(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 October 2004 (14.10.2004)

PCT

(10) International Publication Number
WO 2004/087578 A1

(51) International Patent Classification[7]: C01G 23/047

(21) International Application Number:
PCT/KR2003/001063

(22) International Filing Date: 30 May 2003 (30.05.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10-2003-0021092 3 April 2003 (03.04.2003) KR

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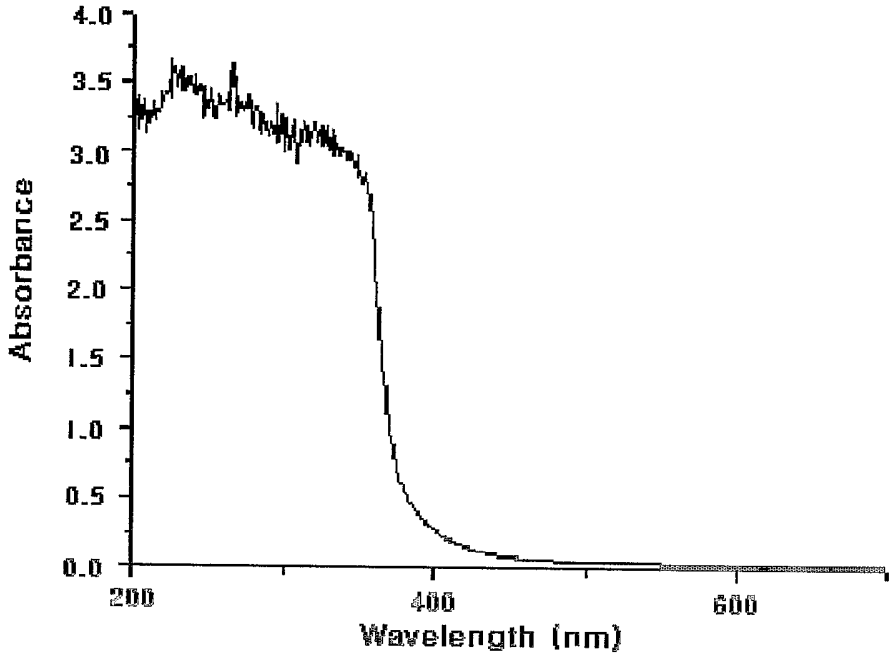
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

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

Published:
— *with international search report*

[Continued on next page]

(54) **Title:** NON-ACIDIC, NON-BASIC COLLOID SOLUTION CONTAINING DISPERSED TITANIUM DIOXIDE, METHOD OF MANUFACTURING THE SAME, AND COATING MATERIAL COMPRISING THE COLLOID SOLUTION



(57) **Abstract:** The present invention relates to a method of manufacturing a neutral and transparent titanium dioxide colloid solution wherein titanium dioxide nano particles is dispersed, and a novel titanium dioxide colloid solution prepared by the method. In addition, the present invention relates to a multifunctional, normal temperature curing-type coating agent comprising the titanium dioxide colloid solution.

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

Non-acidic, non-basic colloid solution containing dispersed titanium dioxide, method of manufacturing the same, and coating material comprising the colloid solution

Field of The Invention

The present invention relates to a method of manufacturing a non-acidic, non-basic, transparent titanium dioxide colloid solution which is dispersed with nano-sized titanium dioxide particles, and improved titanium dioxide colloid solution prepared by the method. Also, the present invention relates to a multifunctional, normal temperature curing-type coating agent comprising a proper additive in addition to the titanium dioxide colloid solution.

Background of The Invention

Titanium dioxide is used in various fields such as optics, pigment, semiconductor, catalyst, ultraviolet blocking agent, polymer filler and ceramics since it is chemically and physically stable. In particular, if the titanium dioxide becomes nano-sized particles, its specific surface area and the number of particles are largely increased, giving it various applications such as photocatalyst, ultraviolet blocking agent, or filler for transparent polymer materials, and the like. For example, when one spherical micron size particle is divided into nano-sized particles, the number of particles can be increased to 1 billion and its specific surface area is increased a million times. Therefore, the UV blocking effect by nano-sized particles is increased (about a billion times) and its catalytic property may be increased to 1 million times that of nano-sized particles of the same weight.

However, if the specific surface area of particles is largely increased, it is accompanied by an increase of the surface tension thereof in the same condition. As a result, the particles may be easily coagulated, which results in an increase of particle size. Since the nano-sized particles are metastable, the state of such particles are unstable. On the other hand, such unstable particles can be easily adsorbed and adhered

onto the surface of other bodies.

The point of zero charge of titanium dioxide particles' surface that suppresses coagulation of the particles in a solution is acidic. For this reason, a strong acidic solution dispersed with titanium dioxide particles has been prepared so as to prevent the titanium dioxide particles from coagulating. This strong acidic property restricts the use of the colloid solution containing dispersed titanium dioxide particles or the solution containing dispersed macro particles, and causes a dangerous problem to the working environment or workers.

A method of manufacturing a neutral titanium dioxide solution to solve the above problems has been developed, but this method is comprised of several steps, such as precipitating titanium dioxide in the aqueous solution, filtering the precipitates and then drying, and re-dispersing it in the solvent by an ultrasonic method or vigorous mechanical stirring method. However, because it is impossible to re-ground and re-disperse the coagulated nano-sized particles by using an ultrasonic method or stirring method, and the filtering step is a time consuming procedure, its productivity is very low and the cost of production is very high. Furthermore, the nano-sized particles can be easily re-coagulated at a little higher temperature, thus a transparent colloid solution which is uniformly dispersed with nano-sized particles of less than 10nm could not be produced by this method.

Furthermore, due to such a coagulation phenomenon, less than 3% of titanium dioxide can be dispersed in the conventional titanium dioxide colloid solution. Such low concentration of titanium dioxide colloid solution causes serious problems of cost, applicability or productivity, etc., due to difficulties in transportation, storage or production.

The present invention provides a method of manufacturing a colloid solution which is dispersed with nano-sized titanium dioxide particles in one step without performing conventional multi-steps, including the filtering or re-dispersing steps. More particularly, the present invention provides a colloid solution which is 1~ 5 % by weight of dispersed titanium dioxide which is superior to the conventional colloid solution, which is 1~3 % by weight of dispersed titanium dioxide.

The titanium dioxide colloid solution prepared by the present method is a high

concentration (3 ~ 5 % by weight) and neutral solution, thus its application field can be greatly extended.

Disclosure of The Invention

An object of the present invention is to provide a method of manufacturing a neutral and transparent titanium dioxide (TiO_2) colloid solution in which nano-sized titanium dioxide particles are dispersed.

Another object of the present invention is to provide a neutral and transparent titanium dioxide (TiO_2) colloid solution_prepared by the present method, in which nano-sized titanium dioxide particles are dispersed.

Yet another object of the present invention is to provide a multifunctional, normal temperature curing-type coating agent containing the said titanium dioxide (TiO_2) colloid solution.

The said objects and other objects may be achieved according to the present invention illustrating herein below.

Brief Description of The Drawings

Figure 1 shows the absorbance of the colloid solution of Example 1 at the wavelength regions of the UV/visible light. When measuring, the colloid solution was diluted with water, and thus contained 1.5% by weight of dispersed titanium dioxide (TiO_2).

Figure 2 shows the absorbance of the colloid solution of Example 9 at the wavelength regions of the UV/visible light. When measuring, the colloid solution was diluted with water, and thus contained 1.5% by weight of dispersed titanium dioxide (TiO_2).

Figure 3 shows the absorbance of the thin film coating of the colloid solution of Example 1 on the glass plate, measured at the wavelength regions of the UV/visible light.

Figure 4 shows the crystallinity of the thin film coating of the colloid solution of

Example 1 on the glass plate, measured by XRD.

Figure 5 shows the morphology of the TiO_2 particles dispersed in the colloid solution of Example 1 measured by transmission electron microscope (TEM).

Figure 6 shows the morphology of the TiO_2 particles dispersed in the colloid solution of Example 9 measured by TEM.

Figure 7 shows the morphology of the TiO_2 particles dispersed in the colloid solution of Example 8 measured by TEM.

Detailed Description of The Invention

In one aspect, the present invention provides a method of manufacturing a neutral and transparent titanium dioxide (TiO_2) colloid solution which is dispersed with nano-sized titanium dioxide particles. The present method can be classified into a water-based method and an alcohol-based method of manufacturing a titanium dioxide colloid solution depending on the kind of solvent used.

A water-based method of manufacturing a titanium dioxide colloid solution comprises the following steps:

(A) adding a titanium compound and a stabilizer to alcohol;

(B) slowly adding the reacted solution to distilled water by stirring;

(C) neutralizing the resulting solution by adding a basic solution; and

(D) heating the neutralized solution at a temperature of above 85℃.

At step (A), a titanium compound and a stabilizer may be added in any order. Furthermore, after adding a titanium compound to an alcohol solution and before adding the stabilizer, 0.01 ~ 2% by weight of 40% aqueous titanium tetrachloride solution based on the total solution can be added to facilitate the hydrolysis. At this time, since a very vigorous exothermic reaction is carried out, the reaction is continued by sufficient stirring until the exothermic reaction is finished.

At step (B), stirring is continued for enough time, preferably more than 1 hour, after adding the distilled water to the reacted solution at room temperature. At step (C), the pH of the resulting solution is adjusted to 6~8 by slowly adding a basic solution. At step (D), after heating the solution for more than 7 hrs, a neutral and transparent

titanium dioxide (TiO_2) colloid solution which is dispersed with titanium dioxide particles of anatase structure and a size of less than 10 nm may be obtained.

The alcohol-based method of manufacturing a titanium dioxide colloid solution comprises the following steps:

(a) adding a titanium compound and a stabilizer into alcohol;

(b) neutralizing the resulting solution by adding a basic solution thereto; and

(c) heating the neutralized solution at a temperature of above 75℃ for more than 7 hrs.

At step (a), a titanium compound and a stabilizer may be added in any order. Furthermore, prior to step (b), 0.01 ~ 2 % by weight of 40% aqueous titanium tetrachloride solution based on the total solution is added, or 2 ~ 10 % by weight of distilled water based on the total solution is added to facilitate the hydrolysis. Also, the solution is stirred for enough time, preferably more than 1 hr at room temperature. At step (b), the pH of the resulting solution is controlled with 6~8 by adding slowly a basic solution. At step (c), after heating the solution for more than 7 hrs, a neutral and transparent titanium dioxide (TiO_2) colloid solution which is dispersed with titanium dioxide particles of anatase structure and a size of less than 10 nm may be obtained.

In the method of manufacturing the above water-based or alcohol-based titanium dioxide colloid solution, the heating procedure of step (D) and step (c) may be replaced with a hydrothermal reaction at a temperature of above 120℃ for 5 hrs in a high temperature, high pressure reactor. This hydrothermal reaction produces a titanium dioxide colloid solution of excellent structural crystallinity, within a short reaction period.

The alcohol to be used in the present invention is a lower alcohol having 1 to 4 carbon atoms such as methanol, ethanol, propanol, isopropanol or butanol. In the water-based system, 1 ~ 50% by weight of alcohol based on 100 % by weight of the resulting titanium dioxide colloid solution is used; and in the alcohol-based system, 50 ~ 90 % by weight of alcohol based on 100 % by weight of the resulting titanium dioxide colloid solution is used.

In the present invention, the titanium compound can be any of the conventional titanium compounds and can be selected depending on the solvent used. However, if an

inorganic titanium compound such as titanium tetrachloride or titanium sulfate is used, an excess of basic compound should be added to neutralize the solution. This results in too high concentration of salts in the solution. Thus, it is preferable to use a mixture of inorganic titanium compound and organic titanium compound rather than an inorganic compound alone. Preferably, titanium(IV) isopropoxide (tetraisopropanol titanium), titanium(IV) butoxide, titanium(IV) ethoxide(titanium tetraethanolate), titanium(IV) methoxide, titanium stearate or a mixture thereof is used. Amongst these titanium compounds, titanium(IV) isopropoxide (tetraisopropanol titanium) is most preferable. Titanium compound is added in such amount that Titanium dioxide of 1 ~ 5 % by weight is dispersed in the resulting titanium dioxide solution.

The suitable stabilizer to be used in the present invention may be an organic acid having an alcohol group and a ketone group, or an organic acid having an alcohol group and an acetate group, and the salts thereof. Examples of the above organic acid include glycolic acid, glycolic salt, organic acid having a similar structure to glycolic acid and the salt thereof, oxalic acid and oxalate, and the salts thereof. Also, the above stabilizer may be selected from the group consisting of pentanediol, pentanedione, butanediol, butanedione, alkylacetoacetate, polyethylenglycol, cetyltrimethyl ammonium hydroxide, polyvinyl acetate, polyvinyl alcohol, trialkylalcohol amine, alkylalcohol ammonium, or the mixture thereof. The amount of the stabilizer to be added is dependent on the molecular weight of the stabilizer used and is usually at least 0.1 % by weight, and preferably 1 ~ 3 % by weight based on 100 % by weight of resulting titanium dioxide colloid solution.

When an aqueous glycolic salt solution is used as a stabilizer, the amount of aqueous alkaline solution to be used in the neutralization may be reduced. When polyethylene glycol is used, the amount of polyethylene glycol to be added is dependent on its molecular weight. When the molecular weight of polyethylene glycol is about 3,000, about 0.1 ~ 2 % by weight of polyethylene glycol is added. When polyethylene glycol and glycolic acid are used together, glycolic acid is added first and then reacted sufficiently, to prevent precipitation, and then polyethylene glycol is added thereto.

When polyvinyl acetate is used, the amount of polyvinyl acetate to be added is

dependent on its molecular weight. When the molecular weight of polyvinyl acetate is about 100,000, about 0.1 ~ 2 % by weight of polyvinyl acetate is added. When the molecular weight of polyvinyl acetate exceeds the above range, its solubility becomes low. It is, therefore, preferable to use polyvinyl acetate of low molecular weight. When polyvinyl alcohol is used, because its solubility is lower than that of polyvinyl acetate, polyvinyl alcohol of low molecular weight is added and then heated. By doing so, it is possible to enhance the solubility of polyvinyl alcohol, resulting in an enhanced stability of the resulting colloid solution.

A solution of any basic compound may be used in the neutralization step. The basic solution may be properly selected according to the required adherence property of the resulting colloid solution and its use. Preferably, a solution of sodium hydroxide, a basic compound of alkaline metals, an ammonium compound, an amine compounds, a basic compound with alkyl ammonium group, a basic compound of alkali earth metal, or a poly basic compound having a cationic ion such as aluminum ion may be used as a basic solution. Ammonia is especially effective in preventing titanium dioxide from coagulating, because it is a strong Lewis base and acts as a strong ligand for titanium ion.

The amount of basic solution to be used may depend on the kind of stabilizer, and the amount is controlled by adjusting the pH of the solution to be 6 ~ 8 with the pH meter mounted on the reactor. Also, water glass or sodium metasilicate can be used instead of a basic solution in the neutralizing step, and the resulting titanium dioxide colloid solution will have excellent adherence.

In the present method of manufacturing the titanium dioxide colloid solution, in addition to the titanium compound, if necessary, organic silicon compound, aluminum compound, zirconium compound, iron compound or the mixture thereof (hereinafter collectively referred as "organic silicon compound and the like") may be added. The silicon compound used in the present invention includes organic silicon compound having alkoxy group, alkyl acetoacetate functional group; organic silicon compound having glycolate, acetate group neighboring alcohol group or ketone group; organic silicon compound having ester and amine groups; and organic silicon compound having ketone and epoxide groups. The aluminum compound used in the present invention

may be aluminum acetate or aluminum chloride.

The organic silicon compound and the like are added to the extent that the ratio of TiO_2:SiO_2, which are dispersed in the resulting colloid solution, is below 2:1 (below 50 % by weight based on the content of titanium dioxide). The hydrolysis of organic silicon compound and the like together with titanium compound results in the improved adherence of the resulting titanium dioxide colloid solution to shaped articles.

The water-based or alcohol-based titanium dioxide colloid solution prepared by the present invention is cooled to room temperature, and 1 ml of the solution is diluted with 5 ml of water or alcohol, respectively. Thereafter the absorbance pattern of the solution is measured and analyzed using UV/visible spectroscope to estimate the size of nano particles and the uniformity of the size.

In another aspect, the present invention provides a new, neutral and transparent water-based or alcohol-based titanium dioxide colloid solution prepared by the said method, which contains 1 ~ 5 % by weight of dispersed nano-sized titanium dioxide particles.

In another aspect, the present invention provides a multifunctional, normal temperature curing-type coating agent with excellent transparency, adherence, crystallinity, absorbance and stability, which comprises a novel, neutral and transparent water-based or alcohol-based titanium dioxide colloid solution prepared by the said method, and in which 1 ~ 5 % by weight of nano-sized titanium dioxide particles are dispersed.

In still another aspect, the present invention provides products coated with the coating agent. The products to be coated include products of polymer, wood, leather, ceramic, metal, glass, paper, tile, wallpaper, fiber, and optical lens.

In another aspect, the present invention provides a neutral and transparent water-based or alcohol-based titanium dioxide colloid composition, in which the composition comprises 1 ~ 5 % by weight of dispersed titanium dioxide; 0.1 % or more by weight of the stabilizer selected from the group consisting of glycolic acid, pentanediol, pentanedione, butanediol, butanedione, aqueous glycolic salt solution, and a mixture thereof; basic solution in the amount capable of neutralizing the stabilizer; and the reminder of solvent such as water or alcohol.

Titanium dioxide colloid solution according to the present invention contains dispersed TiO_2 uniform nano particles below 10nm in size, and it is clear and transparent. The above colloid solution is stable even after it is allowed to stand for a long time (more than 2 years). The solution is also stable without occurring aggregation even at a temperature higher than 100 ℃. Furthermore, since it contains to the extent of 5% by weight of dispersed titanium dioxide particles, if desired, it is possible to use the colloid solution with various concentrations. Also, the colloid solution is very stable without occurring aggregation even if it is mixed with other colloid solutions.

In another aspect, the present invention provides a multifunctional, normal temperature curing-type coating agent, which comprises the titanium dioxide colloid solution. The coating agent comprising the titanium dioxide colloid solution of the present invention has excellent transparency, adherence, crystallinity, absorbance and stability, and can be thus used as a coating agent for polymer, ceramic, fabric, metal, paper or glass-made articles and as a filler for transparent coating paint, and the like.

It is not necessary to use a specific material produced by a specific company to reproduce the Examples, and but it is preferable to use a compound with high purity. In the Examples, the materials of Dupont or Daw Corning Company were mostly used.

Examples

Example 1

175g of tetraisopropanol titanium and 5g of TEOS (TetraEthoxySilane) were added to 100ml of ethanol, and then dissolved. Thereafter, 5ml of 40% aqueous titanium tetrachloride solution were added thereto while the solution was slowly stirred, and the hydrolysis was carried out. 2ml of pentanediol and 6g of glycolic acid were added to the resulting solution and then reacted sufficiently. Thereafter, 750ml of distilled water were added to the above solution by stirring vigorously. The stirring was continued at room temperature for about 1 hr. The pH of this solution was adjusted to 7 by adding slowly 3M aqueous sodium hydroxide solution to the solution. After heating the resulting solution at a temperature of 85℃ for 7 hrs, a clear and transparent colloid solution containing dispersed titanium dioxide nano particles (below 10 nm) having of anatase structure was obtained.

Example 2

After 6g of glycolic acid were dissolved in 100ml of ethanol, 150g of titanium tetraethanolate and 5g of TEOS were also dissolved thereto. 2ml of 40% aqueous titanium tetrachloride solution were added to this solution, and the hydrolysis was carried out. Thereafter, 500ml of distilled water was added slowly by stirring vigorously, and the stirring was continued at room temperature for 1 hour. The pH of the resulting solution was adjusted to 7 by adding slowly 3M aqueous sodium hydroxide solution. The solution was heated at a temperature of 85℃ for 7 hrs to obtain a clear and transparent colloid solution.

Example 3

The procedure of Example 1 was repeated, except that 8g of glycolic acid instead of aqueous titanium tetrachloride solution were added. A clear and transparent colloid solution was obtained.

Example 4

The procedure of Example 1 was repeated, except that as a stabilizer, a mixture of 6g of glycolic acid and 3ml of polyethylene glycol was used. A clear and transparent colloid solution was obtained.

Example 5

After 175g of tetraisopropanol titanium and 5g of TEOS were dissolved in 100ml of ethanol, 6g of glycolic acid and 2g of cetyltrimethyl ammonium chloride were added thereto, and then reacted sufficiently for 1 hr. 750ml of distilled water was slowly added to the above solution while the solution was vigorously stirred. The stirring was continued at room temperature for about 1 hour. Thereafter, pH of the solution was adjusted to 7 by slowly adding 3M aqueous sodium hydroxide solution. After heating the resulting solution at a temperature of 85℃ for 7 hrs, a clear and transparent colloid solution containing dispersed titanium dioxide nano particles (below 10 nm) of antase structure was obtained.

Example 6

The procedure of Example 1 was repeated, except that polyvinyl acetate instead of cetyltrimethyl ammonium chloride was used. A clear and transparent colloid solution was obtained.

Example 7

After 175g of tetraisopropanol titanium and 5g of TEOS were dissolved in 20ml of isopropanol, a solution of 6g of glycolic acid and 2 ml of nitric acid dissolved in 750 ml of distilled water was slowly added to the above isopropanol solution by stirring vigorously. The stirring was continued at room temperature for 1 hour. Thereafter, pH of the solution was adjusted to 7 by slowly adding 3M aqueous sodium hydroxide solution. After heating the resulting solution at a temperature of 85℃ for 7 hrs, a clear and transparent colloid solution containing dispersed titanium dioxide nano particles (below 10 nm) of anatase structure was obtained.

Example 8

The procedure of Example 1 was repeated, except that the hydrothermal reaction was carried out at a temperature of above 120℃ for about 5 hrs in the high temperature and high pressure reactor, instead of heating at a temperature of above 85℃ for about 7 hrs. A clear and transparent colloid solution was obtained.

Example 9

After 2ml of pentanediol and 6g of glycolic acid were dissolved in 800 ml of ethanol, 175g of tetraisopropanol titanium and 5g of TEOS were added thereto. 10ml of 40% aqueous titanium tetrachloride solution were added to this solution by stirring slowly and the hydrolysis was carried out. At this step, a vigorous exothermic reaction occurred, and the reaction was continued until the exothermic reaction stopped. Thereafter, pH of the solution was adjusted to 7 by slowly adding 3M aqueous sodium hydroxide solution. After heating the resulting solution at a temperature of 75℃ for 7 hrs, a clear and transparent colloid solution containing dispersed titanium dioxide nano

particles (below 10 nm) of antase structure was obtained.

Example 10

After 6g of glycolic acid were dissolved in 800ml of ethanol, 150g of titanium tetraethanolate and 5g of TEOS were added thereto. 2ml of 40% aqueous titanium tetrachloride solution was added to this solution, and the hydrolysis was carried out. Thereafter, 500ml of distilled solution was added thereto, and then hydrolyzed sufficiently while the solution was stirred for about 1 hour. pH of the solution was adjusted to 7 by slowly adding 3M aqueous sodium hydroxide solution. After heating the resulting solution at a temperature of 75℃ for 7 hrs, a clear and transparent colloid solution containing dispersed titanium dioxide nano particles (below 10 nm) of anatase structure was obtained.

Example 11

The procedure of Example 9 was repeated, but using 8g of glycolic acid and without adding the aqueous titanium tetrachloride solution. A clear and transparent colloid solution containing dispersed titanium dioxide nano particles (below 10 nm) of anatase structure was obtained.

Example 12

After 175g of tetraisopropanol titanium and 5g of TEOS were dissolved in 800ml of ethanol, 6g of glycolic acid and 2ml of cetyltrimethyl ammonium hydroxide were added thereto and the hydrolysis was sufficiently carried out. Thereafter, pH of the solution was adjusted to 7 by slowly adding 3M aqueous sodium hydroxide solution. After heating the resulting solution at a temperature of above 75℃ for 7 hrs, a clear and transparent colloid solution containing dispersed titanium dioxide nano particles (below 10 nm) of anatase structure was obtained.

Example 13

After 175g of tetraisopropanol titanium and 5g of TEOS were dissolved in 800ml of ethanol, 6g of glycolic acid and 2ml of nitric acid were added thereto. The stirring was continued at room temperature for 1 hour. Thereafter, pH of the solution was

adjusted to 7 by slowly adding 3M aqueous sodium hydroxide solution. After heating the resulting solution at a temperature of above 75℃ for 7 hrs, a clear and transparent colloid solution containing dispersed titanium dioxide nano particles (below 10 nm) of anatase structure was obtained.

Example 14

The procedure of Example 9 was repeated, except that the hydrothermal reaction was carried out at a temperature of above 120℃ for about 5 hrs in the high temperature and high pressure reactor, instead of heating at a temperature of above 75℃ for about 7 hrs. A clear and transparent colloid solution containing dispersed titanium dioxide nano particles (below 10 nm) of anatase structure was obtained.

Example 15

The procedure of Example 9 was repeated, except that pH of the solution was adjusted by using ammonia instead of sodium hydroxide. A clear and transparent colloid solution containing dispersed titanium dioxide nano particles (below 10 nm) of anatase structure was obtained.

The neutral, water-based or alcohol-based titanium dioxide colloid solutions prepared in the Examples were tested for the following properties, and the results were shown in Tables 1 and 2, and Figures 1 to 7.

Transparency

1ml of water-based or alcohol-based titanium dioxide colloid solution was diluted with 5ml of water or alcohol, respectively. The degree of light scattering in the solution was measured by using the UV/visible light spectroscope at the region of 410nm wavelength (the shortest wavelength region in which the light was not absorbed but scattered).

Adherence

1ml of water-based or alcohol-based titanium dioxide colloid solution was diluted with 5ml of water or alcohol, respectively. The solution was applied to the surface of a

glass plate by using a spin coating method, and then heat-treated in the thermostatic bath at a temperature of 110℃, and then rubbed with an eraser. The absorbance was measured by using the UV/visible light spectroscope at 350 nm.

Stability

After one month has elapsed, the degree of variance of the turbidity for titanium dioxide colloid solution was measured. The turbidity was measured with the same method for transparency.

Absorbance

It is a relative absorbance. 1ml of titanium dioxide colloid solution was diluted with 5ml of distilled water and absorbance was measured at 350nm wavelength.

Crystallinity for the nano particles

1ml of water-based or alcohol-based titanium dioxide colloid solution was diluted with 5ml of water or alcohol, respectively. The solution was applied twice on the surface of the glass plate by using a spin coating method, heat-treated at a temperature of 110℃ in the thermostatic bath, and then the crystallinity of the thin film was measured by using the X-ray Diffraction (XRD). The XRD was carried out at 1° because the film was very thin, and 2Θ was measured in the range from 10°to 80°, the scanning rate was 2°/min.

Table 1

Physical properties of water-based TiO_2 colloid solution

Example	Transparency	Adherence	Crystallinity	Absorbance	Stability
1	A	A	B	2.5	A
2	A	A	A	A	A
3	A	A	B	B	A
4	A	B	B	B	A
5	A	B	A	C	A
6	B	B	B	B	B

7	A	A	A	A	A
8	A	A	A	A	A

Note: A: excellent, B: good, C: normal, D: poor

For absorbance, A: higher than 2.5 of the Example 1,

B: same as 2.5 of the Example 1,

C: lower than 2.5 of the Example 1

Table 2

Physical properties of alcohol-based TiO_2 colloid solution

Example	Transparency	Adherence	Crystallinity	Absorbance	Stability
9	A	A	B	2.0	A
10	A	A	B	B	A
11	A	B	B	B	A
12	A	B	B	B	B
13	A	A	A	B	A
14	A	A	A	A	A
15	A	B	A	B	B

Industrial Applicability

A titanium dioxide colloid solution according to the present invention comprises dispersed titanium dioxide nano particles, and the colloid solution is clear and transparent. The colloid solution of the present invention is stable even after it is allowed to stand for a long time (more than two years), and the solution is also stable without occurring aggregation even at a temperature of above 100℃.

Furthermore, since the colloid solution contains to the extent of 5% by weight of dispersed titanium dioxide particles, if desired, it is possible to use the colloid solution with various concentration. Also, the colloid solution is very stable without occurring aggregation even if it is mixed with other colloid solutions.

In addition, a multifunctional, normal temperature curing-type coating agent is provided, which is composed of the titanium dioxide colloid solution. The coating agent, which is titanium dioxide colloid solution according to the present invention, has

excellent transparency, adherence, crystallinity, absorbance and stability, and can be thus used as a coating agent for polymer, wood, leather, metal, ceramic, glass, paper, tile, wallpaper, a fiber, or optical lens article or as a filler for transparent coating paint.

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Claims

1. A method of manufacturing a neutral and transparent water-based titanium dioxide colloid solution containing dispersed titanium dioxide nano particles, comprising the following steps:

(A) adding a titanium compound and a stabilizer to alcohol, wherein the said stabilizer is selected from the group consisting of an organic acid with alcohol group and ketone group, an organic acid with alcohol group and acetate group, and a salt thereof.;

(B) slowly adding the reacted solution to distilled water while the solution is stirred;

(C) neutralizing the resulting solution by adding a basic solution; and

(D) heating the neutralized solution at a temperature of above 85℃,

wherein at step (A), the titanium compound and the stabilizer can be added in any order.

2. The method according to claim 1, characterized in that at step (A), 40 % aqueous titanium tetrachloride solution is added to the solution, prior to the addition of the stabilizer and after adding a titanium compound to the alcohol.

3. The method according to claims 1 or 2, characterized in that the alcohol is added in the amount of 1 ~ 50% by weight, the stabilizer is added in the amount of at least 0.1% by weight based on the total solution, and the titanium compound is added in the amount of 1 ~ 5% by weight, which is calculated in terms of the amount of the TiO_2 dispersed in the resultant titanium colloid solution, and the balance is water.

4. The method according to claims 1 or 2, characterized in that the alcohol is selected from the group consisting of lower alcohol having 1~ 4 carbon atoms such as methanol, ethanol, propanol, isopropanol or butanol.

5. The method according to claims 1 or 2, characterized in that the titanium compound is selected from the group consisting of titanium(IV) isopropoxide (tetraisopropanol titanium), titanium(IV) butoxide, titanium(IV) ethoxide (titanium tetraethanolate), titanium(IV) methoxide, titanium (IV) stearate and a mixture thereof.

6. The method according to claims 1 or 2, characterized in that the stabilizer

further comprises pentanediol, pentanedione, butanediol, butanedione, alkylacetoacetate, polyethylenglycol, cetyltrimethyl ammonium hydroxide, polyvinyl acetate, polyvinyl alcohol, trialkylalcohol amine($(RO)_3N$), or a mixture thereof.

7. The method according to claims 1 or 2, characterized in that the basic solution is a solution of sodium hydroxide, a basic compound of alkaline metal, ammonium compound, an amine compound, a basic compound having an alkyl ammonium group, a basic compound of alkali earth metal, or a poly basic compound having a cationic ion such as aluminum ion.

8. The method according to claims 1 or 2, characterized in that at step (A), in addition to the titanium compound, an organic silicon compound, an aluminum compound, a zirconium compound, an iron compound or a mixture thereof is further added.

9. The method according to claims 1 or 2, characterized in that the heating procedure of step (D) is replaced with a hydrothermal reaction being carried out at a temperature of above 120℃ for 5 hrs in the high temperature, high pressure reactor.

10. A method of manufacturing a neutral and transparent alcohol-based titanium dioxide colloid solution containing dispersed titanium dioxide nano particles, comprising the following steps:

(a) adding a titanium compound and a stabilizer to alcohol, wherein the said stabilizer is selected from the group consisting of an organic acid with alcohol group and ketone group, an organic acid with alcohol group and acetate group and a salt thereof;

(b) neutralizing the resulting solution by adding a basic solution; and

(c) heating the neutralized solution at a temperature of above 75℃ for more than 7 hrs,

wherein at step (a), the titanium compound and the stabilizer can be added in any order.

11. The method according to claim 10, characterized in that prior to step b), 40% aqueous titanium tetrachloride solution is further added to the solution, or a distilled water is further added to the solution.

12. The method according to claims 10 or 11, characterized in that the alcohol

is added in the amount of 50 ~ 90% by weight, the stabilizer be added in the amount of at least 0.1% by weight based on the total solution, and the titanium dioxide compound be added in the amount of 1 ~ 5% by weight, which is calculated in terms of the amount of TiO_2 dispersed in the resultant titanium colloid solution, and the balance is water.

13. The method according to claims 10 or 11, characterized in that the alcohol is selected from the group consisting of lower alcohol having 1~ 4 of carbon atoms such as methanol, ethanol, propanol, isopropanol or butanol.

14. The method according to claims 10 or 11, characterized in that the titanium compound is selected from the group consisting of titanium(IV) isopropoxide (tetraisopropanol titanium), titanium(IV) butoxide, titanium(IV) ethoxide (titanium tetraethanolate), titanium(IV) methoxide, titanium(IV) stearate and a mixture thereof.

15. The method according to claims 10 or 11, characterized in that the stabilizer further comprises pentanediol, pentanedione, butanediol, butanedione, alkylacetoacetate, polyethylenglycol, cetyltrimethyl ammonium hydroxide, polyvinyl acetate, polyvinyl alcohol, trialkylalcohol amine($(RO)_3N$), or a mixture thereof.

16. The method according to claims 10 or 11, characterized in that the basic solution is a soultion of sodium hydroxide, basic compound of alkaline metal, ammonium compound, amine compound, basic compound having an alkyl ammonium group, basic compound of alkali earth metal, or poly basic compound having a cationic ion such as aluminum ion.

17. The method according to claims 10 or 11, characterized in that at step (A), in addition to the titanium compound, an organic silicon compound, an aluminum compound, a zirconium compound, an iron compound or a mixture thereof is further added.

18. The method according to claims 10 or 11, characterized in that the heating procedure of step (c) is replaced with a hydrothermal reaction being carried out at a temperature of above 120℃ for 5 hrs in the high temperature, high pressure reactor.

19. A neutral and transparent titanium dioxide colloid solution prepared by the method according to any one of claims 1 to 18, wherein 1 ~ 5 % by weight of titanium dioxide nano particles of anatase structure is dispersed.

20. A coating agent comprising the titanium dioxide colloid solution according to claim 19, wherein the coating agent has excellent transparency, adherence, crystallinity, absorbance and stability.

21. A product coated on the surface thereof with the coating agent according to claim 20.

22. A neutral, transparent, water-based or alcohol-based composition, wherein 1~5% by weight of TiO_2 is dispersed, and comprises at least 0.1% by weight of a stabilizer selected from the group consisting of glycolic acid, pentanediol, pentanedione, butanediol, butanedione, aqueous glycolic salt solution and a mixture thereof; a basic solution in the amount capable of neutralizing the stabilizer; and the balance of water or alcohol as a solvent.

23. The composition according to claim 22, wherein the stabilizer further contains pentanediol, pentanedione, butanediol, butanedione, alkyl acetoacetate, polyethylene glycol, cetyltrimethyl ammonium hydroxide, polyvinyl acetate, polyvinyl alcohol, trialkylalcohol amine ($(RO)_3N$), or a mixture thereof.

24. The composition according to claims 22 or 23, further comprises an organic silicon compound, an aluminum compound, a zirconium compound, an iron compound or a mixture thereof.

Fig 1

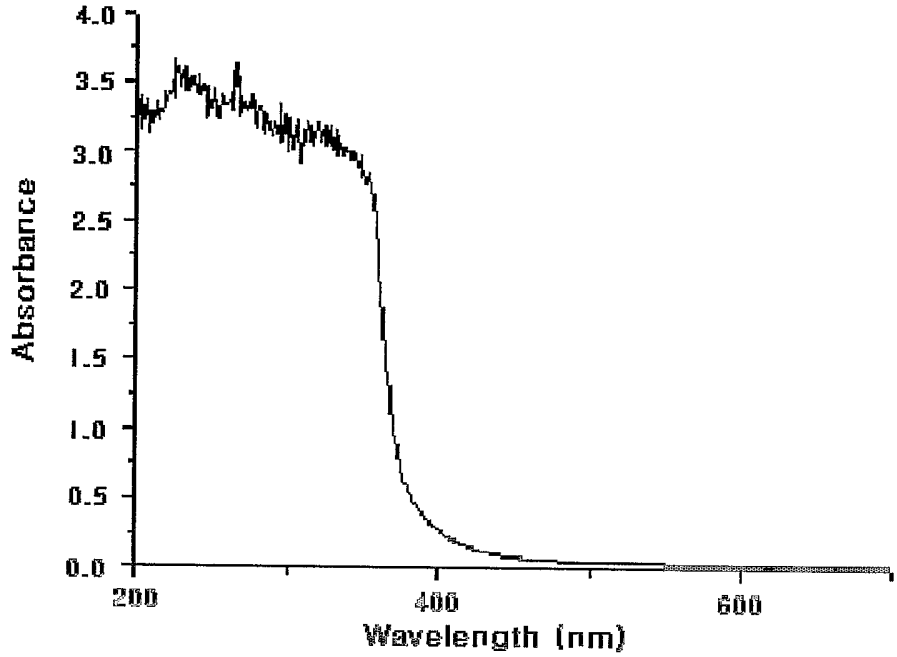

Absorbance
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2.0
1.5
1.0
0.5
0.0
200
400
600
Wavelength (nm)

Fig 2

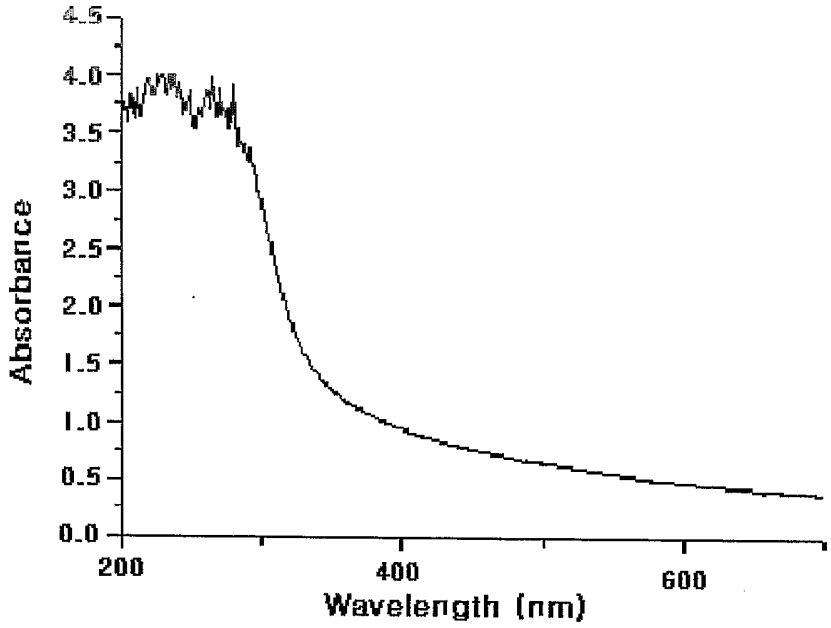

Absorbance
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
200
400
600
Wavelength (nm)

Fig 3

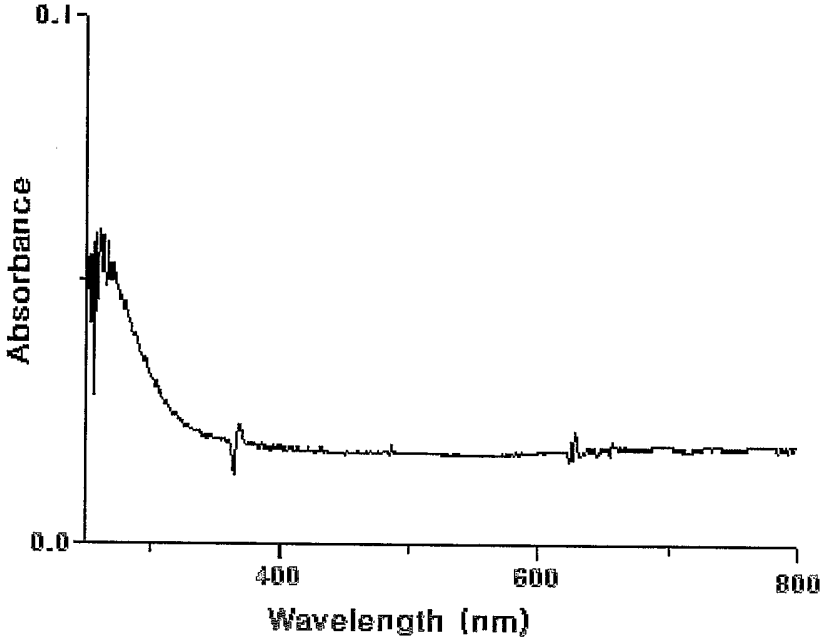

0.1
0.0
Absorbance
400
600
800
Wavelength (nm)

Fig 4

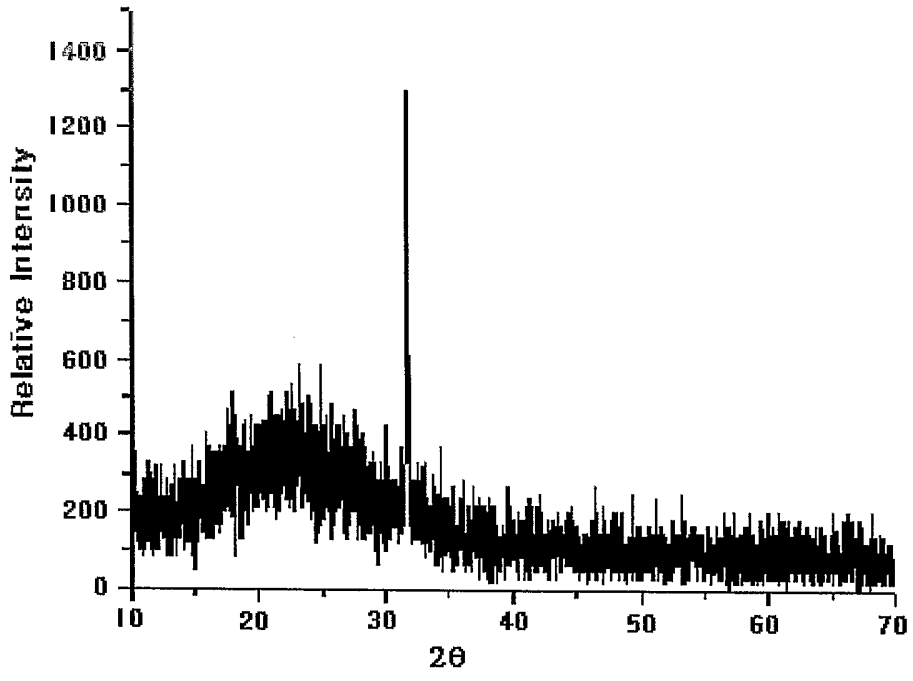

1400
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1000
800
600
400
200
0
Relative Intensity
10
20
30
40
50
60
70
2θ

Fig 5

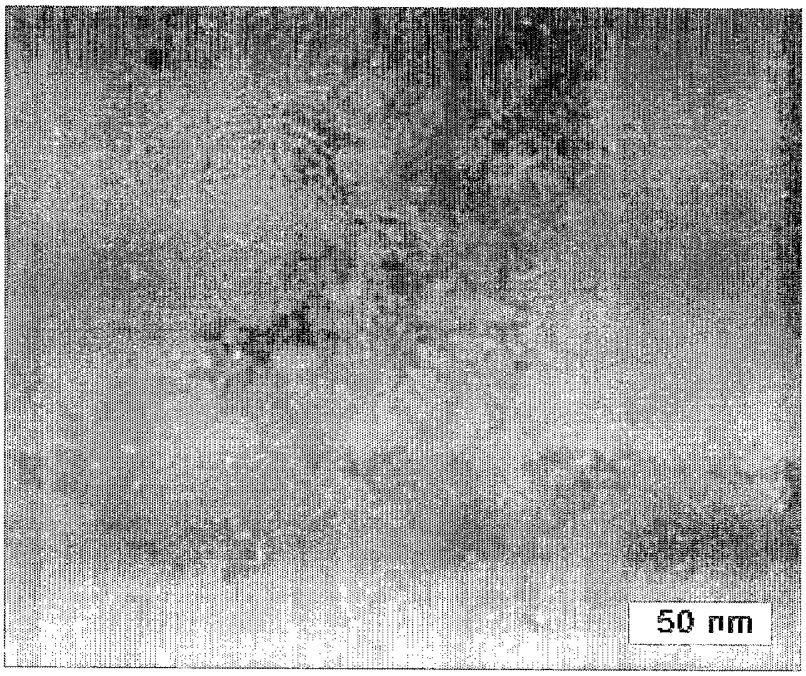


Fig 6

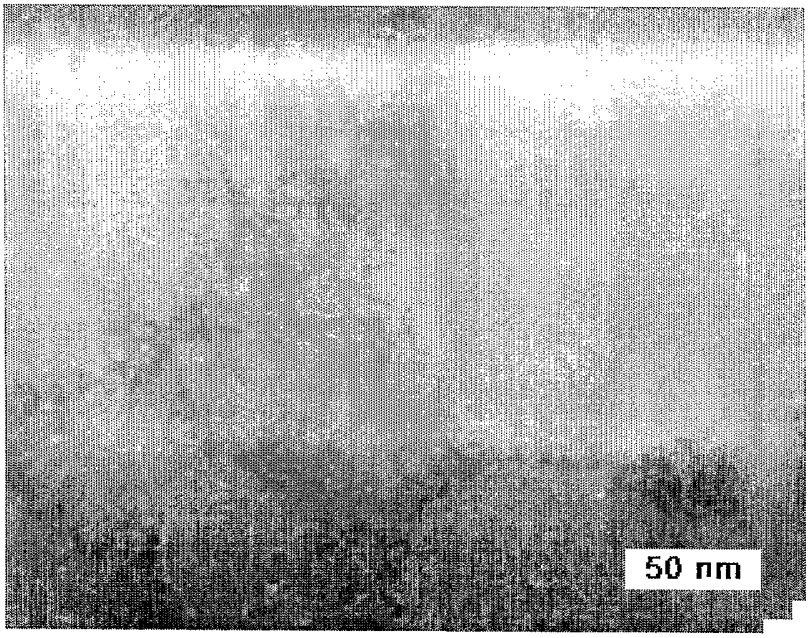
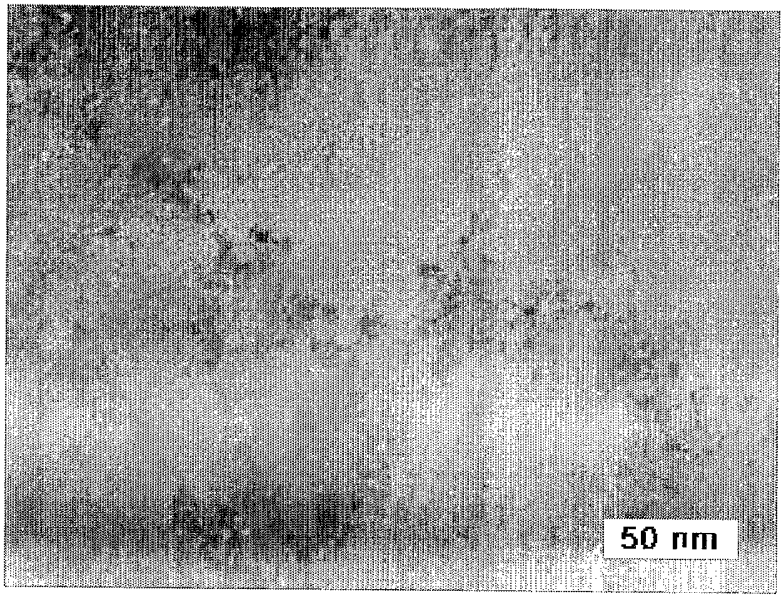


Fig 7



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2003/001063

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C01G 23/047

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)

IPC7 C01G, C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Patents and applications for inventions since 1975, Korean Utility models and applications for Utility models since 1975
Japanese Utility models and applications for Utility models since 1975

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)

eKIPASS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 62-226814 A (Sumitomo Metal Mining Co., Ltd.) 5 October 1987 see the whole document	1, 10
A	US 5,846,511 A (Korea Advanced Institute of Science and Technology) 8 December 1998 see the whole document	1, 10
A	EP 1052225 A1 (Nihon Parkerizing Co., Ltd.) 15 November 2000 see the whole document	19, 22
A	US 6,340,711 B1 (Showa Denko K. K.) 22 January 2002 see the whole document	19, 22

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 JANUARY 2004 (06.01.2004)	06 JANUARY 2004 (06.01.2004)

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Telephone No. 82-42-481-8151

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR2003/001063

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