

PROCESS FOR THE PREPARATION OF TITANIUM DIOXIDE BASED COLORED PIGMENTS

The invention concerns a process for the preparation of titanium dioxide based colored pigments. The invention also concerns the colored pigments obtained through this process.

Rutile phase colored pigments, i.e., composed primarily of rutile titanium dioxide are commonly used as coloring substances in plastic materials, paints and varnishes and also in the cosmetics and galenic fields.

These prior art pigments are generally prepared by (i) mixing anatase titanium dioxide with one or a plurality of pigmentation additives, (ii) grinding then (iii) calcination.

These colored pigments must meet a certain number of criteria and, in particular, must have good stability to temperature, light, and also to decomposition by acid or basic chemical agents. DE 36 04 317 proposes colored pigments having improved thermostability containing from 0.1 to 2 wt.-% magnesium in addition to a ternary system composed of titanium, antimony and chromium.

It is, in fact, essential that the colors of the pigments do not shade off, for instance, when they are added to plastic materials or paints, or when they are subjected to particularly severe climatic conditions. Along the same line of thought, EP 318 783 recommends incorporation of lithium at a rate of 0.01 up to 0.25 wt.-%, to limit the tendency toward discoloration of rutile phase pigments composed of chromium and antimony subjected to a quenching treatment.

However, the colorations from rutile phase pigments used in industry to date are not always satisfactory from the point of view of intensity of the shades and color saturation.

The invention proposes to resolve the problem of intensifying the shades by providing an improved process for the preparation of titanium dioxide based colored pigments. The colored pigments obtained through this process offer a palette of colors that are more intense than those currently available on the market.

To that end, the invention concerns a process for the preparation of titanium dioxide based colored pigments including the calcination of anatase titanium dioxide until complete transformation of the anatase titanium dioxide into rutile titanium dioxide, in which an anatase titanium dioxide with a rutilization temperature of at least 1000°C, preferably at least 1060°C., and a sulfate level, expressed as SO_3 , of at most 1 wt.-%, preferably less than 0.8%, is used.

According to a first essential characteristic of the invention, the titanium dioxide used must have a sulfate level, expressed as SO_3 , of at most 1 wt.-%, preferably less than 0.8%. It was noted that starting with an anatase titanium dioxide with an excessively high sulfate level yields a pigment shade which is not sufficiently intense. The lowest possible sulfate level is more advantageous.

The sulfate level is easily determined by the person skilled in the art using any one of the methods of analysis known in the art, for example, by x-ray fluorescence.

This sulfate content in the anatase titanium dioxide may be controlled during the manufacture of the anatase titanium dioxide.

The starting anatase titanium dioxides that may be used in the process according to the invention are prepared according to methods known to the person skilled in the art. In this regard, reference may be made to the works of Ullman Band (vol. 18, p. 574) and Kirk Othmer (vol. 23, p. 146). Preferably, the anatase titanium dioxide is obtained in three steps through (1) hydrolysis of a titanium sulfate solution, (2) filtration of the hydrolysate, and (3) washing of the filtrate with water.

The sulfate content of the titanium dioxide may be controlled, in particular, during the step (3) of washing of the filtrate.

According to a second essential characteristic of the invention, the titanium dioxide used must have a rutilization temperature of at least 1000°C, preferably at least 1060°C.

Control of the rutilization temperature of a titanium dioxide is generally performed during the synthesis of the titanium dioxide. The degree of purity of the anatase phase titanium dioxide may be a controlling element of this temperature: the closer the level of anatase titanium dioxide is to 100%, the higher the rutilization temperature.

This level of anatase may, in particular, be adjusted in the step (1) by incorporation of seeds into the hydrolysis medium. These serve to direct the nature of the hydrolysate formed: Depending on the nature of the titanium dioxide seeds introduced, the resulting hydrolysate, primarily made up of anatase titanium dioxide, will include a higher or lower percentage of rutile titanium dioxide, *with the objective being to reduce the percentage.*

Anatase titanium dioxides that have the necessary characteristics to be used in the process according to the invention are marketed, for example, by the Rhône Poulenc Company. The titanium dioxide sold by the Rhône Poulenc Company under the reference G5 is a powder; the Rhône Poulenc Company also supplies a titanium dioxide as a sol under the reference S5-300.

The rutilization temperature, which is not always indicated by the manufacturer, is easily determined by the person skilled in the art by implementing the following operating protocol.

The rutilization temperature is generally defined as being that at which 50 wt.-% of the anatase phase of an anatase titanium dioxide has been transformed into the rutile phase through calcination. According to the invention, the rutilization temperature is determined by high temperature x-ray diffractometry.

To avoid the influence of extrinsic parameters (such as the exact conditions of the rise in temperature), this determination takes place under very precise operating conditions: the anatase titanium dioxide sample is placed on a flat platinum substrate and kept in a confined atmosphere (without air currents) during calcination, for example, in a closed chamber. The temperature of the chamber is increased at the rate of 5°C/min. up to 1250°C.

Diffractometry measurements are taken between 650°C and 1250°C. At regular intervals (for example, every 50°C), a diffractogram is drawn, the acquisition time being fixed at 10 seconds over an angular range from 10° to 60° scanned by steps of 0.032°.

Preliminary experiments are performed in this manner with reference samples of

100% of rutile phase and 100% of anatase phase, respectively.

On the reference diffractograms obtained, the bands corresponding to the anatase and rutile titanium dioxides, respectively, are located.

The experiment is then performed under the same conditions with the titanium dioxide sample to be analyzed.

By comparing the surface area of the most intense band of the two phases with those marked on the diffractograms drawn from the reference samples, a calculation is made at each temperature of the proportion of rutile phase formed.

The temperature at which an equal percentage of rutile phase and anatase phase is observed is the rutilization temperature.

According to the invention, the rutilization temperature must be at least 1000°C, preferably at least 1060°C. A temperature of less than 1000°C is insufficient from the point of view of intensification of shades and of color saturation.

According to a preferred embodiment of the invention, the process includes the following steps:

- a) mixing the anatase titanium dioxide with at least one pigmentation additive;
- b) grinding the resulting mixture, and
- c) calcination in an oxidizing atmosphere.

The mixing of anatase titanium dioxide with one or more pigmentation additives may be performed dry or starting from an aqueous suspension.

To facilitate the mixing operation, selection of an anatase titanium dioxide with a BET specific surface of at least 250 g/m² [sic m²/g] is preferred.

BET specific surface is understood to mean the specific surface measured by the BET method, i.e., by nitrogen adsorption, in accordance with ASTM standard 03663-78 established on the basis of the BRUNAUER-EMMETT-TELLER method described in the periodical, "The Journal of the American Society", 60, 309 (1938). When the titanium dioxide is in the form of an aqueous suspension (for example, a sol), the aqueous suspension is first atomized prior to measuring its specific surface.

When the mixing operation a) is performed dry, the anatase titanium dioxide is in the form of a powder composed of agglomerates of particles, with the average size of these agglomerates between 1 and 2 µm and the average size of the particles between 40 and 60 nm.

Such a powder may be obtained by a prior art means, by implementing the steps of:

- hydrolysis of a titanium sulfate solution,
- filtration of the hydrolysate,
- washing of the filtrate with water,
- resuspension of the filtrate in water, and
- atomization of the resulting suspension.

According to another embodiment, the mixing a) may be performed in solution starting from anatase titanium dioxide particles suspended in an aqueous medium, with the average size of the particles ranging between 40 and 60 nm. Prior to grinding and calcination, the water is, in this case, eliminated from the aqueous suspension. This second embodiment is even more advantageous insofar as it results in pigments that have even more intense colors, in comparison to the first embodiment according to which the mixing operation a) is performed dry starting from the corresponding anatase titanium

dioxide powder.

In all cases, a reduction in size of the particles facilitates the mixing operation.

The anatase titanium dioxide based aqueous suspension may be obtained by implementing the following steps:

- hydrolysis of a titanium sulfate solution,
- filtration of the hydrolysate,
- washing of the filtrate with water,
- redispersion of the filtrate in an acidified medium, for example, a nitric acid or hydrochloric acid solution. The use of sulfuric acid will be avoided at this stage so as not to increase the sulfate level.

The pigmentary additives are those generally used in the art. These are chosen, for example, from among the compounds of the transition elements Sb, Cr, Ni, Co, Zn, Cu, Mn and W, and are either in the oxide form (particularly, Sb_2O_3 , Cr_2O_3 , NiO , CuO , MnO and WO_3), or in the form of compounds oxidizable in an oxidizing atmosphere, such as that used during the calcination stage.

Preferably, a mixture of titanium dioxide and compounds of chromium and antimony, in which the molar ratio of antimony to chromium is close to 1, for example, between 0.8 and 1.2, will be selected.

For informational purposes, it should be noted that calcination may take place in an oxygen or air atmosphere, with the calcination temperature advantageously between 800 and 1400°C.

Prior to grinding and calcination of the titanium dioxide based mixture, it is possible to add mineral additives to it (called "mineralizers" in the art), which are, for example, sodium fluoride, sodium chloride, potassium chloride, calcium fluoride or calcium chloride. It is also possible to envisage the addition of lithium compounds such as those described in EP 318 783 (carbonate, fluoride, chloride, oxide, hydroxide, sulfate, nitrate, phosphate, lithium antimonate or lithium titanate) or magnesium compounds, such as are recommended in DE 36 04 317 (magnesium carbonate and oxide).

The invention also concerns the colored pigments obtained through the process described above. These may be used in plastic materials, paints and varnishes, and also in the cosmetics and galenic fields.

And finally, the invention concerns the use of an anatase titanium dioxide with a rutilization temperature of at least 1000°C, preferably at least 1060°C, and a sulfate level, expressed as SO_3 , of at most 1 wt.-%, preferably less than 0.8%, for the preparation of titanium dioxide based colored pigments.

The following examples are for the purpose of facilitating comprehension of the invention without restricting it.

EXAMPLE 1 - Determination of the rutilization temperatures of anatase titanium dioxides.

The samples used in the examples have the following characteristics:

- sample 1: G5 powder marketed by the Rhône Poulenc Company. This titanium dioxide has a BET specific surface of 300 m²/g and a sulfate level, expressed as SO_3 , of less than 0.8 wt.-%; the powder is in the form of an agglomerate of particles, with the

average size of the agglomerates close to 1.5 μm .

- sample 2: comparative powder having a BET specific surface of over 250 m^2/g and a sulfate level, expressed as SO_3 , of 5 wt.-%; it is in the form of agglomerates of particles, with the average size of the agglomerates close to 1.5 μm .

The rutilization temperatures of these samples are measured as follows.

First, the reference samples powders are studied by high temperature x-ray diffraction. As a reference for the location of the bands corresponding to the anatase and rutile phases, 100% anatase and 100% rutile powders are used. Each reference powder to be tested is placed on a flat platinum substrate situated in a closed chamber. The temperature of the chamber is progressively increased at a heating speed of $5^\circ\text{C}/\text{min}$. Diffractograms are drawn at the temperatures of 650, 700, 750, 800, 850, 900, 950, 1000, 1050, 1100, 1150, 1200 and 1250°C , respectively, under the following conditions:

- acquisition time: 10 s
- angular range 10° to 60° in steps of 0.032° .

The bands corresponding to the rutile and anatase phases are located.

The same measurements are made on samples 1 and 2. The diffractograms obtained enable the evaluation of the percentage of the rutile and anatase phases by comparing the surface area of the most intense bands of the two phases with those marked on the diffractograms drawn from the reference samples.

The results are then visualized in the form of curves representing the variation in the percentage of the rutile or anatase phase as a function of temperature. These curves, proposed in figures 1 and 2, enable an easy graphic determination of the rutilization temperature.

Figure 1 corresponds to sample 1, which shows a rutilization temperature of 1080°C .

Figure 2 corresponds to sample 2, which shows a rutilization temperature of 850°C .

Only the powder from sample 1 may be used in the process according to the invention since its rutilization temperature is greater than 1000°C .

EXAMPLE 2 - Preparation of the anatase titanium dioxide based colored pigments with a rutilization temperature of 1080°C .

The anatase titanium dioxide powder of sample 1 (cf. example 1) is mixed with chromium oxide (Cr_2O_3) and antimony oxide (Sb_2O_3). This mixture is formed into pellets.

Then these pellets are calcinated for 12 hrs. at 920°C in an oxygen atmosphere. Next, the pellets are ground prior to calcinating them again, first for 12 hrs. at 980°C in an oxygen atmosphere, then for 4 hrs. at 970°C in air. The resulting powder is ground.

Two samples of orange-colored pigment are prepared in this manner:

- sample 3: this has as a total formula $(\text{Ti}_{0.9}\text{Cr}_{0.05}\text{Sb}_{0.05})\text{O}_2$
- sample 4: this has as a total formula $(\text{Ti}_{0.99}\text{Cr}_{0.005}\text{Sb}_{0.005})\text{O}_2$.

The chemical formula of the final compound is adjusted using the respective quantities of chromium oxide, antimony oxide and titanium dioxide.

The two pigments obtained have been tested from the point of view of color saturation.

The coloration is quantified here by the chromatic coordinates L^* , a^* and b^* of the 1976 CIE system (L^* , a^* , b^*) as defined by the International Commission on Illumination and listed in the Compendium of French Standards (Recueil des Normes Françaises (AFNOR)), colorimetric color no. X08-12 (1983). They are determined using a DATACOLOR colorimeter marketed by the SCIENTIFIC PACIFIC Company.

L^* gives a measurement of reflectance and gives information on the clarity of the color.

a^* and b^* express the colored tendencies:

a value of a^* positive indicates red,

a value of a^* negative indicates green,

a value of b^* positive indicates yellow, and

a value of b^* negative indicates blue.

Thus, schematically, L^* represents the variation from white to black (clarity), a^* the variation from green to red and b^* the variation from blue to yellow.

The measurements taken from samples 3 and 4 yielded the results reported in Table 1 below:

TABLE 1

Pigment	L^*	a^*	b^*
Sample 3	67.5	24	59
Sample 4	84	6	38

EXAMPLE 3 (comparative) - Preparation of anatase titanium dioxide based colored pigments with a rutilization temperature of 850°C.

Two colored pigments (samples 5 and 6) corresponding respectively to total formulas $(\text{Ti}_{0.9}\text{Cr}_{0.05}\text{Sb}_{0.05})\text{O}_2$ and $(\text{Ti}_{0.99}\text{Cr}_{0.005}\text{Sb}_{0.005})\text{O}_2$ are prepared starting from the anatase titanium dioxide of sample 2 as described in example 1 in accordance with the operating mode of example 2.

The measured chromatic data are reported in table 2 below:

TABLE 2

Pigment	L^*	a^*	b^*
Sample 5	66	20	57
Sample 6	85.8	3.2	28.2

It is then noted, by comparing the pigments with the same chemical formula

(samples 3 and 5, on the one hand, and samples 4 and 6, on the other) that the pigments according to the invention have higher values for a^* and b^* and thus, overall, a more intense orange-color.

EXAMPLE 4 - Preparation of anatase titanium dioxide based colored pigments with a rutilization temperature of 1080°C.

The anatase titanium dioxide used is in sol form. It is marketed by the Rhône Poulenc Company under reference S5-300. The titanium dioxide in question is characterized by a BET specific surface of 300 m²/g and a sulfate level, expressed as SO₃, of less than 0.8 wt.-% and a rutilization temperature of 1080°C. The dry extract of the S5-300 sol is 20 wt.-%.

The titanium dioxide colored pigments are prepared by (i) mixing the S5-300 sol with chromium nitrate and antimony nitrate, (ii) atomization of the resulting aqueous mixture, and (iii) calcination/grinding as in example 2.

Two orange-colored samples are thus prepared:

- sample 7 has as a total formula: (Ti_{0.9}Cr_{0.05}Sb_{0.05})O₂.

- sample 8 has as a total formula: (Ti_{0.99}Cr_{0.005}Sb_{0.005})O₂.

The chemical formula of the pigments is adjusted using the respective quantities of antimony nitrate, chromium nitrate and S5-300 sol.

Samples 7 and 8 were analyzed from the point of view of color saturation. The results obtained are reported in Table 3.

TABLE 3

Pigment	L*	a*	b*
Sample 7	68	24	61.5
Sample 8	85	8	41.2

A comparison of the values for a^* and b^* in the case of samples 3 and 7, on the one hand, and 4 and 8, on the other, reveals a more intense coloration of the pigments of samples 7 and 8.

Thus, it is verified that pigments prepared from an anatase titanium dioxide sol according to the invention result in an intensification of shades.

CLAIMS

1. A process for the preparation of titanium dioxide based colored pigments including the calcination of anatase titanium dioxide until complete transformation of the anatase titanium dioxide into rutile titanium dioxide, characterized in that an anatase titanium dioxide with a rutilization temperature of at least 1000°C, preferably at least 1060°C, and a sulfate level, expressed as SO₃, of at most 1 wt.-%, preferably less than 0.8%, is used.

2. The process according to Claim 1, characterized in that it includes the steps of:

(samples 3 and 5, on the one hand, and samples 4 and 6, on the other) that the pigments according to the invention have higher values for a^* and b^* and thus, overall, a more intense orange-color.

EXAMPLE 4 - Preparation of anatase titanium dioxide based colored pigments with a rutilization temperature of 1080°C.

The anatase titanium dioxide used is in sol form. It is marketed by the Rhône Poulenc Company under reference S5-300. The titanium dioxide in question is characterized by a BET specific surface of 300 m²/g and a sulfate level, expressed as SO₃, of less than 0.8 wt.-% and a rutilization temperature of 1080°C. The dry extract of the S5-300 sol is 20 wt.-%.

The titanium dioxide colored pigments are prepared by (i) mixing the S5-300 sol with chromium nitrate and antimony nitrate, (ii) atomization of the resulting aqueous mixture, and (iii) calcination/grinding as in example 2.

Two orange-colored samples are thus prepared:

- sample 7 has as a total formula: $(\text{Ti}_{0.9}\text{Cr}_{0.05}\text{Sb}_{0.05})\text{O}_2$

- sample 8 has as a total formula: $(\text{Ti}_{0.99}\text{Cr}_{0.005}\text{Sb}_{0.005})\text{O}_2$.

The chemical formula of the pigments is adjusted using the respective quantities of antimony nitrate, chromium nitrate and S5-300 sol.

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Thus, it is verified that pigments prepared from an anatase titanium dioxide sol according to the invention result in an intensification of shades.

CLAIMS

1. A process for the preparation of titanium dioxide based colored pigments including the calcination of anatase titanium dioxide until complete transformation of the anatase titanium dioxide into rutile titanium dioxide, characterized in that an anatase titanium dioxide with a rutilization temperature of at least 1000°C, preferably at least 1060°C, and a sulfate level, expressed as SO₃, of at most 1 wt.-%, preferably less than 0.8%, is used.
2. The process according to Claim 1, characterized in that it includes the steps of:



- a) mixing of said anatase titanium dioxide with at least one pigmentation additive,
- b) grinding of the resulting mixture, and
- c) calcination in an oxidizing atmosphere.

3. The process according to either of Claims 1 or 2, characterized in that the BET specific surface of the anatase titanium dioxide is at least 250 m²/g.

4. The process according to either of Claims 2 or 3, characterized in that in step a) the mixing is performed dry starting with an anatase titanium dioxide powder.

5. The process according to Claim 4, characterized in that said powder is composed of agglomerates of titanium dioxide particles, with the average size of these agglomerates between 1 and 2 µm and the average size of the particles between 40 and 60 nm.

6. The process according to either of Claims 2 or 3, characterized in that in step a) the mixing is performed starting from an aqueous suspension of anatase titanium dioxide, with the water of the suspension eliminated prior to grinding the mixture.

7. The process according to Claim 6, characterized in that the aqueous suspension includes suspended anatase titanium dioxide particles with an average size between 40 and 60 nm.

8. The process according to any one of Claims 2 through 7, characterized in that said pigmentation additive is chosen from among the compounds of the transition elements Sb, Cr, Ni, Co, Zn, Cu, Mn and W, which are either in the form of oxides or in the form of compounds oxidizable in an oxidizing atmosphere.

9. The process according to Claim 8, characterized in that in step a), said anatase titanium dioxide is mixed with compounds of antimony and chromium, with the molar ratio of antimony to chromium between 0.8 to 1.2, preferably equal to 1.

10. The process according to any one of Claims 2 through 9, characterized in that calcination occurs at a temperature between 800 and 1400°C.

11. Titanium dioxide based colored pigments obtained by implementing a process according to any one of Claims 1 to 10.

12. Use of an anatase titanium dioxide showing a rutilization temperature of at least 1000°C, preferably at least 1060°C, and a sulfate level, expressed as SO₃, of at the most 1 wt.-%, preferably less than 0.8%, for the preparation of titanium dioxide based colored pigments.



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