containing 30% of NH_4OH was then added to the container until the mixed solution in the container had a pH of about 7. The mixed solution in the container was let stand at room temperature until hydrous titanium oxide precipitated. The content in the container was then washed with water until the conductivity of the liquid content reached 6 to 20 $\mu\text{S/m}$, as measured by a conductivity meter. The precipitates in the container were separated from the liquid content to form a hydrous titanium oxide cake,

which weighed 94 g and contained about 9.3% of solid TiO₂ particles.

[0057] A mixed solution of NH₄OH and a 12 ml solution containing 30 w% of H₂O₂ was prepared. In the mixed solution, the concentration of NH₄OH was 300 ppm. The mixed solution was ice-cooled and stirred. The HTO cake was added to the mixed solution slowly. Small pieces of the cake were added one by one. A subsequent piece was only added after the previous piece had completely dissolved. A total of 12 g of the HTO cake was added. The final solution was cooled using ice to maintain a low temperature and was stirred for a few hours, resulting in a clear orange PTC solution, which had a pH of around 2.25.

[0058] Example II

[0059] Different PTC solutions were prepared in a similar procedure as described in Example I, except the ammonium hydroxide concentration in the mixed solution was changed to 0, 100, 200, 400, 600, 800, 1,000, 1,200, 1,400, or 1,500 ppm respectively. Further, two PTC solutions were prepared in a similar procedure, but the ammonium hydroxide was replaced with an amine, ethanolamine (H₂NCH₂CH₂OH), at concentrations of 500, and 1,000 ppm respectively.

[0060] It was found that the concentration of ammonium in the mixed solution had significant effects on the final appearance of the solution and the time required to form a clear solution. The results of two series of tests are respectively listed in **Tables IA** and **IB**. As can be seen from **Tables IA** and **IB**, it is possible to obtain clear PTC solution with up to 600 ppm NH₄OH concentration. While in one test, the sample solution with 500 ppm NH₄OH showed precipitation, it is believed that the precipitation in this case was likely caused by experimental or procedural errors.

Table IA. Effect of concentration of ammonium catalyst

Catalyst Concentration (ppm)	Appearance of PTC Solution	Time for solution to become clear (hours)
NH_4OH		
0	Clear	~ 24
0	Translucent	> 24
0	Translucent	> 24
30	Translucent	6
50	clear	4
100	Clear	4
200	Clear	3
300	Clear	3
400	Clear	3
600	Clear	3
800	Precipitate	(Did not turn clear)
1,000	Precipitate	(Did not turn clear)
1,200	Precipitate	(Did not turn clear)
1,400	Precipitate	(Did not turn clear)
1,600	Precipitate	(Did not turn clear)
$\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$		
500	Clear	3
1,000	Precipitate	(Did not turn clear)

Table IB. Effect of concentration of ammonium hydroxide

NH ₄ OH Concentration (ppm)	Appearance of PTC Solution	NH ₄ OH Concentration (ppm)	Appearance of PTC Solution
0	Clear	300	Clear
0	Translucent	300	Clear
0	Translucent	331	Clear
132	Clear	331	Clear
164	Clear	331	Clear
189	Clear	>500	Precipitate
240	Clear	662	Translucent
250	Clear	>750	Precipitate
257.3	Clear	1,324	Gel
265	Clear	1,500	Precipitate
265	Clear	1,501	Precipitate

[0061] Example III

[0062] A PTC solution was prepared as described in Example I with 300 ppm of NH₄OH, except that the final solution was aged without stirring. It was observed that the viscosity of the PTC solution increased over time and the solution became translucent over time. Gelation occurred in the solution when its pH reached around 5.

[0063] Example IV

[0064] PTC solutions were prepared as in Example I, with 300 ppm of NH₄OH in the mixed solution. Each PTC solution was then diluted with deionized water, with a dilution factor of 2, 4, 6, 8, 10, 12, or 15, respectively.

The diluted PTC solutions were stirred and aged at room temperature for 3 to 5 hours. The stability of observed transparency of these solutions after stirring and aging is shown in **FIG. 5**, where a higher y-value indicates a higher stability. It was observed that when the dilution factor is 8 or greater, the diluted solution became completely clear after stirring and aging. Further, even when the diluted solution was re-concentrated after stirring and aging, the re-concentrated solution remained transparent over time.

[0065] Another diluted PTC solution was prepared as above with a dilution factor of 4, and was aged at a temperature of about 4 °C in a refrigerator for two weeks. The transparency, pH values, and UV spectrum of this solution were observed or measured daily. The results are shown in **Table II** and **FIG. 6**.

Table II. Relationships between pH and Optical Properties

pH	Color	Transparency	Peaks in Spectrum	Peak wavelength (nm)
0.65	Dark-red	Translucent	Two peaks	397 & 281
0.99	Red orange	Translucent	Two peaks	397 & 281
2.21	Orange	Translucent	No sharp peak	-
3.90	Light orange	Translucent	No sharp peak	-
5.80	Yellow	Cloudy	One peak	245
6.70	Pale yellow	Translucent	One peak	245
8.37	Pale yellow	Translucent	One peak	245

[0066] Example V

[0067] A diluted PTC solution was prepared as in Example IV, with a dilution factor of 8. This diluted PTC solution was found to be very stable, and had a pH of around 7.8.

[0068] A portion of the diluted solution without being subjected to hydrothermal treatment was sprayed on glass slides to form a coating completely covering the slides. The haze level of the coating was about 0.6 to 0.8, which was measured according to the ASTM standard (D1003-95). The coating on a first slide was heated to 110°C for 30 minute. The coating on a second slide was dried at room temperature. The two coated slides were then exposed to sunlight and light from a Xenon lamp, respectively. The water contact angles for each coated slide after different periods of exposure to sunlight or light from the Xenon lamp were measured, and are shown in **FIGS. 7** (sunlight) and **8** (Xenon lamp). The diamond points represent the data for the first, heated slide, and the square points represent the data for the

second, unheated slide. The triangle points represent data for a third, control sample slide, which will be described below in Example VI. As shown in **FIG. 7**, the water contact angles decreased substantially after exposure to sunlight for both the first and second slides, from about 50° or above to below about 5° after 50 minutes of exposure. **FIG. 8** similarly shows that the water angles in both cases decreased significantly after about 20 minutes of irradiation. As shown, both heated and unheated coating surfaces exhibited substantial super-hydrophilicity after about one hour exposure. The results indicate that it is not necessary to heat the TiO₂ coating to obtain substantial super-hydrophilicity. This indicates that application at room temperature is possible. It is generally expected that the TiO₂ in the PTC particles in the unheated coating were in the amorphous phase. Heat treatment is needed for producing anatase TiO₂, making it difficult for on-site application.

[0069] The diluted PTC solution was subjected to a hydrothermal treatment at 100°C for up to 8 hours. The pH values of the solution were monitored during the hydrothermal treatment and the measured values were 8.5, 8.9, 9.5, and 9.6 after 2, 4, 6, and 8 hours of treatment, respectively. XRD spectra were also obtained at these time intervals, which are shown in **FIG. 9**. As shown, there is a peak at $2\theta = 25.4^\circ$ for the heated samples, but there is no peak for the control sample. The amplitude of the peak also increases with the treatment time. The peak at $2\theta = 25.4^\circ$ indicates the formation of anatase TiO₂.

[0070] After the hydrothermal treatment, the treated solution was dried by removing water from the solution, using a rotary evaporator. About two third of the water in the solution was removed. The concentrated solution had a measured pH of around 7.2.

[0071] A portion of the concentrated solution was sprayed onto a ceramic tile surface to form a coating. Two coated samples were prepared. One coated sample was heated at 450 °C for 30 minutes and the other was not heated. The coating was then covered with methylene violate dye (MV; 0.05% aqueous). The surfaces of both coated samples were irradiated with blacklight blue (BLB) UV light and color change on the surfaces was monitored. The UV

light had a wavelength of 300 to 400 nm at a power density of 1.5 mW/cm², which were measured using a spectro-radiometer made by 4D Controls™ Ltd. The results of color change (ΔE) are shown in **FIG. 10** (triangles for the unheated sample and diamonds for the heated sample), along with results obtained from a control sample (lighter squares) and two comparison samples (circles and dark squares). Here, the control sample was not coated with any PTC particles, and the comparison samples were coated with TK100 (1%) sold by Techno Corp, Japan. As shown, the coating surfaces of both heated and unheated samples exhibited drastic color change, indicating extensive photocatalytic oxidation reactivity in the coating. In comparison, the control sample and comparison samples exhibited much less change in color.

[0072] In **FIG. 11**, color change during exposure to visible light for the heated sample and the control sample is shown. Here, the visible light was obtained by using a cut-off filter. The results showed that photocatalytic oxidation was induced by visible light in the sample coatings prepared according to an embodiment of the present invention, which was surprising. This means that it could be used indoor, for example, for de-odorization.

[0073] The concentrated solution was diluted again by a factor of 100. Images of the solution were obtained using a TEM before and after the hydrothermal treatment, which are shown in **FIGS. 12** (before heating) and **13** (after heating). As can be seen, the particle size of the PTC particles shown in **FIGS. 12** and **13** are much smaller than those prepared by a conventional technique where the dissolved PTC particles were pre-heated to temperatures up to 80°C. Before the heat treatment, the shape of the PTC was not very clear. After heating, the shapes and sizes of the PTC particles became more uniform and had sizes from 20 to 25 nm. It is believed that such heating cause large leaf-shaped particles to form.

[0074] In the above examples, it was found that the product solution remained stable even when the concentration of the PTC particles in the solution was up to 8 wt%.

[0075] Example VI (Comparison)

[0076] A comparison PTC solution prepared according a conventional technique was coated on a glass slide. The haze level of the coating was measured in the same way as in Example V, which was found to be about 1.3 to 1.5.

[0077] The change in water contact angles of the untreated samples is also shown in **FIGS. 7 and 8** (triangles). As shown, the water contact angles did not change much after about 50 minutes of exposure to sunlight, and even increased after exposure to light from the Xenon lamp.

[0078] Other features, benefits and advantages of the embodiments described herein not expressly mentioned above can be understood from this description and the drawings by those skilled in the art.

[0079] The contents of each reference cited above are hereby incorporated herein by reference.

[0080] Of course, the above described embodiments are intended to be illustrative only and in no way limiting. The described embodiments are susceptible to many modifications of form, arrangement of parts, details and order of operation. The invention, rather, is intended to encompass all such modification within its scope, as defined by the claims.

WHAT IS CLAIMED IS:

1. A method of preparing a solution comprising titanium dioxide particles, said method comprising:

reacting hydrous titanium oxide (HTO) and hydrogen peroxide (H_2O_2) in a solution, in the presence of a volatile base catalyst, to form a peroxy-titanium-complex (PTC);

diluting said solution comprising said PTC by a factor of at least 2, resulting in a diluted solution comprising said PTC; and

removing, by evaporation, a portion of said volatile catalyst from said diluted solution, to form particles that comprise titanium dioxide and said PTC adsorbed to said titanium dioxide, so that, after said removing, said solution has a pH of about 7 and is transparent.
2. The method of claim 1, wherein said pH of about 7 is from 5.5 to 8.5.
3. The method of claim 1, wherein said pH of about 7 is from 6.5 to 7.5.
4. The method of any one of claims 1 to 3, comprising agitating said solution during said reacting and agitating said diluted solution during said removing.
5. The method of any one of claims 1 to 4, wherein said catalyst is a weak base.
6. The method of claim 5, wherein said weak base is selected from ammonium hydroxide and amine.
7. The method of claim 6, wherein said solution comprises, before said reacting, from about 50 to about 600 ppm of said catalyst.
8. The method of any one of claims 1 to 7, comprising cooling said solution.
9. The method of any one of claims 1 to 8, wherein said solution is cooled to a temperature below about 5°C before said reacting.

10. The method of any one of claims 1 to 9, wherein said solution is cooled to a temperature of about 7 °C during said reacting.
11. The method of any one of claims 1 to 10, wherein said diluting comprises diluting said solution by a factor of 2 to 100.
12. The method of any one of claims 1 to 10, wherein said diluting comprises diluting said solution by a factor of 6 to 15.
13. The method of any one of claims 1 to 12, wherein said diluting comprises adding deionized water to said solution.
14. The method of claim 13, wherein said deionized water has a temperature between 5°C and room temperature.
15. The method of any one of claims 1 to 14, comprising heating said particles to form anatase TiO₂.
16. The method of any one of claims 1 to 15, comprising, after said removing, heating said particles to a temperature from about 90 to about 130 °C.
17. The method of claim 16, wherein said particles are heated for about 30 minutes to about 10 hours.
18. The method of any one of claims 1 to 17, wherein said particles are heated in said diluted solution.
19. The method of any one of claims 1 to 18, wherein said evaporation comprises evaporation of said diluted solution for about 30 minutes to about 4 hours.
20. The method of any one of claims 1 to 19, wherein said hydrous titanium oxide is prepared by a process comprising

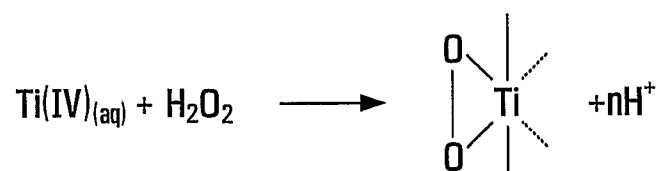
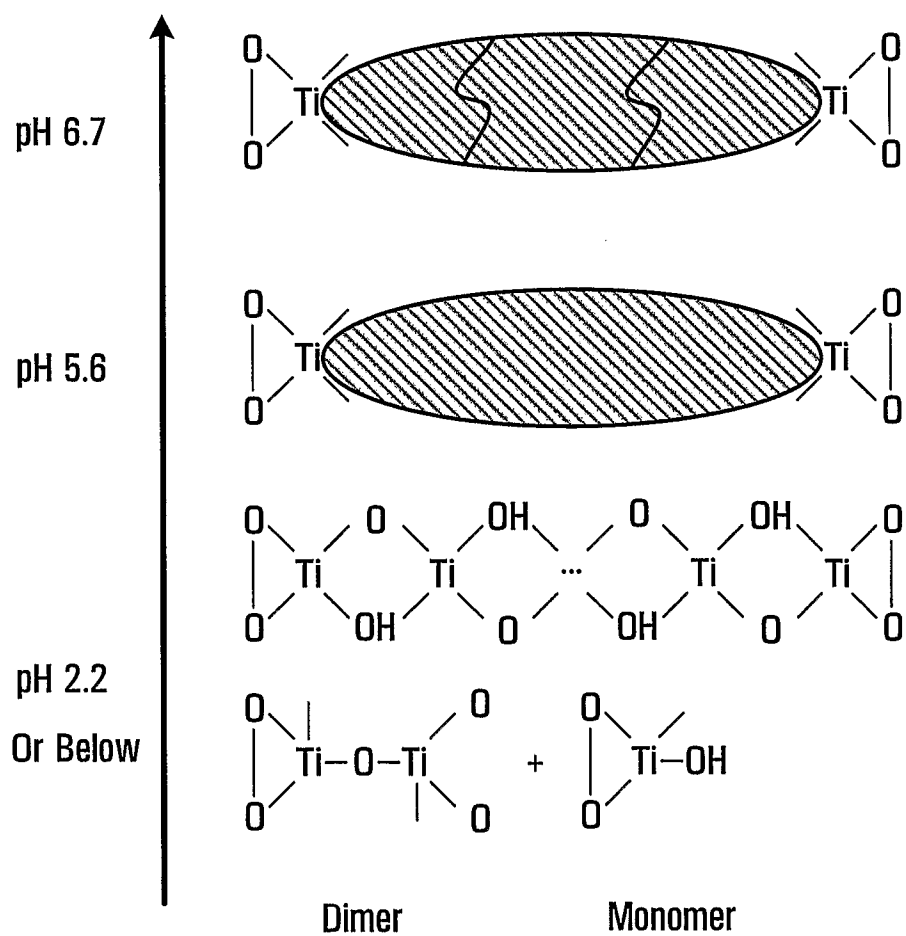
mixing a Ti(IV) source and a basic substance in an aqueous solution, said basic substance being present in an amount such that said aqueous solution has a pH from 6 to 7, to form a precipitate comprising hydrous titanium oxide; and

recovering said precipitate.

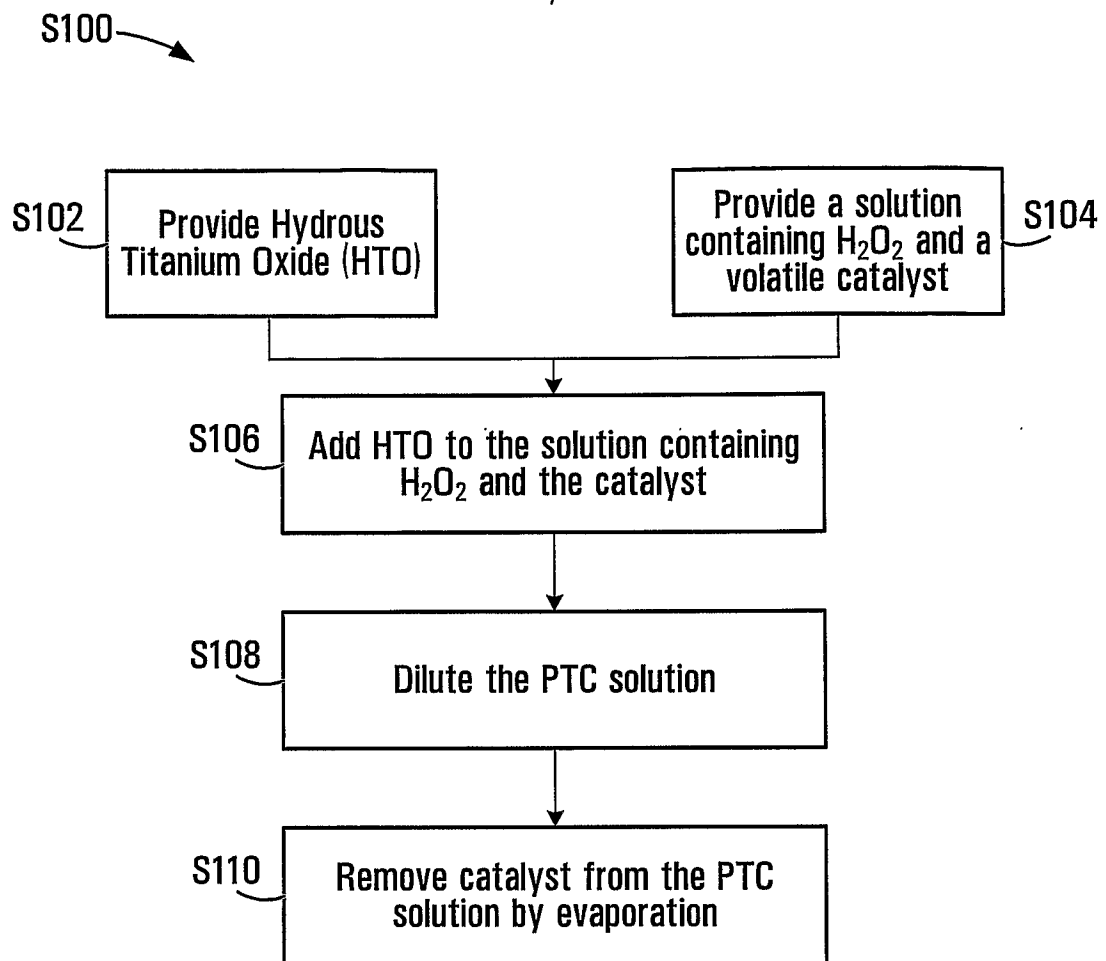
21. The method of claim 20, wherein said basic substance is a volatile weak base.
22. The method of claim 21, wherein said basic substance comprises ammonium hydroxide.
23. The method of any one of claims 20 to 22, wherein said mixing comprises:
- dissolving said Ti(IV) source in acidified water to form a Ti solution;
 - adding a dilute solution of said basic substance to said Ti solution; and
 - subsequently
 - adding a concentrated solution of said basic substance to said Ti solution.
24. The method of claim 23, wherein said dilute solution comprises 0.1 to 5 wt% of said basic substance and said concentrated solution comprises 15 to 30 wt% of said basic substance.
25. The method of any one of claims 20 to 24, comprising washing said precipitate with deionized water.
26. The method of any one of claims 20 to 25, wherein said Ti(IV) source is a titanium salt selected from titanium tetrachloride (TiCl_4), titanium tetrafluoride (TiF_4), titanium sulphate (TiOSO_4), titanium tetranitrate ($\text{Ti}(\text{NO}_3)_4$), and alkoxy titanium ($\text{Ti}(\text{OR})_4$).
27. The method of claim 26, wherein said titanium salt is TiCl_4 .
28. A solution comprising titanium dioxide particles, prepared according to the method of any one of claims 1 to 27, wherein said titanium dioxide particles comprise titanium dioxide and PTC adsorbed to said titanium dioxide and have a zeta potential of -60 to -80 mV.
29. The solution of claim 28, wherein said particles in said solution have particle sizes from 10 nm to 25 nm.

30. The solution of claim 28 or claim 29, wherein the concentration of said particles in said solution is from 6 to 8 wt%.
31. The solution of claim 28 or claim 29, wherein the concentration of said particles in said solution is higher than 4 wt%.
32. A solution comprising:
- an aqueous solvent; and
 - titanium dioxide (TiO_2) particles dispersed in said solvent, said TiO_2 particles comprising titanium dioxide and peroxo-titanium complex (PTC) adsorbed to said titanium dioxide, said PTC comprising peroxo-ligands bonded to Ti(IV), said TiO_2 particles having particle sizes from 10 nm to 25 nm and a zeta potential from -60 to -80 mV, the concentration of said TiO_2 particles in said solution being higher than 4 wt%;
- wherein said solution has a pH of about 7 and is transparent.
33. The solution of claim 32, wherein said solution has a pH of about 7.
34. The solution of claim 32 or claim 33, wherein said TiO_2 particles comprise anatase TiO_2 .
35. The solution of claim 32 or claim 33, wherein said TiO_2 particles comprise amorphous TiO_2 .
36. The solution of any one of claims 32 to 35, wherein said TiO_2 particles in said solution exhibit photocatalytic activities in response to irradiation of visible light.
37. The solution of any one of claims 32 to 36, wherein said concentration of said TiO_2 particles in said solution is from 6 to 8 wt%.

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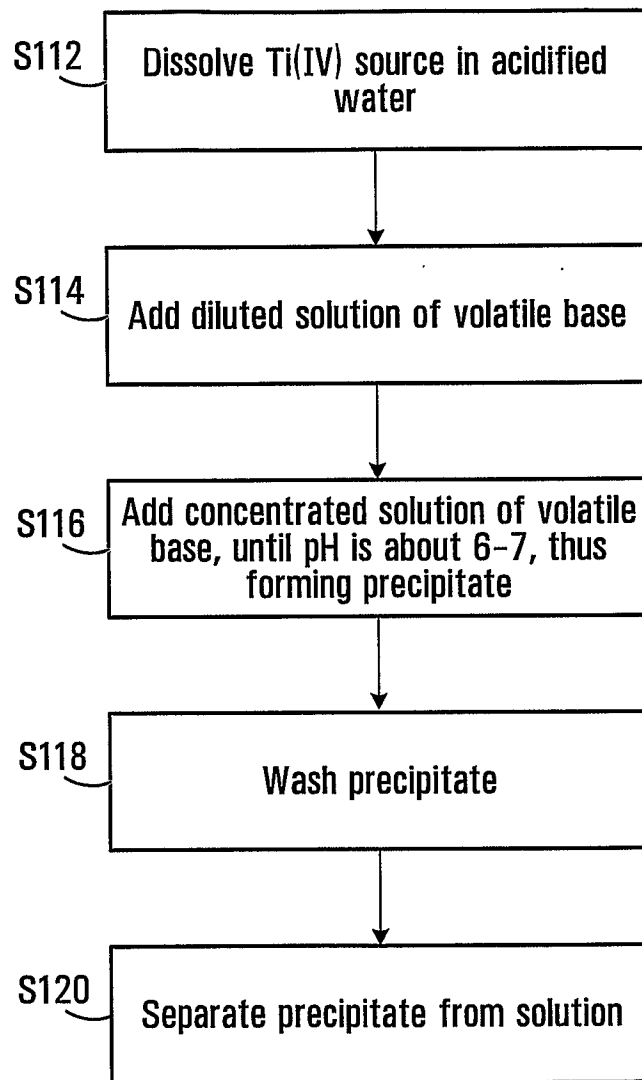
**FIG. 1****FIG. 2**

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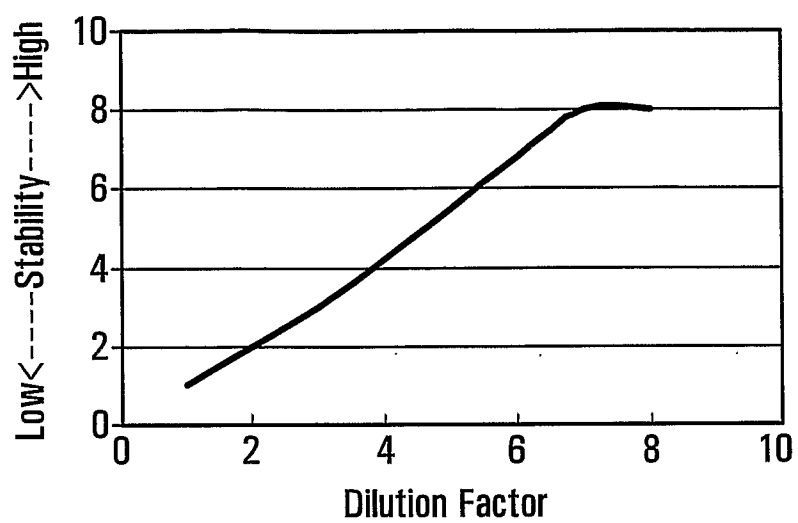
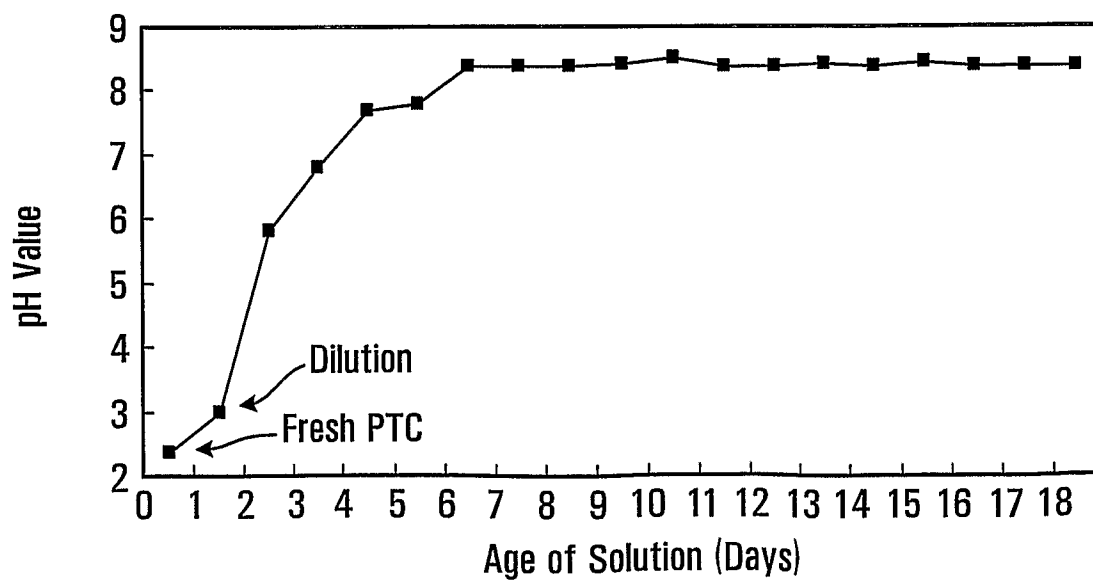
**FIG. 3**

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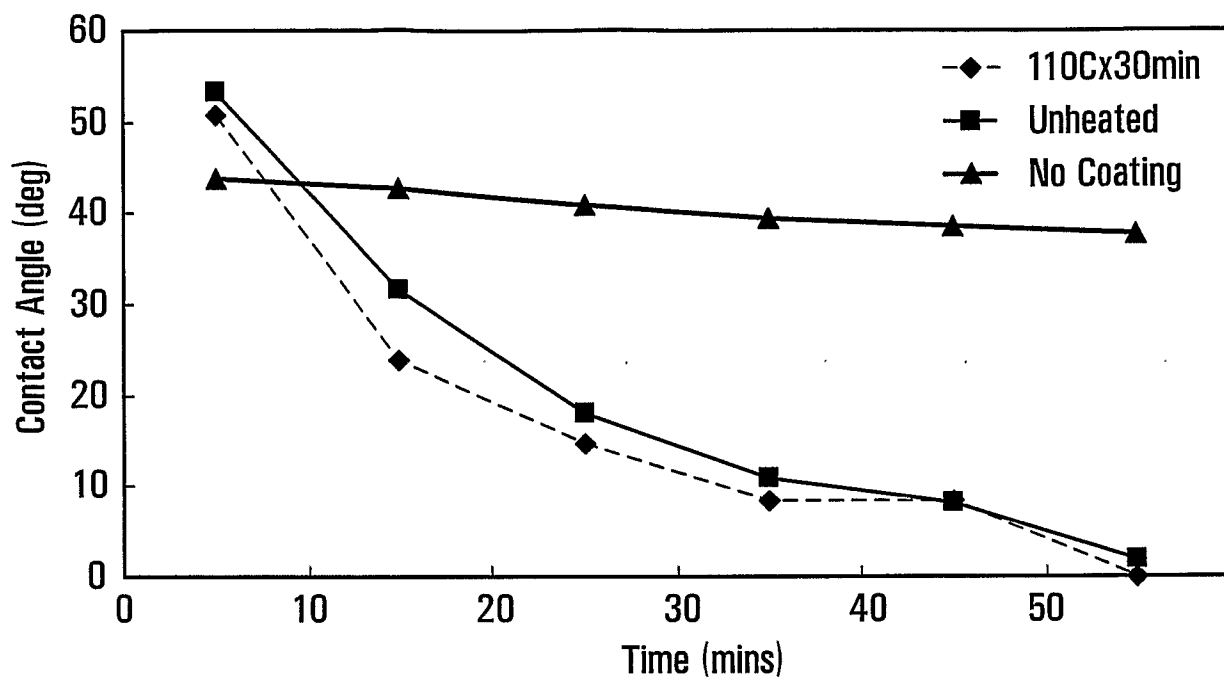
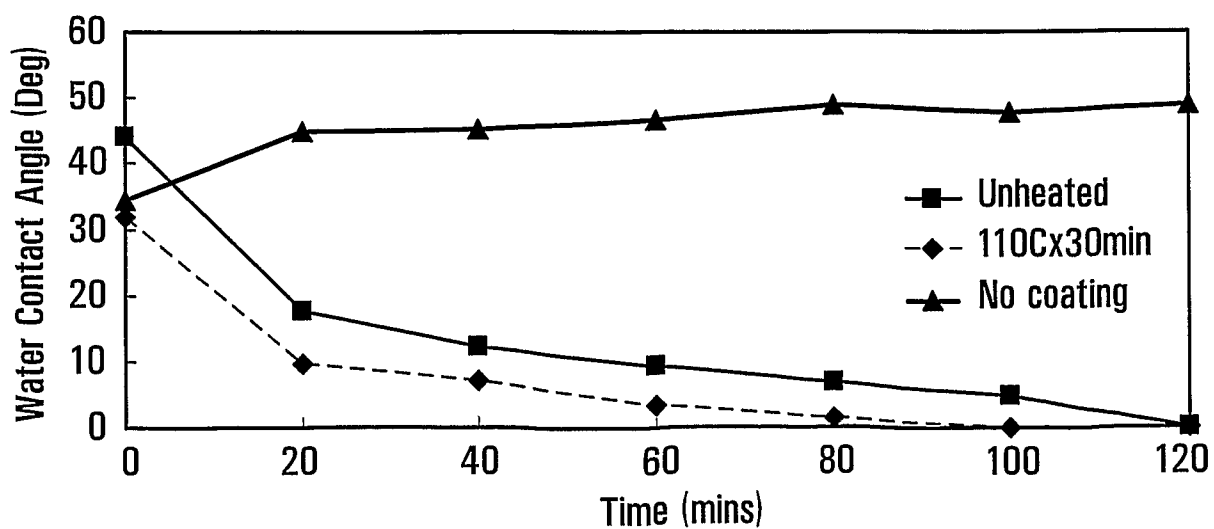
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**FIG. 4**

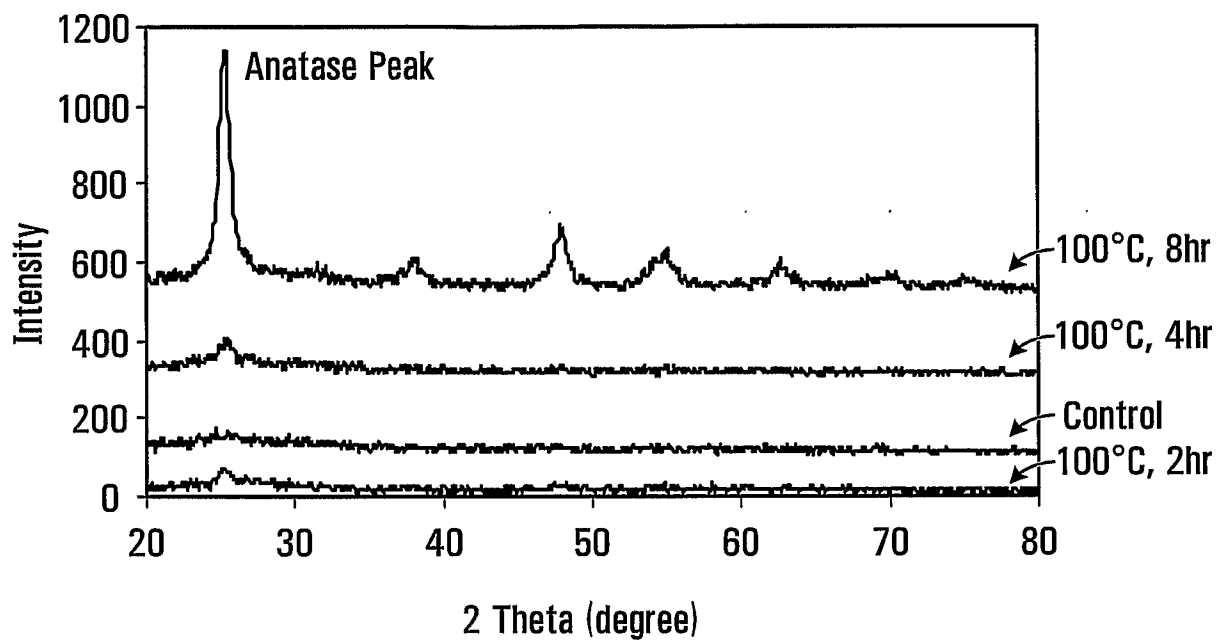
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**FIG. 5****FIG. 6**

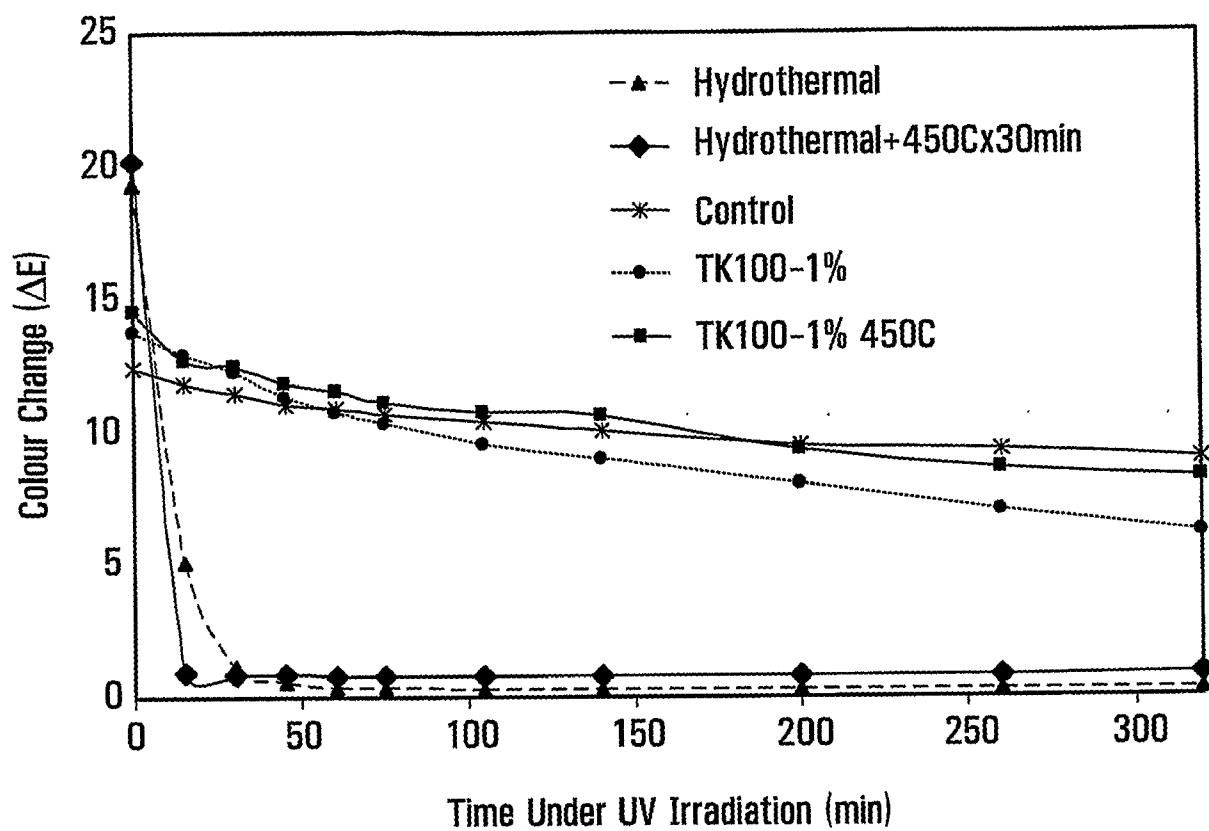
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**FIG. 7****FIG. 8**

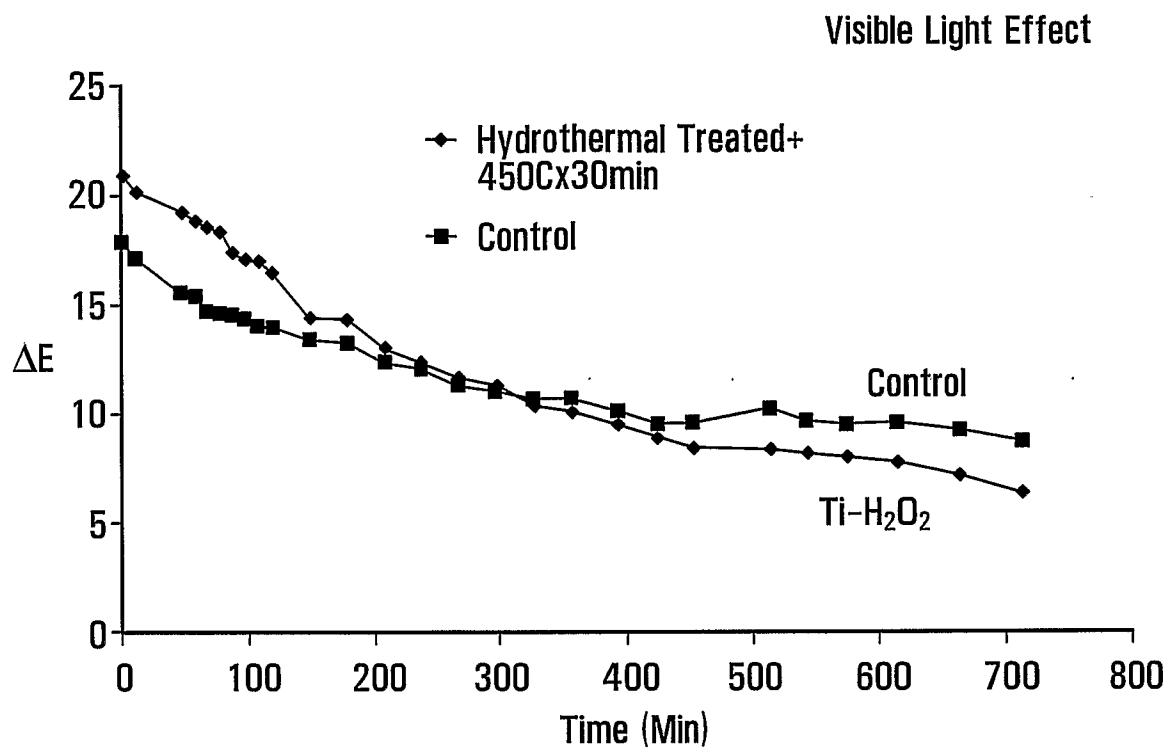
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**FIG. 9**

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**FIG. 10**

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**FIG. 11**

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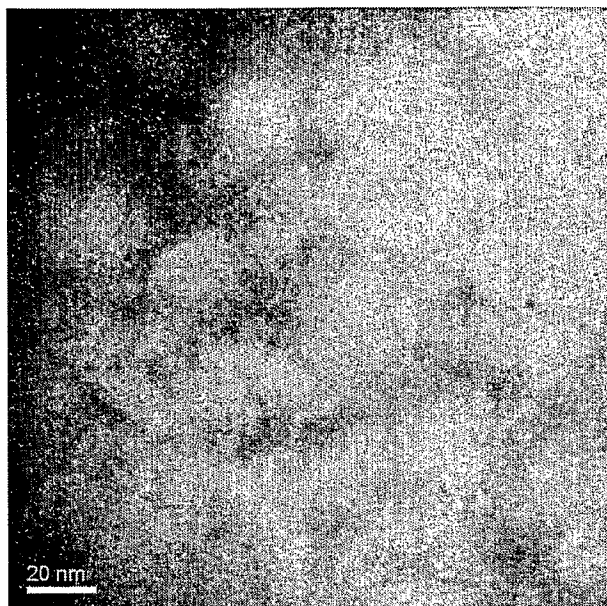


FIG. 12

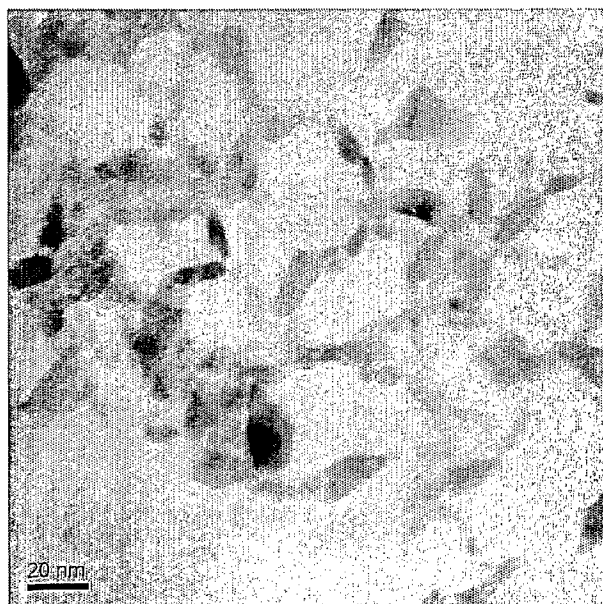


FIG. 13

INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2007/000221

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C01G 23/00 (2006.01) C01G 23/047 (2006.01) C01G 23/053 (2006.01)

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)

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)

CAPLUS, WPIDS, JAPIO: Keywords (TITANIA, TITANIUM OXIDE, PEROXO, HYDROGEN PEROXIDE) and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1031538 A1 (SAGA PREFECTURE) 30 August 2000 Whole document	1-37
A	EP 1449891 A1 (KANSAI PAINT CO LTD) 25 August 2004 Whole document	1-37



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	"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
"E" earlier application or patent 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

31 August 2007

Date of mailing of the international search report

14 SEP 2007

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2007/000221

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	Lei Ge et al, "Preparation of TiO ₂ thin films using inorganic peroxo titanic complex and autoclaved sols as precursors", Key Engineering Materials, Vols 280-283 (2005) 809-812 Whole document	1-37
A	Patent Abstracts of Japan, JP 01-224220 (CATALYST & CHEM IND CO LTD) 7 September 1989 Abstract	1-37
A	Patent Abstracts of Japan, JP 11-349330 (MURATA MFG CO LTD) 21 December 1999 Abstract	1-37

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SG2007/000221

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
EP	1031538	CA	2299187	JP	2000247638	JP	2000247639
		JP	2001048538	KR	2001000668	US	6602918
JP	11349330						
JP	1224220						
EP	1449891	CN	1578814	US	7077895	US	2004244648
		US	2005205165	WO	03037996		
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.							
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