

**Method for coating the surface of inorganic solid particles,
in particular titanium dioxide pigment particles**

5 Field of the invention

The invention relates to a method for coating the surface of inorganic solid particles in an aqueous suspension. It especially relates to the coating of titanium dioxide pigment particles with a smooth, homogeneous silicon dioxide skin.

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Technological background of the invention

15 The surface of fine, inorganic solid particles is frequently coated in order to modify specific properties, such as abrasion resistance, surface charge, dispersing properties, acid or light resistance. For example, US 2,885,366 describes the application of a dense silicon dioxide coating to substrate particles, such as nickel or iron powder, glass fibres or titanium dioxide. Colour and white pigments are regularly coated with various oxides and hydroxides (e.g. EP 0 130 272 A1, US Re. 27818).

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Surface treatment, particularly of TiO_2 pigments, is customarily performed in the aqueous phase, where metal oxides, hydroxides, phosphates or similar compounds are deposited on the particle surface. The method is customarily operated as a batch process and starts with an aqueous pigment particle suspension which first of all is disagglomerated, customarily in a media mill. Subsequently, metal salts are added in dissolved form as so-called precursors, and the pH value of the suspension is set by means of alkaline or acidic substances in such a way that the precursors are precipitated as oxides, hydroxides, etc.

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In the classical method, there is the risk of particle reagglomeration in the suspension, meaning that the deposited coating substances do not enclose the individual particle, but often an agglomerate. The agglomerates are disintegrated again during final dry milling, as a result of which not all particles in the end product are provided with a continuous skin, but instead also display uncoated surface areas. Moreover, part of the coating substances is not fixed on the particle surface, but forms floccules alongside the particles. These floccules can no longer be removed from the suspension and have a negative impact on the optical properties of the pigments, such as the tinting strength (TS).

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US 5,993,533 discloses a method in which titanium dioxide pigment is coated with SiO_2 and Al_2O_3 in an inline mixer. Treatment is performed in two consecutive maturation stages at 80 to 100 °C and pH values of > 9.5 and < 8.5.

5 GB 1 340 045 describes a batch method for coating the surface of titanium dioxide pigment, where a suspension of the pigment is subjected to intensive agitation in a mixing vessel for up to two hours, during which time the coating substances are added and applied.

10 WO 2008/071382 A1 describes a further method, in which inorganic particles are surface-coated during continuous feeding through an agitator mill. Particularly smooth and homogeneous surface-coating of the individual particles is achieved in this case.

Summary of the invention

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The object of the invention is to indicate an alternative method by means of which a smooth, homogeneous and continuous surface coating can be produced on solid particles.

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The object is solved by a method for coating inorganic solid particles in an aqueous suspension with at least one coating substance, comprising the steps:

- a) Disagglomeration of the solid particles contained in aqueous suspension,
- b) Addition of a water-soluble precursor of the coating substance to the suspension,
- c) Immediately following Step b) homogenisation of the suspension, where the temperature and pH value of the suspension do not change significantly in Steps a) to c),
- 25 d) Feeding the slurry into a tank and precipitation of the coating substance onto the particle surface and, optionally, application of further coatings,
- e) Separation of the solid particles from the suspension.

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Further advantageous embodiments of the invention are described in the sub-claims.

The subject matter of the invention is thus a method for coating the surface of solid particles with a smooth, homogeneous and continuous skin consisting of at least one inorganic or organic compound.

Brief description of the drawings

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Figure 1 is a TEM view of titanium dioxide pigment particles of Example 1.

Figure 2 is a TEM view of titanium dioxide pigment particles of Reference Example 1.

Detailed description of the preferred embodiments

The method according to the invention is based on an aqueous suspension of untreated inorganic solid particles, also referred to as base material below. Suitable for this purpose are fine, inorganic solids that have a particle size in the range of roughly 0.001 to 1 μm and are processed in aqueous suspensions, such as pigments (titanium dioxide, colour pigments, effect pigments, etc.), fillers, titanates, iron, nickel or other magnetic particles.

Open to consideration as the coating are oxides, hydroxides, phosphates and similar compounds of the familiar elements Si, Ti, Al, Zr, Sn, Mn, Ce and other elements. Here and below, the term "oxide" is also to be taken to mean the respective hydroxide or hydrous oxide. In particular, inorganic coatings are involved.

In a special embodiment of the invention, untreated titanium dioxide pigment particles (TiO_2 base material) are used. TiO_2 base material manufactured by either the sulphate process or the chloride process can be used. The TiO_2 base material can have an anatase or rutile structure. Rutile is preferred. The TiO_2 base material is customarily doped with familiar elements, e.g. Al, to improve the photostability of the TiO_2 pigment. In the chloride process, for example, such a quantity of AlCl_3 is oxidised together with TiCl_4 that the TiO_2 base material contains roughly 0.5 to 2.0% by weight Al, calculated as Al_2O_3 . When manufacturing titanium dioxide by the sulphate process, the hydrolysed titanyl sulphate is mixed with calcining additives, such as potassium hydroxide or phosphoric acid, and subsequently calcined. TiO_2 base material from the sulphate process customarily contains roughly 0.2 to 0.3% by weight K, as well as 0.05 to 0.4% by weight P, calculated as oxide in each case.

The method according to the invention is characterised by the fact that the particles are in an optimum state of dispersion during surface-coating in the aqueous suspension. The method is thus based on an aqueous suspension of untreated, inorganic solid particles that are subjected to intensive disagglomeration in a first step (Step a)).

Disagglomeration can, for example, be performed in agitator mills, such as bead mills or sand mills, or in ultrasonic mills.

A dispersant is customarily added. Suitable dispersants are familiar to the person skilled in the art. For example, sodium silicate or sodium hexametaphosphate is used with preference as the dispersant when disagglomerating TiO_2 base material in sand mills. The dispersant concentration is customarily in the range from 0.05 to 5.0 kg/t TiO_2 .

The pH value of the suspension is customarily also set as a function of the particle type and the dispersant. For example, the pH value is set to values of roughly 9 to 12, or of roughly 2 to 5, when disagglomerating TiO_2 base material from the chloride process. The temperature of TiO_2 base material suspensions is customarily roughly 40 to 80 °C.

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The disagglomerated suspension is classified to eliminate grinding media, their fragments or feedstock which has not been comminuted adequately. Sieves and hydrocyclones are used for this purpose. The fines from hydrocyclone classification can subsequently be used for surface-coating, while the coarse material can be returned to the disagglomeration process step.

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In a Step b), a precursor of the coating substances is added to the suspension in an aqueous solution, customarily, as in the classical methods, in the form of water-soluble salts (referred to as metal salts below). The person skilled in the art is familiar with the corresponding metal salts. For example, sodium or potassium silicate (waterglass) can be used as the precursor for coating with SiO_2 .

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Furthermore, organometallic compounds can also be used as precursors, such as alkoxysilanes for coating with SiO_2 .

The precursor can be added either to a pipeline or batchwise to a tank.

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The method according to the invention is characterized in that the addition follows so fast after disagglomeration and classification, that the temperature and pH value cannot change significantly. A "significant" change is taken to mean a temperature difference of more than 10 °C and a pH value difference greater than 1. Addition preferably takes place no later than eight hours preferably no later than one hour after disagglomeration and classification. It is advantageous to avoid sedimentation of the particles in the period prior to addition of the precursor.

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Following addition of the precursor, the suspension is homogenised in a dispersing machine in a Step c). Inline dispersing machines are preferably used, such as rotor-stator systems, or static mixers. No significant change in the temperature and pH value of the suspension occurs during homogenisation. Homogenisation ensures that a uniform, adsorbed layer of the precursor already forms around the individual particles. Precipitation of the coating substance takes place in Step d).

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In Step d), the suspension is fed into a tank and the coating substance precipitated on the particle surface by setting a suitable pH value. Accordingly, an acid or alkaline-reacting

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substance, such as an acid or a lye, is added to the suspension in accordance with familiar methods. The person skilled in the art is familiar with the precipitation conditions for the individual coating substances.

Optionally, further inorganic or organic coatings can additionally be applied to the particle surface by familiar methods.

In a Step e), the coated particles are separated from the suspension, washed if appropriate, dried and fine-ground by familiar methods.

10 In a special embodiment of the method, titanium dioxide base material particles are coated with SiO_2 or Al_2O_3 , preferably with SiO_2 . To this end, a suspension of TiO_2 base material particles is set to an alkaline pH value, mixed with dispersant, disagglomerated in a sand mill and subsequently classified. The suspension subsequently has a pH value of roughly 9 to 12 and a temperature of roughly 40 to 80 °C.

15 For coating with SiO_2 , sodium silicate solution is added to the suspension as the precursor, in a quantity of roughly 0.1 to 5.0% by weight SiO_2 , referred to TiO_2 . For coating with Al_2O_3 , suitable precursors are, for example, aluminates, particularly sodium aluminate. Addition preferably takes place no later than eight hours preferably no later than one hour after disagglomeration and classification, so that the temperature and pH value have not changed significantly. The suspension mixed with silicate is homogenised in an inline dispersing machine immediately afterwards. The temperature and pH value of the suspension do not change significantly during homogenisation.

20 The suspension is subsequently pumped into a tank and the pH value set to roughly 1 to 8 by adding an appropriate quantity of acid, such as HCl. As a result, SiO_2 or Al_2O_3 is precipitated on the particle surface.

25 Familiar methods can subsequently be used to apply further surface coatings, e.g. oxides, hydroxides, oxide hydrates or phosphates of Si, Al, Zr, Sn, Ti, Mn, Ce, etc. Preferably, an Al compound is finally applied in a quantity of roughly 0.5 to 8% by weight, calculated as Al_2O_3 and referred to TiO_2 .

30 Compared to the familiar surface-coating methods, the method according to the invention achieves very smooth, homogeneous and continuous enclosure of the individual particles. Moreover, the suspension of SiO_2 or Al_2O_3 -coated TiO_2 particles, produced in Step c) of the method according to the invention, demonstrates particularly good storage stability compared to conventionally disagglomerated and classified suspension, since the silicon dioxide hydrate layer, or the aluminium oxide hydrate layer, on the TiO_2 particles increases the

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negative surface charge density of the particles under the prevailing conditions (temperature of roughly 40 to 80 °C, pH value of roughly 9 to 12). This prevents reagglomeration of the titanium dioxide during subsequent precipitation in Step d) and prior to further coating.

With the method according to the invention, there is less uncoated particle surface and less separately precipitated coating substance following final fine-grinding.

Moreover, the filtration properties of the suspension produced by the method according to the invention compare well to those of the suspension produced by the classical method (Reference Example 1).

TiO₂ pigments treated according to the invention display improved photostability and substantially improved tinting strength (TS). The TiO₂ pigments are eminently suited to use in plastics, particularly masterbatches, as well as in coatings, particularly paints, and in laminates.

Examples

The invention is explained in more detail below on the basis of examples, although these are not to be interpreted as a limitation. The quantities indicated refer to the TiO₂ base material in each case.

Example 1

An aqueous suspension of TiO₂ base material from the chloride process with a concentration of 550 kg/m³ and a temperature of 55 °C was prepared, set to a pH value of roughly 11 with NaOH and mixed with sodium hexametaphosphate as dispersant. The suspension obtained in this way was disagglomerated in an agitator mill, using zirconium dioxide grinding media, and classified by means of sieves and hydrocyclones to eliminate coarse material. The fines from the disagglomerated suspension were collected in a tank and displayed a pH value of 10.5 and a temperature of 55 °C. The suspension was subsequently fed through an inline dispersing machine (rotor-stator system: Ytron Z250.3). 0.5% by weight aqueous sodium silicate solution, calculated as SiO₂ and referred to TiO₂, was added to the suspension via a pipe in the feed line of the inline dispersing machine.

The suspension was subsequently collected in a further tank. The temperature of the suspension was 55 °C, the pH value being 10.5. HCl was subsequently added while stirring, and the pH value set to roughly 3.5.

After stirring for 30 minutes, a further 0.7% SiO₂ was added in the form of sodium silicate solution, and finally 2.0% Al₂O₃ in the form of sodium aluminate solution. A pH value of

roughly 6 was obtained. The suspension was subsequently filtered, washed and dried. The dried material was micronised in a spiral jet mill with added silicone oil.

The composition of the TiO_2 pigment was analysed with the help of XRF (X-ray fluorescence) and was 95% by weight TiO_2 , 1.25% by weight SiO_2 and 3.3% by weight Al_2O_3 .

- 5 Examination under the transmission electron microscope revealed that the pigment displays a very homogeneous, smooth and continuous coating (Fig. 1). There is no flocculated coating material alongside the particles.

The tinting strength (TS) of the pigment produced in this way was roughly 103 points.

10 Example 2

The procedure was the same as in Example 1, the only difference being that 0.5% by weight Al_2O_3 in the form of sodium aluminate solution was added to the feed line of the inline dispersing machine, instead of SiO_2 . In the further course, SiO_2 and Al_2O_3 were added in such quantities that a TiO_2 pigment was obtained with the composition 96% by weight TiO_2 ,

- 15 1.8% by weight SiO_2 and 2.2% by weight Al_2O_3 .

Reference Example 1 (classical method)

An aqueous suspension of TiO_2 base material from the chloride process with a concentration of 550 kg/m³ and a temperature of 55 °C was prepared, set to a pH value of roughly 11 with
20 NaOH and mixed with sodium hexametaphosphate as dispersant. The suspension obtained in this way was disagglomerated in an agitator mill, using zirconium dioxide grinding media, and classified by means of sieves and hydrocyclones to eliminate coarse material. The fines from the disagglomerated suspension were collected in a tank and displayed a pH value of 10.5 and a temperature of 55 °C.

- 25 The suspension was subsequently collected in a tank. The temperature of the suspension was 55 °C, the pH value being 10.5.

1.25% SiO_2 was then added in the form of sodium silicate solution, the pH value lowered to approx. 5 by adding HCl and, finally, 2.0% Al_2O_3 added in the form of sodium aluminate solution. A pH value of roughly 6 was obtained. The suspension was subsequently filtered,
30 washed and dried. The dried material was micronised in a spiral jet mill with added silicone oil.

The composition of the TiO_2 pigment was analysed with the help of XRF (X-ray fluorescence) and was 95% by weight TiO_2 , 1.25% by weight SiO_2 and 3.3% by weight Al_2O_3 . Examination under the transmission electron microscope revealed that the pigment displays an
35 inhomogeneous coating compared to Example 1 (Fig. 2). There is flocculated coating material alongside the particles.

The tinting strength (TS) of the pigment produced in this way was 99 points.

Reference Example 2 (so-called TDD method)

An aqueous suspension of TiO_2 base material from the chloride process with a concentration of 550 kg/m³ and a temperature of 55 °C was prepared, set to a pH value of roughly 11 with NaOH and mixed with sodium hexametaphosphate as dispersant. This was followed by addition of 0.5% by weight aqueous sodium silicate solution, calculated as SiO_2 and referred to TiO_2 . The suspension obtained in this way was disagglomerated in an agitator mill, using sand grinding media, and classified by means of sieves and hydrocyclones to eliminate coarse material. The fines from the disagglomerated suspension were collected in a tank and displayed a pH value of 10.5 and a temperature of 55 °C.

HCl was subsequently added while stirring, and the pH value set to roughly 3.5.

After stirring for 30 minutes, a further 0.7% SiO_2 was added in the form of sodium silicate solution, and finally 2.0% Al_2O_3 in the form of sodium aluminate solution. A pH value of roughly 6 was obtained. The suspension was subsequently filtered, washed and dried. The dried material was micronised in a spiral jet mill with added silicone oil.

The composition of the TiO_2 pigment was analysed with the help of XRF (X-ray fluorescence) and was 95% by weight TiO_2 , 1.25% by weight SiO_2 and 3.3% by weight Al_2O_3 .

Examination under the transmission electron microscope revealed that the pigment displays a similarly homogeneous, smooth and continuous coating compared to Example 1. There is no flocculated coating material alongside the particles.

The tinting strength (TS) of the pigment produced in this way was roughly 103 points.

Test methods

Tinting strength (TS)

The tinting strength (TS) of the pigments in the examples and the reference examples is determined after incorporation into a Vinnol black paste at a pigment volume concentration of 1.22% (so-called VIG method).

The titanium dioxide pigment to be tested is pasted with a ready-made Vinnol black paste on an automatic muller.

The grey paste obtained is applied to a chart with a film applicator.

The reflectance values of the film are measured with a HunterLab PD-9000 colorimeter in wet state and referred to an internal standard.

Transmission electron microscopy (TEM)

The coating of the titanium dioxide particles can be visualised with the help of transmission electron microscopy (TEM).

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Conclusion

10 The method according to the invention leads to pigments with a very homogeneous, smooth and continuous coating (Fig. 1). There is no flocculated coating material alongside the particles. The coating produced in accordance with the invention is thus substantially improved compared to that in Reference Example 1 (Fig. 2), produced by the classical method, and comparable to that in Reference Example 2, produced by the so-called TDD method.

15 At the same time, however, the method according to the invention is characterised by the fact that the suspension displays similarly good filtration properties as in the classical method (Reference Example 1), whereas the suspension produced according to the TDD method (Reference Example 2) can, owing to thixotropy and formation of a very compact filter cake, only be filtered by reducing the throughput by roughly 30%.

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CLAIMS

- 5 1. Method for coating inorganic solid particles in an aqueous suspension with at least one coating substance, comprising the steps:
 - a) Disagglomeration solid particles contained in an aqueous suspension,
 - b) Addition of a water-soluble precursor of the coating substance to the suspension,
 - 10 c) Immediately following Step b) homogenisation of the suspension, where the temperature and pH value of the suspension do not change significantly in Steps a) to c),
 - d) Feeding the slurry into a tank and recipitation of the coating substance onto the particle surface and, optionally, application of further coatings,
 - 15 e) Separation of the solid particles from the suspension.
2. Method according to Claim 1, characterised in that the solid particles are titanium dioxide particles.
- 20 3. Method according to Claim 1 or 2, characterised in that coating is performed with at least one inorganic coating substance.
4. Method according to Claim 3, characterised in that the coating substance is SiO_2 or Al_2O_3 .
- 25 5. Method according to one or more of Claims 1 to 4, characterised in that an agitator mill is used in Step a).
6. Method according to one or more of Claims 1 to 5, characterised in that the suspension displays a pH value of roughly 9 to 12, or of roughly 2 to 5, in
30 Step a).
7. Method according to one or more of Claims 1 to 6, characterised in that the suspension displays a temperature of roughly 40 to 80 °C in Step a).
- 35 8. Method according to one or more of Claims 1 to 7, characterised in that coarse material is removed from the suspension by a classification step after

disagglomeration in Step a).

- 5 9. Method according to Claim 4, characterised in that
SiO₂ is added in a quantity of roughly 0.1 to 5% by weight, referred to the
particle mass.
- 10 10. Method according to one or more of Claims 1 to 9, characterised in that
the precursor is added (Step b)) no later than eight hours, particularly no later
than one hour, after Step a).
- 15 11. Method according to one or more of Claims 1 to 10, characterised in that
the precursor is added to a tank or to a pipeline in Step b).
12. Method according to one or more of Claims 1 to 11, characterised in that
an inline dispersing machine is used in Step c).
- 20 13. Method according to Claim 12, characterised in that
the inline dispersing machine is a rotor-stator system or a static mixer.
- 25 14. Method according to one or more of Claims 1 to 13, characterised in that
further coating with oxides, hydroxides, oxide hydrates or phosphates of Si,
Al, Zr, Sn, Ti, Mn or Ce is performed in Step d).
- 30 15. Method according to Claim 14, characterised in that,
finally, coating is performed with a quantity of roughly 0.5 to 8% by weight Al,
calculated as Al₂O₃ and referred to the particle mass.
- 35 16. Coated, inorganic solid particles, manufactured according to one or more of
Claims 1 to 15.
17. Particles according to Claim 16, characterised in that
the particles are titanium dioxide pigment particles.
18. Use of the titanium dioxide pigment particles according to Claim 17 in plastics,
coatings and laminates.