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PROCESS FOR PRODUCING PARTICLES AND COATING FILMS  
OF TITANIUM OXIDE



## PROCESS FOR PRODUCING PARTICLES AND COATING FILMS OF TITANIUM OXIDE

### 1 BACKGROUND OF THE INVENTION

#### Field of the Invention

The present invention relates to a process for producing particles and coating films of titanium oxide and more particularly to a process for producing particles and coating films of titanium oxide which are used for pigments, ultraviolet absorbers, fillers, optical materials, electronic materials, optoelectric transducers, decorative materials, catalysts, photocatalysts, catalyst carriers, adsorbents, bioreactors and the like.

#### Description of Related Art

Titanium oxide particles are useful as pigments, ultraviolet absorbers, fillers and the like. Furthermore, titanium oxide coating films comprising titanium oxide particles allowed to firmly adhere to a support are useful as photocatalysts, sensors and materials for semiconductor electrodes such as solar batteries utilizing the photosemiconductor characteristics of titanium oxide and as sealing materials utilizing its dielectric characteristics. Moreover, titanium oxide coating films are used as heat ray reflecting glasses and decorative materials because of high light reflectance and beautiful silvery reflective color tone and furthermore as catalysts, photocatalysts,



1 catalyst carriers, adsorbents and bioreactors utilizing  
the porosity of the titanium oxide coating films. The  
titanium oxide coating films can be produced, for exam-  
ple, by a process which comprises immersing a support in  
5 a solution containing titanium isopropoxide or the like,  
taking it out and then heating the support at a high  
temperature to form a film, a process which comprises  
blowing titanium tetrachloride vapor against the surface  
of a support at a high temperature to form a film, a  
10 process which comprises spraying a solution containing an  
organotitanium compound such as titanium acetylacetonato,  
titanium alkoxide or the like to the surface of a support  
at a high temperature to form a film.

According to the above-mentioned conventional  
15 processes, a titanium compound is reacted on a support to  
form a titanium oxide film. Therefore, the size of  
titanium oxide primary particles which constitute the  
resulting titanium oxide film is several nm and such  
titanium oxide particles show volume shrinkage at the  
20 time of sintering to cause occurrence of cracks in the  
resulting film. The film having cracks is apt to peel  
off from the support and is low in endurance and wear  
resistance and furthermore, inferior in optical charac-  
teristics. In addition, according to the conventional  
25 processes, it is difficult to make porous titanium oxide  
coating films having a large thickness and a large  
specific surface area which are suitable for optoelectric  
transducing materials, catalysts, photocatalysts and

1 adsorbents. The conventional processes have further  
problems that the working atmosphere becomes worse due to  
the vapors of organic solvents and titanium compounds and  
there are dangers in working such as firing.

5 SUMMARY OF THE INVENTION

An object of the present invention is to  
provide titanium oxide particles excellent in crystal-  
linity and extremely excellent in various properties.  
Another object of the present invention is to provide  
10 titanium oxide coating films less in cracks and high in  
adhesion to a support.

The present invention is a process for produc-  
ing titanium oxide particles which comprises subjecting  
titanium oxide fine particles to a hydrothermal treatment  
15 at a temperature of 100°C or higher, characterized by  
carrying out the hydrothermal treatment using (1) a sus-  
pension of titanium oxide fine particles containing  
rutile-type titanium oxide, (2) a suspension of titanium  
oxide fine particles containing anatase-type titanium  
20 oxide obtained by hydrolyzing titanyl sulfate or (3) a  
suspension in which various titanium oxide fine particles  
such as hydrous titanium oxide fine particles of  
metatitanic acid or orthotitanic acid in addition to the  
above-mentioned titanium oxide fine particles are highly  
25 dispersed. Furthermore, the present invention is a  
process for producing a titanium oxide coating film on a  
support using the above titanium oxide particles.



1 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a optical photomicrograph (x 1000) which shows the surface morphologic structure of the titanium oxide coating film obtained in Example 3.

5 Fig. 2 is an electron photomicrograph (x 8000) which shows the layer structure of a section of the titanium oxide coating film obtained in Example 7.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The inventors have conducted intensive research  
10 in an attempt to obtain a titanium oxide coating film strong in adhesion to a support and excellent in optical properties and as a result, have found that (1) by using titanium oxide particles obtained by carrying out crystal growth of titanium oxide fine particles, volume shrinkage  
15 at the time of formation of the film can be reduced, occurrence of cracks can be reduced and adhesion to the support can be improved, (2) the titanium oxide particles which are allowed to firmly adhere are desirably those which have an average particle size of 10 to 100 nm,  
20 preferably 10 to 30 nm, especially preferably 15 to 25 nm because these are excellent in adhesion to the support, (3) for carrying out the crystal growth of titanium oxide fine particles, there are the following methods of (a) heating titanium oxide fine particles at a temperature of  
25 200 to 600°C, (b) subjecting the titanium oxide fine particles to a hydrothermal treatment at a temperature of 100°C or higher, and (c) subjecting a suspension in which





1 the titanium oxide fine particles are highly dispersed to  
a hydrothermal treatment at a temperature of 100°C or  
higher, and these methods are preferred because the  
crystals of the titanium oxide fine particles can be  
5 uniformly grown, and especially preferred is the method  
(b) in which titanium oxide fine particles containing  
rutile-type titanium oxide or titanium oxide fine parti-  
cles obtained by hydrolyzing titanyl sulfate are  
subjected to a hydrothermal treatment, and (4) in the  
10 case of forming a titanium oxide coating film by allowing  
titanium oxide particles obtained by crystal growth of  
titanium oxide fine particles to firmly adhere to a  
support, the packing density of the titanium oxide coat-  
ing film can be enhanced and adhesion to the support can  
15 be further improved by using a suspension in which said  
titanium oxide particles are highly dispersed. Thus, the  
present invention has been accomplished.

In the present invention, the "titanium oxide"  
means various titanium oxides such as anatase-type  
20 titanium oxide, rutile-type titanium oxide, amorphous  
titanium oxide, metatitanic acid, orthotitanic acid and  
the like and hydrous titanium oxide. Moreover, the  
"titanium oxide fine particles" means those which have a  
fine average particle size of 3 to 20 nm, preferably 5 to  
25 15 nm and the "titanium oxide particles" means those  
having an average particle size of 10 to 100 nm, prefer-  
ably 10 to 30 nm, especially preferably 15 to 25 nm  
obtained by crystal growth of said titanium oxide fine



1 particles. The said titanium oxide fine particles are  
obtained by known processes, for example, by hydrolyzing  
or neutralizing titanium compounds such as titanyl  
sulfate, titanium chloride, titanium acetate, titanium  
5 alkoxide and the like, if necessary, in the presence of a  
seed. Then, the thus obtained titanium oxide fine parti-  
cles are preferably filtrated and washed for removing  
impurities such as sulfates, chlorine and alkalis.

The "titanium oxide fine particles containing  
10 rutile-type titanium oxide" used herein means titanium  
oxide comprising 0.5 to 50% by weight, preferably 1 to  
30% by weight of fine particles of titanium oxide which  
can be identified to be rutile-type crystal in the X-ray  
diffraction pattern and the balance being mostly amor-  
15 phous. One example corresponding thereto is the rutile  
transition accelerating seed used in preparation of  
titanium dioxide pigments. The said titanium oxide fine  
particles containing rutile-type titanium oxide can be  
prepared, for example, by the following processes: (1) A  
20 titanium compound such as titanyl sulfate, titanium  
acetate or titanium tetrachloride is neutralized with an  
alkali or hydrolyzed, if necessary, in the presence of  
nucleus crystals to obtain a precipitate and the result-  
ing precipitate is heated, if necessary, with addition of  
25 an alkali and then is aged at a temperature of from 50°C  
to the boiling point with addition of an inorganic acid  
such as hydrochloric acid or nitric acid or an organic  
acid such as citric acid. (2) A Titanium chloride is

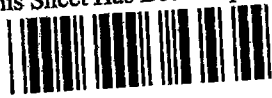
1 neutralized with an alkali at a pH of 4 to 7.

③ Titanium chloride is hydrolyzed by heating under the condition of 11% or higher in hydrochloric acid concentration. ④ Titanium chloride is subjected to an  
5 oxidative thermal decomposition in vapor phase.

The "titanium oxide fine particles obtained by hydrolysis of titanyl sulfate" used herein means titanium oxide fine particles containing anatase-type titanium oxide obtained by hydrolyzing titanyl sulfate with heat-  
10 ing at 60 to 110°C, especially 80 to 110°C. This contains a slight amount of amorphous titanium oxide, but contains mostly titanium oxide which can be identified to be anatase-type crystal in the X-ray diffraction pattern.

When the heating temperature at the time of  
15 hydrolysis is lower than 60°C, hydrolysis of titanyl sulfate is not sufficiently performed or a long time is required for hydrolysis. The concentration of titanyl sulfate in the solution and the heating time can be optionally set, but a titanyl sulfate concentration of 50  
20 to 250 g/l in terms of  $\text{TiO}_2$  is suitable and a heating time of about 1 to 10 hours is suitable. The pressure at the time of heating is preferably atmospheric pressure, but the heating may be conducted under application of pressure. Furthermore, if necessary, a seed may be  
25 present in the solution of titanyl sulfate. Preferably, the thus obtained titanium oxide fine particles are filtrated and washed to remove impurities such as sulfate radicals.





1           The "suspension in which titanium oxide fine  
particles are highly dispersed" used herein is obtained  
by allowing an acid to be present in a suspension of  
titanium oxide fine particles to adjust the pH to 4 or  
5 lower, preferably 2 or lower or allowing an alkali to be  
present in a suspension of titanium oxide fine particles  
to adjust the pH to 9 or higher, preferably 10 or higher  
and dispersing titanium oxide fine particles or by  
grinding the powders of titanium oxide fine particles and  
10 then preparing a suspension thereof, or by suspending  
titanium oxide fine particles in a suspension with grind-  
ing the fine particles by a grinder or a classifier, or  
by allowing a dispersant to be present in the suspension.

          When acid or alkali is allowed to be present,  
15 if pH of the suspension is higher than 4 and lower than  
9, titanium oxide fine particles are dispersed with  
difficulty and cannot be made to a colloid solution. For  
adjusting the pH to 4 or lower, at least one acid optio-  
nally selected from inorganic acids such as hydrochloric  
20 acid, nitric acid, sulfuric acid, phosphoric acid and  
carbonic acid and organic acids such as citric acid,  
malic acid, acetic acid and lactic acid is added to the  
suspension. Hydrochloric acid or nitric acid is prefer-  
red. For adjusting the pH to 9 or higher, at least one  
25 alkali optionally selected from sodium hydroxide, potas-  
sium hydroxide, sodium carbonate, ammonium carbonate,  
ammonia and amines is allowed to be present. The  
grinders used are preferably wet grinders such as sand



1 mill, ball mill, Henschel mixer and paint shaker. As the  
dispersant when this is used, mention may be made of, for  
example, inorganic dispersants such as sodium hexameta-  
phosphate and sodium silicate and organic dispersants  
5 such as sodium polycarboxylates, polyethylene glycol and  
acetylacetone. These dispersants may be used each alone  
or in combination of two or more. In the present inven-  
tion, organic dispersants are especially preferred and  
sodium polycarboxylates such as OROTAN 850 (manufactured  
10 by Rohm & Haas Co.) and polyethylene glycol are espe-  
cially preferred among the organic dispersants. These  
dispersants can be added optionally to the suspension of  
titanium oxide fine particles before coating of the  
suspension on a support, thereby to allow them to be  
15 present in the suspension. The amount of the dispersant  
to be added is preferably about 0.1 to 40% by weight in  
terms of the effective ingredient based on the weight of  
the titanium oxide fine particles. In the present inven-  
tion, preferred are the process of allowing an acid to be  
20 present in the suspension of titanium oxide fine parti-  
cles to adjust the pH to 4 or lower, preferably 2 or  
lower or allowing an alkali to be present in the suspen-  
sion of titanium oxide fine particles to adjust the pH to  
9 or higher, preferably 10 or higher and dispersing the  
25 titanium oxide fine particles.

The hydrothermal treatment is carried out by  
heating the suspension or highly dispersed suspension of  
titanium oxide fine particles to a temperature of 100°C



1 or higher, preferably 100 to 250°C. By this hydrothermal  
treatment, crystals of the titanium oxide fine particles  
are grown to an average particle size of 10 to 100 nm,  
preferably 10 to 30 nm, especially preferably 15 to 25  
5 nm. Furthermore, by this hydrothermal treatment, the  
titanium oxide fine particles containing rutile-type  
titanium oxide become rutile-type titanium oxide  
particles and X-ray diffraction of this rutile-type  
titanium oxide particles reveals no anatase-type crystal  
10 and this rutile-type titanium oxide particles have  
substantially rutile-type crystal structure. The  
titanium oxide fine particles containing anatase-type  
titanium oxide become anatase-type titanium oxide  
particles by the hydrothermal treatment. X-ray diffrac-  
15 tion of this anatase-type titanium oxide particles  
reveals that the particles show substantially anatase-  
type crystal structure. The thus obtained rutile-type  
titanium oxide particles or anatase-type titanium oxide  
particles can have the desired particle size by suitably  
20 setting the temperature and time of the hydrothermal  
treatment. By subjecting the suspension in which  
titanium oxide fine particles are highly dispersed to the  
hydrothermal treatment, the effect of the hydrothermal  
treatment can be further enhanced.

25 The hydrothermal treatment is preferably  
carried out under about saturated vapor pressure, but can  
also be carried out under higher than the saturated vapor  
pressure or under about atmospheric pressure and can



1 normally be carried out by industrially employed heat-resisting and pressure-resisting apparatuses. The time for the hydrothermal treatment can be optionally set, but is suitably about 1 to 48 hours.

5 If necessary, the titanium oxide particles obtained by the hydrothermal treatment are filtrated and washed to remove impurities such as sulfate radicals, chlorine and alkalis, and dried to make dry powders. The drying can be carried out at optional temperatures, but  
10 suitable is 100 to 500°C. Furthermore, it is also possible depending on the using sites to use the titanium oxide particles by supporting or coating them on a support or by grinding or molding the above dry powders. It is also possible depending on the catalytic reactions  
15 used to support transition metals such as gold, platinum, rhodium and palladium on the surface of the titanium oxide particles.

The present invention further relates to a process for producing a titanium oxide coating film by  
20 coating on a support the titanium oxide particles obtained by carrying out the crystal growth of the titanium oxide fine particles and firing the coated particles. The "titanium oxide coating film" in the present invention means a coating film containing  
25 substantially no resin, being different from the general coating films comprising a titanium oxide pigment and a resin medium. Furthermore, it has a large specific surface area of about 10 to 200 cm<sup>2</sup> per 1 cm<sup>2</sup> of the



1 support and 1  $\mu\text{m}$  of a film thickness. The titanium oxide  
coating film of the present invention can be optionally  
changed in its thickness, transparency and porosity  
expressed by specific surface area by suitably setting  
5 the conditions such as concentration of titanium oxide  
suspension and particle size of the titanium oxide  
particles explained hereinafter. Moreover, the titanium  
oxide coating film of either anatase-type or rutile-type  
can be formed by suitably selecting the crystal system of  
10 the titanium oxide particles used or by suitably setting  
the firing conditions. Furthermore, it is also possible  
to form a coating film comprising a mixture of anatase-  
type titanium oxide particles and rutile-type titanium  
oxide particles at an optional proportion. The thickness  
15 of the film can be, for example, about 0.5 to 20  $\mu\text{m}$ . The  
titanium oxide particles having an average particle size  
of 10 to 100 nm, preferably 10 to 30 nm, especially  
preferably 15 to 25 nm are superior in adhesion to the  
support.

20 The method for growing the crystals of the  
titanium oxide fine particles includes, for example, (a)  
a method of heating them at a temperature of 200 to  
600°C, preferably 300 to 500°C, especially preferably 300  
to 450°C and (b) the above-mentioned method of subjecting  
25 them to hydrothermal treatment at a temperature of 100°C  
or higher, preferably 100 to 250°C.

When the heating temperature is lower than  
200°C, crystal growth of the titanium oxide fine



1 particles is not sufficient and volume shrinkage of titanium oxide particles when allowed to firmly adhere to a support is great and cracks are apt to occur and adhesion to the support becomes inferior. When the heating  
5 temperature is higher than 600°C, the crystals of the titanium oxide fine particles grow too much and adhesion to the support is deteriorated or the specific surface area of the titanium oxide coating film decreases. The heating time is suitably 0.5 to 2 hours.

10 By carrying out the above heating treatment or hydrothermal treatment, crystals of the titanium oxide fine particles grow and crystallinity is improved and uniform titanium oxide particles of suitable size can be obtained. Thus, the desired titanium oxide coating film  
15 can be obtained.

In the present invention, the titanium oxide particles obtained by carrying out the crystal growth of the titanium oxide particles are first suspended in a solvent such as water, alcohol, toluene or the like. As  
20 the solvent, water is especially preferred from the point of working atmosphere. The concentration of the titanium oxide particles in the suspension can be optionally set, but a concentration of 10 to 1200 g/l in terms of  $\text{TiO}_2$  is preferred. When the concentration is lower than 10 g/l,  
25 it becomes difficult to increase the thickness of the titanium oxide coating film. When it is higher than 1200 g/l, viscosity of the suspension increases and the suspension can be coated on a support with difficulty. In



1 the present invention, it is preferred to increase the  
concentration by subjecting the titanium oxide particles  
in the suspension to the aforementioned dispersion  
treatment. Furthermore, the suspension of the titanium  
5 oxide particles obtained by the hydrothermal treatment  
can be coated as it is or after adjusting the concen-  
tration of the titanium oxide particles without carrying  
out the filtration of the titanium oxide particles on a  
support by various coating methods mentioned hereafter  
10 and thus, a titanium oxide coating film can be obtained.

The resulting suspension of titanium oxide  
particles is coated on a support by usual methods such as  
dip coating, spray coating, spinner coating, blade  
coating, roller coating, wire bar coating and reverse  
15 roll coating and, if necessary, dried and fired to remove  
the solvent, and the titanium oxide particles are allowed  
to firmly adhere to the support. Material, shape and  
size of the support on which the titanium oxide film is  
formed can be optionally selected depending on the object  
20 and its use. As the material there may be used glass,  
metals, ceramics and others, and as the shape and size  
mention may be made of a card board, a small fragment,  
spheres such as beads. The firing is carried out at  
100°C or higher, preferably 200 to 800°C, especially  
25 preferably 300 to 800°C. When the firing temperature is  
lower than 100°C, adhesion to the support deteriorates.  
The upper limit of the firing temperature depends on the  
use and cannot be generically specified, but the firing

1 temperature higher than 800°C is not preferred in so  
me case because crystal growth of the titanium oxide  
particles is too much or the specific surface area of the  
titanium oxide coating film is small. In the case of  
5 carrying out the heating for crystal growth, the firing  
is carried out at a temperature higher than the heating  
temperature. When the firing temperature for adhesion of  
the particles is lower than the heating temperature for  
the crystal growth, adhesion to the support is inferior.

10 In the present invention, it is preferred to  
use titanium oxide particles obtained by subjecting the  
suspension in which the titanium oxide fine particles are  
highly dispersed to the hydrothermal treatment. Further-  
more, for producing a titanium oxide coating film  
15 comprising rutile-type titanium oxide particles, it is  
preferred to use the titanium oxide particles comprising  
substantially rutile-type titanium oxide obtained by  
subjecting the titanium oxide fine particles containing  
rutile-type titanium oxide to a hydrothermal treatment at  
20 a temperature of 100°C or higher. For producing a  
titanium oxide coating film of anatase-type titanium  
oxide, it is preferred to use the substantially anatase-  
type titanium oxide particles obtained by hydrolyzing  
titanyl sulfate and then subjecting the resulting  
25 titanium oxide fine particles to a hydrothermal treatment  
at a temperature of 100°C or higher.

In this way, the titanium oxide film of the  
present invention is obtained.

This Sheet Has Been Replaced





1           The present invention is illustrated by the  
following examples.

Example 1

One liter of an aqueous solution containing 200  
5 g/l of titanium tetrachloride was added dropwise to 2  
liters of an aqueous solution containing 222 g/l of  
sodium carbonate with stirring to neutralize titanium  
tetrachloride at room temperature. Subsequently, to the  
above aqueous solution was added citric acid in an amount  
10 of 5% by weight based on the weight of  $TiO_2$  of the  
neutralization precipitate. Then, the aqueous solution  
was heated to 70°C and aged for 20 minutes. (A part of  
the resulting titanium oxide fine particles were taken,  
filtrated and dried. X-ray diffraction thereof showed  
15 that they contained 15% by weight of titanium oxide fine  
particles having rutile-type crystal structure, the  
balance being amorphous.).

The thus obtained titanium oxide fine particles  
were filtrated, washed and then dispersed in water to  
20 prepare a suspension of 250 g/l in terms of  $TiO_2$ . Then,  
aqueous nitric acid solution was added to this suspension  
to adjust to a pH of 1.3. Thereafter, the suspension was  
charged in an autoclave and subjected to a hydrothermal  
treatment at 150°C for 13 hours under a saturated vapor  
25 pressure. The resulting product was filtrated, washed  
and dried to obtain the titanium oxide particles of the  
present invention (Sample A). X-ray diffraction of this



- 1 Sample A showed that it had substantially the rutile-type  
crystal structure and had a particle size of 18 nm.  
Furthermore, it had a cubic form which is euhedral for  
the rutile-type crystal according to observation under an  
5 electron microscope.

#### Comparative Example 1

- Aqueous ammonia was added to 1 liter of a  
solution containing 80 g/l of titanium tetrachloride with  
stirring to adjust the pH to 7.0 to obtain a gel. This  
10 gel was filtrated, washed and then dispersed in water to  
prepare a suspension of 250 g/l in terms of  $\text{TiO}_2$ . This  
suspension was charged in an autoclave and subjected to a  
hydrothermal treatment at  $150^\circ\text{C}$  for 13 hours under a  
saturated vapor pressure. The resulting product was  
15 filtrated, washed and dried to obtain titanium oxide par-  
ticles (Sample B). X-ray diffraction of this Sample B  
showed that it had an anatase-type crystal structure and  
had a particle size of 10.5 nm.

#### Comparative Example 2

- 20 The commercially available titanium oxide  
catalyst P-25 (a mixture of rutile-type and anatase-type,  
particle size: 22 nm, manufactured by Japan Aerosil Co.)  
was employed as Sample C.

- The catalytic activity of Samples A-C obtained  
25 in Example 1 and Comparative Examples 1 and 2 was  
examined in the following manner. Each of the samples



1 was dispersed in water to prepare a suspension of 4 g/l  
in terms of  $\text{TiO}_2$ . To 25 ml of the resulting suspension  
was added 10  $\mu\text{l}$  of tetrachloroethylene and then, the  
suspension was irradiated with a light from a xenon lamp  
5 of 150 W for 30 minutes to carry out a photocatalytic  
decomposition reaction of tetrachloroethylene. The  
decomposition rate of tetrachloroethylene with the sample  
was calculated from the concentration of tetrachloro-  
ethylene before the reaction and that of tetrachloro-  
10 ethylene after the reaction. The results are shown in  
Table 1. As can be seen from the results, the rutile-  
type titanium oxide particles of the present invention  
are superior in the catalytic activity.

Table 1

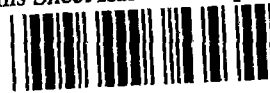
|                       | Sample | Decomposition rate (%) |
|-----------------------|--------|------------------------|
| Example               | A      | 72                     |
| Comparative Example 1 | B      | 42                     |
| Comparative Example 2 | C      | 48                     |

Furthermore, crystallinity of Samples A-C was  
15 examined by spectroscopic means using a photo-acoustic  
spectroscopic method. That is, when 0.5 g of the sample  
is charged in a closed container and irradiated with a  
light of a given wavelength, the sample absorbs the light  
depending on the wavelength. In the case of emitting the  
20 energy of this absorbed light as a heat by nonradiative



1 process, the atmosphere around the sample vibrates and  
generates a sound wave due to the thermal expansion of  
the sample with increase of the vibration energy of  
crystal lattice. The sound wave generated in this case  
5 is detected by a high-sensitivity microphone. The  
wavelength of the light with which the sample is irradi-  
ated is changed from 300 to 1600 nm and the output of the  
high-sensitivity microphone is measured to obtain a  
photo-acoustic spectrum of each sample.

10 It is generally said that rutile-type titanium  
oxide has an energy gap of 3.0 eV. When an energy  
corresponding to this energy gap is converted into a  
light energy, this is a light of 413 nm in wavelength.  
Therefore, theoretically, when a light slightly shorter  
15 in wavelength than 413 nm is irradiated, the light is  
completely absorbed by titanium oxide and when a light  
slightly longer than 413 nm is irradiated, the light is  
utterly not absorbed by titanium oxide. However,  
titanium oxide inferior in crystallinity has a defect  
20 level capable of absorbing an energy smaller than 3.0 eV  
and absorbs even the light slightly longer than 413 nm.  
From this fact, superiority or inferiority of crys-  
tallinity of the samples can be determined by comparing  
the state of this specific light absorption edge using  
25 the above-mentioned photo-acoustic spectrum. From the  
fact that the photo-acoustic spectrum of the rutile-type  
titanium oxide particles of the present invention was  
sharp in rising of the specific light absorption edge, it



1 was seen that the rutile-type titanium oxide particles of  
the present invention were superior in crystallinity.

#### Example 2

One liter of a solution containing 80 g/l of  
5 titanyl sulfate was heated to 85°C and kept for 3 hours  
to hydrolyze titanyl sulfate. (A part of the resulting  
titanium oxide fine particles were taken, filtrated and  
dried. X-ray diffraction of the product showed that it  
had an anatase-type crystal structure and had a particle  
10 size of 5 nm.)

The thus obtained titanium oxide fine particles  
were filtrated, washed and then dispersed in water to  
prepare a suspension of 250 g/l in terms of  $\text{TiO}_2$ . Then,  
aqueous hydrochloric acid solution was added to this  
15 suspension to adjust the pH to 1.0. Thereafter, the  
suspension was charged in an autoclave and subjected to a  
hydrothermal treatment at 150°C for 13 hours under a  
saturated vapor pressure. The resulting product was  
filtrated, washed and dried to obtain the titanium oxide  
20 particles of the present invention (Sample D). X-ray  
diffraction of this Sample D showed that it had an  
anatase-type crystal structure and had a particle size of  
13 nm.

#### Comparative Example 3

25 Titanium oxide fine particles were obtained in  
the same manner as in Example 2 except that the hydro-



1 thermal treatment was not conducted (Sample E). X-ray  
diffraction of this Sample E showed that it had an  
anatase-type crystal structure and a particle size of 5  
nm.

5 Comparative Example 4

The titanium oxide fine particles obtained in  
Comparative Example 3 were fired at 450°C for 30 minutes  
to obtain Sample F. X-ray diffraction of this Sample F  
showed that it had an anatase-type crystal structure and  
10 a particle size of 12 nm.

The catalytic activity of Samples B-F obtained  
in Example 2 and Comparative Examples 1-4 was examined in  
the following manner. Each of the samples was dispersed  
in water to prepare a suspension of 4 g/l in terms of  
15 TiO<sub>2</sub>. To 25 ml of the resulting suspension was added 25  
μl of 2-propanol and then, the suspension was irradiated  
with a light from a xenon lamp of 150 W for 2 hours to  
carry out a photocatalytic decomposition reaction of 2-  
propanol. The decomposition rate of 2-propanol with the  
20 sample was calculated from the concentrations of 2-  
propanol before and after the reaction. The results are  
shown in Table 2. As can be seen from the results, the  
anatase-type titanium oxide particles of the present  
invention are superior in the catalytic activity.



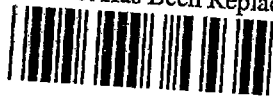
Table 2

|                       | Sample | Decomposition Rate (R)                  |                                        |
|-----------------------|--------|-----------------------------------------|----------------------------------------|
|                       |        | One hour after starting of the reaction | 2 hours after starting of the reaction |
| Example 2             | D      | 33.5                                    | 54.7                                   |
| Comparative Example 1 | B      | 11.3                                    | 24.4                                   |
| Comparative Example 2 | C      | 24.6                                    | 40.8                                   |
| Comparative Example 3 | E      | 12.2                                    | 26.0                                   |
| Comparative Example 4 | F      | 22.5                                    | 35.5                                   |

1 Furthermore, the catalytic activity for the decomposition reaction of tetrachloroethylene was examined in the same manner as above. The results are shown in Table 3. As can be seen from the results, the  
5 anatase-type titanium oxide particles of the present invention are superior in catalytic activity.

Table 3

|                       | Sample | Decomposition Rate (R)                    |                                           |
|-----------------------|--------|-------------------------------------------|-------------------------------------------|
|                       |        | 15 minutes after starting of the reaction | 30 minutes after starting of the reaction |
| Example 2             | D      | 41.9                                      | 71.3                                      |
| Comparative Example 2 | C      | 28.8                                      | 47.5                                      |



1           The crystallinity of the Samples B-F was  
examined as mentioned hereinbefore. From the fact that  
the photo-acoustic spectrum of the anatase-type titanium  
oxide particles of the present invention was sharp in  
5   rising of the specific light absorption edge, it was seen  
that the anatase-type titanium oxide particles of the  
present invention were superior in crystallinity.

As mentioned above, the rutile-type titanium  
oxide particles and the anatase-type titanium oxide  
10   particles of the present invention are higher in cata-  
lytic activity than conventional ones. The reason is not  
clear, but can be considered as follows: The rutile-type  
titanium oxide particles and the anatase-type titanium  
oxide particles of the present invention are superior in  
15   crystallinity and a few lattice defects are present  
inside the titanium oxide particles. Since conventional  
rutile-type titanium oxide particles and anatase-type  
titanium oxide particles have many lattice defects, many  
electrons or holes generated by irradiation with ultra-  
20   violet rays or the like retain in the lattice defects and  
only a few electrons or holes can participate in the  
catalytic reaction. On the other hand, since the rutile-  
type titanium oxide particles and anatase-type titanium  
oxide particles of the present invention have only a few  
25   lattice defects, the electrons and holes generated hardly  
retain in the lattice defects and in addition, the charge  
separation between the electrons and holes generated  
becomes easy and the amount of electrons or holes capable



1 of participating in the catalytic reaction increases.  
Furthermore, since the anatase-type titanium oxide  
particles of the present invention are obtained by  
subjecting the titanium oxide fine particles obtained by  
5 hydrolyzing titanyl sulfate to a hydrothermal treatment,  
many acid points are present on the surface of the  
resulting anatase-type titanium oxide particles and these  
acid points act as adsorption active points for the  
reactants to further enhance the catalytic activity.

10 Example 3

One liter of a solution containing 80 g/l of  
titanyl sulfate was heated to 85°C to carry out hydro-  
lysis. Then, the product was filtrated and washed to  
obtain a wet cake. Successively, water in this wet cake  
15 was replaced with acetone and then, the cake was sub-  
jected to vacuum drying at 60°C to obtain titanium oxide  
fine particle powders. (X-ray diffraction of the  
resulting titanium oxide fine particles showed that the  
product had anatase-type crystal structure and had a  
20 particle size of 5 nm.)

Then, the titanium oxide fine particle powders  
were heated at 300°C for 1 hour to obtain titanium oxide  
particles having anatase-type crystal structure of 11 nm  
in particle size. Then, the resulting titanium oxide  
25 particles were ground by an attritor and introduced into  
water. Thereafter, to this water was added polyethylene  
glycol (average molecular weight: 15000-25000) in an



1 amount of 20% by weight of  $\text{TiO}_2$ , followed by sufficient  
shaking by a paint conditioner (manufactured by Red Davil  
Co.) to obtain a suspension containing 500 g/l of tita-  
nium oxide particles. Then, this suspension was coated  
5 on a glass plate by a doctor blade (slit: 60  $\mu\text{m}$ ) and  
air-dried and then, fired at 450°C for 2 hours to obtain  
a titanium oxide coating film (anatase-type crystal,  
hazed) of the present invention.

This titanium oxide coating film firmly adhered  
10 to the glass plate (support) and the film was observed  
under a light microscope to find substantially no cracks  
on the surface. This titanium oxide coating film had a  
thickness of 10  $\mu\text{m}$  measured by a feeler type film thick-  
ness gauge and had a specific surface area of 80 to 100  
15  $\text{cm}^2$  per 1  $\text{cm}^2$  of the support and 1  $\mu\text{m}$  of the film  
thickness which was measured by nitrogen gas adsorption  
method.

#### Example 4

A titanium oxide coating film (anatase-type  
20 crystal, hazed) of the present invention was obtained in  
the same manner as in Example 3 except that the calci-  
nation temperature was 400°C.

The resulting titanium oxide coating film  
firmly adhered to the glass plate (support) and the film  
25 was observed under a light microscope to find substan-  
tially no cracks. This titanium oxide coating film had a  
thickness of 10  $\mu\text{m}$  and had a specific surface area of 80



- 1 to 100 cm<sup>2</sup> per 1 cm<sup>2</sup> of the support and 1 μm of the film thickness.

#### Example 5

An acid titania sol (CS-N, titanium oxide fine particles of anatase-type crystal and 5 nm in particle size, manufactured by Ishihara Sangyo Kaisha, Ltd.) was dried at 110°C for 5 hours. The resulting titanium oxide fine particle powders were heated at 300°C for 1 hour in the air to obtain titanium oxide particle powders (anatase-type crystal, particle size 11 nm). Then, the following components were shaken in a paint shaker for 5 hours to sufficiently mix and disperse them. This was coated on a glass plate of 100 cm<sup>2</sup> by a doctor blade and dried and then, was fired at 450°C for 30 minutes to obtain a titanium oxide coating film (anatase-type crystal, translucent) of the present invention.

The resulting titanium oxide coating film firmly adhered to the glass plate (support) and the film was observed under a light microscope to find substantially no cracks. This titanium oxide coating film had a thickness of 2.0 μm.

|                                                 |         |
|-------------------------------------------------|---------|
| Titanium oxide particle powders                 | 8.0 g   |
| Polyethylene glycol<br>(molecular weight 20000) | 3.2 g   |
| Pure water                                      | 14.0 ml |
| Concentrated nitric acid                        | 0.5 ml  |



1 Catalytic activity of the resulting titanium  
oxide coating film was examined in the following manner.  
The titanium oxide coating film was put in a glass  
container of 8 liters and acetaldehyde which was a  
5 malodorous component was added thereto at a concentration  
of 50 ppm. Then, the glass container was sealed. The  
titanium oxide coating film was irradiated with a black  
light for 2 hours so that ultraviolet intensity on the  
surface of the film reached  $1 \text{ mW/cm}^2$  and the  
10 concentration of acetaldehyde after the irradiation was  
measured to obtain 15 ppm. From this result, it can be  
seen that the titanium oxide coating film of the present  
invention is superior in photocatalytic activity.

#### Comparative Example 5

15 Water was added to the wet cake which was  
obtained in the same manner as in Example 3, but was not  
subjected to the heating and furthermore, polyethylene  
glycol (average molecular weight: 15000-25000) was added  
thereto in an amount of 20% by weight based on the tita-  
20 nium oxide, followed by stirring to obtain a suspension  
containing 300 g/l of titanium oxide fine particles.

Then, this suspension was coated on a glass  
plate by a doctor blade and air-dried. Thereafter, the  
coat was fired at  $450^\circ\text{C}$  for 2 hours. As a result, the  
25 titanium oxide fine particles peeled off from the glass  
plate in the form of fragments and a titanium oxide  
coating film was not able to be formed on the support.



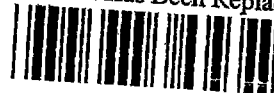
## 1 Example 6

One liter of a solution containing 80 g/l of  
titanyl sulfate was heated to 85°C and kept at that  
temperature for 3 hours to hydrolyze titanyl sulfate to  
5 obtain titanium oxide fine particles. (A part of the  
resulting titanium oxide fine particles were taken and  
filtrated, washed and dried. X-ray diffraction of the  
resulting product showed that the product had anatase-  
type crystal structure and had a particle size of 6 nm.)

10 The resulting titanium oxide fine particles  
were filtrated, washed and then dispersed in water to  
prepare a suspension of 200 g/l in terms of  $\text{TiO}_2$ . Then,  
aqueous hydrochloric acid solution was added to this  
suspension to adjust the pH to 1.0. Thereafter, the  
15 suspension was charged in an autoclave and subjected to a  
hydrothermal treatment at 200°C for 13 hours under a  
saturated vapor pressure. (A part of the resulting  
suspension of titanium oxide particles was taken and  
filtrated, washed and dried. X-ray diffraction of the  
20 resulting product showed that the product had anatase-  
type crystal structure and had a particle size of 20 nm.)

Then, the suspension of titanium oxide  
particles obtained by the hydrothermal treatment was  
coated on a glass plate by a doctor blade and air-dried.  
25 Thereafter, the coat was fired at 450°C for 3 hours to  
obtain a titanium oxide coating film (anatase-type  
crystal, transparent) of the present invention.

This titanium oxide coating film firmly adhered



1 to the glass plate (support). The film was observed  
under a light microscope to find substantially no cracks.  
This titanium oxide coating film had a thickness of 6  $\mu\text{m}$   
and had a specific surface area of 80 to 100  $\text{cm}^2$  per 1  
5  $\text{cm}^2$  of the support and 1  $\mu\text{m}$  of the film thickness.

#### Example 7

Titanyl sulfate was hydrolyzed in accordance  
with the process mentioned in Example 6 to obtain  
titanium oxide fine particles. (A part of the resulting  
10 titanium oxide fine particles were taken and filtrated,  
washed and dried. X-ray diffraction of the resulting  
product showed that it had anatase-type crystal structure  
and had a particle size of 5 nm.)

The resulting titanium oxide fine particles  
15 were filtrated, washed and then dispersed in water to  
prepare a suspension of 250 g/l in terms of  $\text{TiO}_2$ . Then,  
aqueous nitric acid solution was added to this suspension  
to adjust the pH to 1.2. Thereafter, the suspension was  
charged in an autoclave and subjected to a hydrothermal  
20 treatment at 150°C for 13 hours under a saturated vapor  
pressure. (A part of the resulting suspension of tita-  
nium oxide particles was taken and filtrated, washed and  
dried. X-ray diffraction of the resulting product showed  
that it had anatase-type crystal structure and had a  
25 particle size of 13 nm.)

To the suspension of the titanium oxide  
particles obtained by the above hydrothermal treatment



1 was added polyethylene glycol (average molecular weight:  
20000) in an amount of 40% by weight based on  $\text{TiO}_2$  in the  
suspension, followed by heating to  $60^\circ\text{C}$ . Then, in the  
same manner as in Example 6, the suspension was coated on  
5 a glass plate, air-dried, and then fired to obtain a  
titanium oxide coating film (anatase-type crystal,  
transparent) of the present invention.

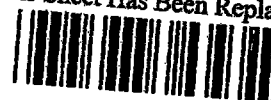
This titanium oxide coating film firmly adhered  
to the glass plate (support). The film was observed  
10 under a light microscope to find substantially no cracks.  
This titanium oxide coating film had a thickness of  $7.5\ \mu\text{m}$   
and had a specific surface area of 100 to  $120\ \text{cm}^2$  per  
 $1\ \text{cm}^2$  of the support and  $1\ \mu\text{m}$  of the film thickness.

#### Example 8

15 Water was added to the suspension of titanium  
oxide particles obtained in accordance with the process  
mentioned in Example 7 to adjust the concentration to 12  
g/l based on  $\text{TiO}_2$ . To 200 ml of this suspension were  
added 10 g of commercially available hollow glass beads  
20 (B28/750 manufactured by 3M Co.) and then, water was  
removed by an evaporator. The resulting product was  
dried at  $100^\circ\text{C}$  for 2 hours and then, fired at  $300^\circ\text{C}$  for 1  
hour to obtain a titanium oxide coating film (anatase-  
type crystal, transparent) of the present invention.

25 This titanium oxide coating film firmly adhered  
to the hollow glass beads (support) and substantially no  
cracks were found according to the observation by a light

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1 microscope.

#### Example 9

A titanium oxide coating film (anatase-type crystal, transparent) of the present invention was  
5 obtained in the same manner as in Example 8 except that solid glass beads (GB503M manufactured by Toshiba Balotyni Co.) were used in place of the hollow glass beads.

This titanium oxide coating film firmly adhered  
10 to the solid glass beads (support) and substantially no cracks were found according to the observation by a light microscope.

#### Example 10

A titanium oxide coating film (anatase-type  
15 crystal, transparent) of the present invention was obtained in the same manner as in Example 8 except that a ceramic honeycomb structure (HONEYCERAM manufactured by Nihon Gaishi K.K.) was used in place of the hollow glass beads.

20 This titanium oxide coating film firmly adhered to the honeycomb structure (support) and substantially no cracks were found according to the observation by a light microscope.

#### Example 11

25 Sodium hydroxide was added to an acid titania



1 sol (CS-N, titanium oxide fine particles of anatase-type  
crystal having a particle size of 6 nm, manufactured by  
Ishihara Sangyo Kaisha, Ltd.) to adjust the pH to 7,  
followed by carrying out filtration and washing. Water  
5 was added to the resulting wet cake to prepare a suspen-  
sion of titanium oxide fine particles having a concentra-  
tion of 100 g/l in terms of  $\text{TiO}_2$ . Then, sodium hydroxide  
was added to the suspension to adjust the pH to 10 and  
the suspension was charged in an autoclave and subjected  
10 to a hydrothermal treatment at  $150^\circ\text{C}$  for 3 hours under a  
saturated vapor pressure.

Then, nitric acid was added to the suspension  
of titanium oxide particles (anatase-type crystal,  
particle size 18 nm) after subjected to the hydrothermal  
15 treatment to neutralize to a pH of 7, followed by carry-  
ing out filtration and water washing. Water was further  
added to the resulting cake of titanium oxide particles  
to prepare a suspension of titanium oxide particles  
having a concentration of 500 g/l in terms of  $\text{TiO}_2$ .  
20 Nitric acid was added to the suspension to adjust the pH  
to 1. This suspension was coated on a glass plate of 100  
 $\text{cm}^2$  by a spin coater and dried and then, fired at  $500^\circ\text{C}$   
for 3 hours to obtain a titanium oxide coating film  
(anatase-type crystal structure, translucent).

25 This titanium oxide coating film firmly adhered  
to the glass plate (support) and substantially no cracks  
were found according to the observation by a light  
microscope. This titanium oxide coating film of the



1 present invention had a thickness of 1.0  $\mu\text{m}$ .

The catalytic activity of the resulting titanium oxide coating film was examined by the method used in Example 5. As a result, the acetaldehyde concentration after irradiated with light was 13 ppm. It can be seen from the result that the titanium oxide coating film of the present invention is superior in photocatalytic activity.

The process of the present invention is an industrially very useful process according to which titanium oxide particles excellent in crystallinity and furthermore, in optical properties, optoelectric transducing properties and catalytic properties can be produced simply and easily. Furthermore, a titanium oxide coating film having a large specific surface area, less in occurrence of cracks and good in adhesion to a support can be produced by allowing the titanium oxide particles of the present invention to firmly adhere to a support.

The titanium oxide coating film of the present invention is also excellent in optical properties, optoelectric transducing properties and catalytic properties and is useful for optical materials, electronic materials, optoelectric transducing materials, decorative materials, catalysts, photocatalysts, catalyst carriers, adsorbents and bioreactors. The titanium oxide coating film of the present invention is especially excellent in photocatalytic activity, and injurious materials can be

1 rapidly and efficiently removed utilizing the excellent  
photocatalytic activity. Thus, it is markedly useful not  
only for industrial uses, but also as household deodor-  
ants and the like. In addition, the titanium oxide  
5 coating film of the present invention can be used for a  
long period of time, is high in safety, can be applied to  
removal of a wide variety of injurious materials and does  
not pollute the environment even if it is abandoned.  
Therefore, it is industrially very useful.

10 Moreover, according to the process of the ,  
present invention, the titanium oxide coating film can be  
simply allowed to adhere to supports such as glass,  
metals, ceramics and plastics and further, the resulting  
film has a stable quality.

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## WHAT IS CLAIMED IS:

1. A process for producing a titanium oxide coating film which comprises carrying out crystal growth of titanium oxide fine particles to prepare titanium oxide particles, coating the resulting titanium oxide particles on a support and firing the coated support to allow the particles to firmly adhere to the support.
2. A process according to claim 1 wherein the titanium oxide particles have an average particle size of 10 to 100 nm.
3. A process according to claim 1 which comprises carrying out the crystal growth of the titanium oxide fine particles by heating the fine particles at a temperature of 200 to 600°C to prepare titanium oxide particles, then coating the resulting titanium oxide particles on a support and firing the coated support at a temperature higher than the heating temperature for the crystal growth to allow the particles to firmly adhere to the support.
4. A process according to claim 1 wherein the titanium oxide fine particles is subjected to a hydrothermal treatment at 100°C or higher to carry out the crystal growth of the fine particles.
5. A process according to claim 1 wherein a suspension of the titanium oxide fine particles is adjusted to a pH of 4 or lower or 9 or higher and then, the suspension is subjected to a hydrothermal treatment at 100°C or higher to carry out the crystal growth of the





titanium oxide fine particles.

6. A process according to claim 1 wherein the titanium oxide fine particles containing rutile-type titanium oxide is subjected to a hydrothermal treatment at 100°C or higher to carry out the crystal growth of the fine particles.

7. A process according to claim 1 wherein titanyl sulfate is hydrolyzed to obtain the titanium oxide fine particles and the resulting titanium oxide fine particles are subjected to a hydrothermal treatment at 100°C or higher to carry out the crystal growth of the fine particles.

8. A process according to claim 1 wherein a suspension of the titanium oxide particles is adjusted to a pH of 4 or lower or 9 or higher and then the suspension is coated on a support and fired to allow the titanium oxide particles to firmly adhere to the support.

9. A process for producing titanium oxide particles which comprises adjusting a suspension of titanium oxide fine particles to a pH of 4 or lower or 9 or higher and then, subjecting the suspension to a hydrothermal treatment at 100°C or higher to carry out crystal growth of the fine particles.

10. A process for producing titanium oxide particles which comprises subjecting titanium oxide fine particles containing rutile-type titanium oxide to a hydrothermal treatment at 100°C or higher to carry out crystal growth of the fine particles.



11. A process for producing titanium oxide particles which comprises hydrolyzing titanyl sulfate to obtain titanium oxide fine particles and subjecting the resulting titanium oxide fine particles to a hydrothermal treatment at 100°C or higher to carry out crystal growth of the fine particles.

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