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"TITANIUM DIOXIDE PIGMENT AND
PROCESS FOR PRODUCING SAME"

5. This invention relates to a titanium dioxide pigment coated with hydrous oxides of tin, zirconium and aluminium and of improved durability and dispersibility, as well as to a process for producing the said titanium dioxide pigment.

10. Recently, the application of the higher finished coatings are increasing as seen in products such as automobiles, domestic electrical articles, and industrial articles. As the titanium dioxide pigment used in the coatings, a pigment having an excellent photochemical stability i.e. durability and an ability to impart a high gloss to the coating is intensely required. With regard to the development of a titanium dioxide pigment capable of satisfying these

15. requirements, a variety of proposals have been made hitherto. For example, coating the pigment with dense amorphous silica together with other inorganic compounds is known as the most effective method for imparting durability. Though this titanium dioxide

20. pigment has excellent durability, it is insufficient in gloss of coating, and particularly in the case of water born paints its application is sometimes restricted. Further, there is also known another proposal to make the aforementioned improvement with-

25. out coating the pigment with the said dense amorphous silica. Although the durability is improved by this method, gloss and dispersibility may be reduced, so that the aforementioned improvement is not yet fully achieved by this proposal.

30. It is an object of this invention to provide a

titanium dioxide pigment of improve durability without deteriorating gloss and dispersibility.

5. The present inventors have found that a coated titanium dioxide pigment in which the titanium dioxide particles have coated thereon a given amount of inorganic compounds in a specific combination is excellent in both durability and gloss, and its pigment properties such as colour tone, hiding power, dispersibility and so on are not reduced.
10. According to the present invention, there is provided a titanium dioxide pigment which comprises (1) a pigmentary titanium dioxide core particle, (2) an inner coating of 0.1-3% by weight of hydrous tin oxide and 0.1-5% by weight of hydrous zirconium oxide, both
15. based on the weight of the said core particle and calculated as SnO_2 and ZrO_2 , respectively, and (3) an outer coating of 0.1-8% by weight of hydrous aluminium oxide, based on the weight of the said core particle and calculated as Al_2O_3 .
20. As referred to in this invention, the term "pigmentary titanium dioxide core particle" means usual pigmentary powder having a mean particle size of about 0.1 - 0.3 μ and a good whiteness, the crystal form of which may be anatase or rutile, and may also
25. be a mixture thereof. The titanium dioxide core may be a product of the so-called sulphate process, according to which a titanium sulphate solution is hydrolyzed, or the product of the so-called chloride process, according to which a titanium halide is oxidized in
30. the vapour phase. When titanium dioxide prepared by

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- the sulphate process is used, it is preferred that the hydrous titanium dioxide formed by the hydrolysis is calcined in the presence of phosphorus or a metal such as zinc, potassium, aluminium, lithium, niobium, or magnesium, to obtain stabilized crystals of titanium dioxide.
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- In the present invention, the amount of inorganic compounds coated on the surface of the titanium dioxide core particles is as follows: As the inner coating,
10. hydrous tin oxide is used in an amount of 0.1-3%, preferably 0.2-1.5% and particularly preferably 0.3-1.0%, by weight calculated as SnO_2 , and hydrous zirconium oxide is used in an amount of 0.1-5%, preferably 0.3-3% and particularly preferably 0.5-2%,
15. by weight calculated as ZrO_2 , based on the weight of core particle. As the outer coating, hydrous aluminium oxide is used in an amount of 0.1-8%, preferably 0.3-5% and particularly preferably 0.5-3% by weight, calculated as Al_2O_3 on the same basis. If the amount
20. of hydrous tin oxide coated is less than the above-mentioned range, the durability effect intended in this invention is not obtained. The use of too large an amount is also undesirable in that discolouration of titanium dioxide pigment can occur and it is disadvantageous economically, too. If the amount of hydrous
25. zirconium oxide coated is less than the above-mentioned range, no improvement in durability can be expected. If it is too large, the gloss is decreased and an economic disadvantage arises.
30. If the amount of hydrous aluminium oxide coated

- is less than the above-mentioned range, a decrease in durability, gloss and dispersibility is unavoidable, which is undesirable. If it is too large, an effect proportional to the amount cannot be expected, and
5. furthermore there is a decrease particularly in gloss. In the present invention, it is most preferred that the amounts of the hydrous oxides of tin, zirconium and aluminium coated fall in the above-mentioned ranges and the weight ratio of SnO_2 : ZrO_2 : Al_2O_3 is 1 : 1-3 :
10. 1-8 and particularly 1 : 1-2 : 2-6. In the present invention, the coating on the core particle is in the state that the outer coating is present around the inner coating. They may be in the form of either a continuous coated layer or a discontinuous coated layer.
15. In the present invention, organic agents such as polyols, or alkanolamines or inorganic compounds such as silicon, titanium, zinc, antimony, or cerium may optionally be coated to be present on the pigment unless they adversely affect the fundamental characteristics
20. of this invention.
- The titanium dioxide pigment of this invention is excellent in dispersibility, gloss and durability, and is useful as a colourant in various fields such as coating material, ink, plastics, and paper. Particu-
25. larly, it is quite suitable for use not only as a colourant in solvent type coating materials for the higher finished coating requiring high gloss, durability and excellent pigment dispersibility, but also as a colourant in water soluble type coating materials.
30. Further, this invention provides a process for

producing a coated titanium dioxide pigment by the following steps:

5. In producing the pigment of this invention, soluble compounds of tin and zirconium are preferably first added to an aqueous slurry of pigmentary titanium dioxide core particles and neutralized with an acid or an alkali, whereby the hydrous oxides of tin and zirconium are precipitated on the surface of titanium oxide to form an inner coating. The pigment
10. concentration of the aqueous titanium dioxide slurry is usually 100-800 g/litre and preferably 200-400 g/litre, and its temperature may be maintained at 40-90°C and preferably 60-80°C. To this aqueous slurry of titanium dioxide were added the desired quantities,
15. based on the weight of the core particles, of the water soluble compounds of tin and zirconium. As said water soluble compound of tin, there may be used acidic compounds such as tin chloride, tin sulphate, tin acetate, tin oxychloride, potassium stannate, or
20. sodium stannate or mixtures thereof. As said water soluble compounds of zirconium, there may be used acidic compounds such as zirconium chloride, zirconium sulphate, zirconium nitrate, zirconium acetate, zirconium carbonate, zirconium oxychloride, or
25. zirconium oxysulphate or mixtures thereof. In order to precipitate the coating agent thus added to the aqueous slurry of titanium dioxide, in the form of a hydrous oxide onto the surface of the said core particles, the pH value of the slurry is adjusted to 6-8 by adding an acidic
30. compound when the slurry is alkaline or adding an

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alkaline compound when the slurry is acidic.

- In the process of the present invention, the inner coating may be formed by simultaneously precipitating hydrous oxides of tin and zirconium, or it may also be
5. formed by precipitating at least a portion of them separately and then precipitating the remainders simultaneously, or separately precipitating the whole of them. However, a desirable effect on durability can, in some cases, be brought about by, for example,
 10. adding a water soluble tin compound to an aqueous slurry of core particles, adjusting the pH of the slurry so that at least a part of the tin first precipitates as a hydrous oxide onto the surface of the particles, and then adding a water soluble zirconium
 15. compound and adjusting the pH of the slurry so that a hydrous oxide of zirconium precipitates to form an inner coating. As the said acidic compound used as the neutralizing agent, there may be mentioned mineral acids such as sulphuric acid, and hydrochloric acid.
 20. As the said alkaline compounds, there may be used bases such as hydroxides and carbonates of alkali metals and alkaline earth metals, as well as ammonia, and amines. The neutralized slurry is preferably aged for a predetermined period of time (usually 10-60
 25. minutes) at a temperature of 40-90°C.
- Then, a given quantity of water soluble aluminium compound is added to the slurry having been subjected to the above-mentioned inner coating treatment, and it is neutralized with an acid or an alkali, whereby
30. hydrous aluminium oxide precipitates to form the

outer coating. As the said soluble aluminium compound, there may be used such compounds as alkali aluminate, aluminium chloride, or aluminium sulphate or mixtures thereof. In order to precipitate the added aluminium compound as a

5. hydrous oxide onto the said core particles, the pH may be adjusted to 6-8 by neutralizing it with an acid or alkali in the same manner as above.

The titanium dioxide pigment slurry which has been subjected to a coating treatment as mentioned above is

10. preferably aged for a given period of time (usually 10-60 minutes) at a temperature of 40-90°C, filtered and washed, then dried, and then subjected to the usual pulverization treatment to obtain a product of titanium dioxide pigment.

15. The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

EXAMPLE 1

20. An aqueous slurry of titanium dioxide core particles prepared by oxidizing titanium tetrachloride in the vapour phase (TiO_2 concentration 400 g/litre) was heated to 70°C, and the pH value of the slurry was adjusted to 2 by adding sulphuric acid. Then, a solu-

25. tion of stannous chloride was added in an amount of 0.5% by weight based on the weight of the core particles and calculated as SnO_2 , and the resulting mixture was stirred for 10 minutes, after which a solution of zirconium sulphate was added in an amount of 0.7% by

30. weight, on the same basis as above and calculated as



- ZrO₂, and the resulting mixture was stirred for 10 minutes. Subsequently, the pH value of the slurry was adjusted to 7 by adding a solution of sodium hydroxide to precipitate hydrous oxides of tin and zirconium on the surface of the core particles. After stirring the mixture for 10 minutes, a solution of sodium aluminate was added in an amount of 2.5% by weight as calculated as Al₂O₃, and the resulting mixture was stirred for 10 minutes, and the pH value of the slurry was adjusted to 7 by adding sulphuric acid, whereby hydrous aluminium oxide was precipitated. Then, the mixture was aged for 60 minutes, filtered, washed, dried at 120°C for 5 hours and pulverized by means of a micronizer to obtain a titanium dioxide pigment coated with the oxides of tin, zirconium and aluminium, which is within the scope of this invention (pigment A).

EXAMPLE 2

- Another titanium dioxide pigment which is within the scope of this invention (pigment B) was prepared by repeating the coating treatment of Example 1, except that a rutile type titanium dioxide produced by hydrolyzing a solution of titanium sulphate into hydrous titanium oxide, calcining, pulverizing and classifying was used as the titanium dioxide and a solution of stannic chloride was used as the tin chloride solution.

EXAMPLE 3

- A further titanium dioxide pigment which is within the scope of this invention (pigment C) was produced by repeating the coating treatment of Example

1, except that the procedure was altered so that the solution of zirconium sulphate was added while maintaining the pH value of slurry at 10-10.5 and then the solution of stannous chloride was added.

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EXAMPLE 4

A further titanium dioxide pigment which is within the scope of this invention (pigment D) was produced by repeating the coating treatment of Example 1, except that, after addition of the stannous chloride solution, the pH value of the slurry was adjusted to 7 by adding a solution of sodium hydroxide, the mixture was stirred for 10 minutes and then the zirconium sulphate was added.

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EXAMPLE 5

A still further titanium dioxide pigment which is within the scope of this invention (pigment E) was produced by repeating the coating treatment of Example 1, except that the stannous chloride solution was added in an amount of 1% by weight as calculated as SnO_2 and the zirconium sulphate solution was added in an amount of 2% by weight as calculated as ZrO_2 , both based on the weight of core particles.

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COMPARATIVE EXAMPLES 6 TO 14

For comparison with the pigments of this invention of Examples 1-5, pigments F-N were produced in the following manner:

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EXAMPLE 6

F: The treatment of Example 1 was repeated, except that the coating with hydrous tin oxide was omitted, to produce pigment F.

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EXAMPLE 7

G: The treatment of Example 1 was repeated, except that the coating with hydrous zirconium oxide was omitted to produce pigment G.

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EXAMPLE 8

H: The treatment of Example 1 was repeated, except that the coating with hydrous aluminium oxide was omitted to produce pigment H.

EXAMPLE 9

10.

I: The treatment of Comparative Example 8 was repeated, except that the hydrous tin oxide was coated in an amount of 5% by weight as calculated as SnO_2 , and the hydrous zirconium oxide was coated in an amount of 1% by weight as calculated as ZrO_2 to produce pigment I.

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EXAMPLE 10

J: The treatment of Example 1 was repeated, except that a solution of sodium silicate was substituted for the solution of stannous chloride and hydrous silicon oxide was coated in an amount of 0.5% by weight as calculated as SiO_2 to produce pigment J.

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EXAMPLE 11

K: The treatment of Example 1 was repeated, except that an ortho-phosphoric acid solution was substituted for the solution of stannous chloride and hydrous phosphorus oxide was coated in an amount of 0.5% by weight as calculated as P_2O_5 to produce pigment K.

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EXAMPLE 12

L: The treatment of Example 1 was repeated, except that a solution of titanium tetrachloride was

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substituted for the solution of stannous chloride and the hydrous titanium oxide was coated in an amount of 1% by weight as calculated as TiO_2 to produce pigment L.

EXAMPLE 13

5. M: The treatment of Example 1 was repeated, except that a solution of cerium chloride was substituted for the hydrous tin oxide and hydrous cerium oxide was coated in an amount of 0.05% by weight as calculated as CeO_2 to produce pigment M.

10. EXAMPLE 14

N: The treatment of Example 5 was repeated, except that the coating treatment with hydrous aluminium oxide was omitted to produce pigment N.

EXAMPLES 15A TO 15N

15. The performances of the titanium dioxide pigments A to N mentioned in the preceding Examples 1 to 14 were tested and the results obtained are shown in Table 1.

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Table 1

Example	Pigment	Initial gloss		Durability			
				Gloss retention (60°-60° gloss)		Chalking resistance	
		20°-20°	60°-60°	360 hrs	560 hrs	Starting time of chalking (hrs)	Chalking degree after 600 hrs
1	A	81	89	83	55	680	10
2	B	78	88	79	50	680	10
3	C	80	88	80	50	640	10
4	D	82	90	83	54	680	10
5	E	79	89	81	55	720	10
6	F	73	88	65	40	560	8
7	G	78	88	60	35	480	4
8	H	74	88	62	40	520	4
9	I	76	88	67	42	560	8
10	J	70	86	65	42	560	6
11	K	70	86	67	45	600	8
12	L	72	87	62	38	520	6
13	M	75	88	75	46	600	8
14	N	76	88	67	45	600	8

It is apparent from Table 1 that the titanium dioxide pigments of this invention exhibit excellent performance in both gloss and durability when used in a solvent type coating material.

5. The performances listed in Table 1 were evaluated by the following procedures:

Preparation of Test Panel

10. The titanium dioxide pigments were separately mixed with a coconut oil-modified short oil alkyd resin/butylated melamine resin (7/3 by weight varnish) and dispersed in the varnish by means of a paint shaker to give a coating material (Examples 15A to 15N). Then, each coating material in turn was coated on a zinc phosphate-treated steel plate (7 cm x 15 cm) so as to
15. have a thickness (as a dry coating) of about 60 μ (microns) and baked at 130°C for 30 minutes. Thus, white coloured test panels were obtained.

Measurement of Specular Gloss

20. The initial gloss (20° - 20° and 60° - 60° specular glosses) of each white coloured test panel was measured by means of a gloss meter.

Evaluation of Durability

25. Gloss retention was evaluated by subjecting each white coloured test panel to an accelerated weathering (water was sprayed for 12 minutes every 60 minute exposure, and the black panel temperature was 63 $\pm$ 3°C) in a carbon arc type sun-shine weather-o-meter and measuring the 60° - 60° specular gloss at predetermined time intervals. Chalking resistance was evaluated
30. based on the starting time of chalking as well as the

extent of chalking appearing on the coating surface after exposure for 600 hours which was measured according to the standard for evaluation of paint film of JAPAN PAINT INSPECTING ASSOCIATION. That the extent of chalking is 10 means that chalking does not appear, and a smaller number means that the extent of chalking is the greater.

EXAMPLE 16

The titanium dioxide pigment A of this invention obtained in Example 1 was mixed with a solution of a resin mixture consisting of a water soluble acrylic resin and a water soluble melamine resin (3/1 by weight) and dispersed in the solution by means of a ball mill to obtain a coating material (Example 16). Then, it was coated on an aluminium plate (7 cm x 15 cm) so as to have a thickness of about 60 μ (microns) (as a dry film) and baked at 150°C for 30 minutes to obtain a white coloured test panel.

Gloss and durability of this white coloured test panel were evaluated in the same manner as in Examples 15A to 15N. The results are shown in Table 2.

TABLE 2

Example	Dispersibility	Initial gloss		Chalking resistance
	Time (hr)	20°-20°	60°-60°	Chalking degree after 600 hrs
16	5	75	88	10
17	13	51	81	8
18	6	75	88	4

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Note: Dispersibility: The time required until the coarse particle fraction in the paint dispersion reaches a size of $7\ \mu$ or less. (A shorter time means a better initial dispersibility.)

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Control: Examples 17 and 18 are both commercial products produced by the chloride process. Example 17 is of the durable grade (coated with SiO_2 and Al_2O_3), and Example 18 is of the general purpose grade for water soluble paint (coated with Al_2O_3).

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It is apparent from Table 2 that the titanium dioxide pigment of this invention exhibits excellent performance in respect of dispersibility into water soluble type paints, gloss and durability.

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CLAIMS

1. A titanium dioxide pigment which comprises (1) pigmentary titanium dioxide core particle, (2) an inner coating formed of 0.1 - 3% by weight, based on the weight of the said core particle and calculated as SnO_2 , of hydrous tin oxide and 0.1 - 5% by weight, based on the weight of the said core particle and calculated as ZrO_2 , of hydrous zirconium oxide and (3) an outer coating formed of 0.1 - 8% by weight, based on the weight of the said core particle and calculated as Al_2O_3 , of hydrous aluminium oxide.

2. A titanium dioxide pigment as claimed in Claim 1 in which the amount of the coating of hydrous tin oxide is 0.2 - 1.5% by weight based on the weight of the said core particle and calculated as SnO_2 .

3. A titanium dioxide pigment as claimed in Claim 1 in which the amount of the coating of hydrous tin oxide is 0.3 - 1% by weight based on the weight of the said core particle and calculated as SnO_2 .

4. A titanium dioxide pigment as claimed in any one of Claims 1 to 3 in which the amount of the coating of hydrous zirconium oxide is 0.3 - 3% by weight based on the weight of the said core particle and calculated as ZrO_2 .

5. A titanium dioxide pigment as claimed in Claim 4 in which the amount of the coating of hydrous zirconium oxide is 0.5 - 2% by weight based on the weight of the said core particle and calculated as ZrO_2 .



6. A titanium dioxide pigment as claimed in any one of Claims 1 to 5 in which the amount of the coating of hydrous aluminium oxide is 0.3 - 5% by weight based on the weight of the said core particle and calculated as Al_2O_3 .

7. A titanium dioxide pigment as claimed in Claim 6 in which the amount of the coating of hydrous aluminium oxide is 0.5 - 3% by weight based on the weight of the said core particle and calculated as Al_2O_3 .

8. A titanium dioxide pigment as claimed in any one of Claims 1 to 7 in which the weight ratio of the amounts of the coatings of the hydrous oxides of tin, zirconium and aluminium, calculated as $\text{SnO}_2 : \text{ZrO}_2 : \text{Al}_2\text{O}_3$, is 1 : 1-3 : 1-8.

9. A titanium dioxide pigment as claimed in Claim 8 in which the weight ratio of the amounts of the coatings of hydrous oxides of tin, zirconium and aluminium, calculated as $\text{SnO}_2 : \text{ZrO}_2 : \text{Al}_2\text{O}_3$, is 1 : 1-2 : 2-6.

10. A titanium dioxide pigment as claimed in any one of Claims 1 to 9 in which an organic agent is adsorbed around the outer coating of hydrous aluminium oxide.

11. A titanium dioxide pigment as claimed in Claim 10 in which the said organic agent is a polyol or an alkanolamine.



12. A titanium dioxide pigment as claimed in Claim 1 substantially as specifically described herein with reference to any one of Examples 1 to 5.

13. A process for producing a titanium dioxide pigment which comprises (1) forming an aqueous slurry of pigmentary titanium dioxide core particles, (2) adding, to the said slurry, water soluble compounds of tin and zirconium and an acid or an alkali to precipitate hydrous oxides of tin and zirconium on the surfaces of the said core particles, thereby forming an inner coating comprising 0.1 - 3% by weight of tin oxide and 0.1 - 5% by weight of zirconium oxide, both based on the weight of the said core particles and calculated as SnO_2 and ZrO_2 , respectively, and then (3) adding a water soluble compound of aluminium and an acid or an alkali to precipitate hydrous aluminium oxide, thereby forming an outer coating comprising 0.1 - 8% by weight of aluminium oxide, based on the weight of the said core particles and calculated as Al_2O_3 .

14. A process for producing a titanium dioxide pigment as claimed in Claim 13 in which said tin compound comprises tin chloride, tin sulphate, tin acetate, tin oxychloride, potassium stannate or sodium stannate or mixtures thereof.

15. A process for producing titanium dioxide pigment as claimed in Claim 13 or Claim 14 in which the said zirconium compound comprises zirconium chloride, zirconium sulphate, zirconium nitrate,

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zirconium acetate, zirconium carbonate, zirconium oxychloride or zirconium oxysulphate or mixtures thereof.

16. A process for producing titanium dioxide pigment as claimed in any one of Claims 13 to 15 in which the said aluminium compound comprises alkali aluminates, aluminium chloride or aluminium sulphate, or mixtures thereof.

17. A process for producing titanium dioxide pigment as claimed in any one of Claims 13 to 16 in which tin chloride is used as the said tin compound, zirconium sulphate is used as the said zirconium compound and sodium aluminate is used as the said aluminium compound.

18. A process for producing titanium dioxide pigment as claimed in any one of Claims 13 to 17 in which in step (1), the aqueous slurry of pigmentary titanium dioxide core particles is adjusted to an acidic condition and, in step (2), an aqueous solution of acidic tin compound and an aqueous solution of acidic zirconium compound are added to the slurry, and the pH value of the slurry is then adjusted to 6 - 8 by adding an aqueous solution of an alkali.

19. A process for producing titanium dioxide pigment as claimed in any one of Claims 13 to 17 in which an inner coating is formed by adding a water soluble compound of tin to the aqueous slurry of the



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core particles, adjusting the pH value of the said slurry to precipitate at least a part of the tin as hydrous oxide onto the surface of the said core particles, then adding a water soluble compound of zirconium and adjusting the pH value of the said slurry to precipitate hydrous zirconium oxide.

20. A process for producing titanium dioxide pigment as claimed in any one of Claims 13 to 19 in which the coating treatment with hydrous oxides of tin, zirconium and aluminium is carried out while maintaining the temperature of the said slurry at 40 - 90°C.

21. A process for producing titanium dioxide pigment as claimed in any one of Claims 13 to 20 in which the outer coating of hydrous oxide of aluminium is formed and an organic agent is thereafter adsorbed thereon.

22. A process as claimed in Claim 13 substantially as specifically described herein with reference to any one of Examples 1 to 5.

23. A titanium dioxide pigment whenever produced by a process as claimed in any one of Claims 13 to 22.

24. A coating material incorporating a titanium dioxide pigment as claimed in any one of Claims 1 to 12 or 23.

25. A coating material as claimed in Claim 24 substantially as specifically described herein with reference to any one of Examples 15A to 15E or 16.