

Method for manufacturing titanium dioxide by oxidising titanium tetrachloride

5 Field of the invention

The invention relates to the manufacture of titanium dioxide by oxidising titanium tetrachloride and subsequently cooling the titanium dioxide particle/gas mixture in a cooling section, where the gas/particle flow is caused to rotate.

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Technological background of the invention

A commercially applied method for manufacturing titanium dioxide pigment, known as the chloride process, is based on titanium tetrachloride (TiCl_4) being converted into titanium dioxide and chlorine gas in a tubular reactor using a preheated, oxidising gas, such as oxygen, air, etc., and certain additives. The oxidation reaction is highly exothermic, meaning that the reaction mixture displays temperatures of more than 1,500 °C following complete conversion. In a downstream reactor cooling section, the TiO_2 pigment particles formed are cooled to below roughly 400 °C and separated from the gas flow. Cooling directly after the completion of particle formation must take place rapidly in order to prevent further particle growth. To this end, the tubular reactor or the reactor cooling section is externally cooled with water from this point onwards.

However, the transfer of heat to the cooling water is severely impeded by the accumulation of TiO_2 pigment particles on the inner wall of the tubular reactor or the reactor cooling section. According to US 2,721,626, scrub solids are introduced into the reactor cooling section for this reason, with the intention of detaching pigment accumulating on the inner walls. The scrub solids used in this patent are abrasive particles, such as quartz sand or aggregated TiO_2 particles with particle sizes of roughly 0.15 to 6.35 mm. The scrub solids are introduced into the TiO_2 /gas suspension at one or more points in the reactor cooling section.

Because of their weight, the scrub solids begin to concentrate in the lower one-third of the tube circumference in the horizontal reactor cooling section just a short time after being added. While this area of the inner wall is thoroughly cleaned of adhering pigment, the higher areas of the circumference are insufficiently cleaned, and the cooling of the gas suspension is inadequate. In order nevertheless to achieve sufficient heat transfer, it is standard practice

to substantially increase the amount of scrub solids added. This increases the burden on the system for manufacturing, adding and eliminating the scrub solids, thus giving rise to higher costs for energy consumption and maintenance, among other things.

5 US 6,419,893 B1 describes a method for more efficient removal of the TiO_2 deposits on the inner wall of the reactor cooling section. According to US 6,419,893 B1, at least a partial area of the reactor cooling section is provided with ribs that run in helical fashion on the inner wall and serve as guide elements, as a result of which the scrub solids are guided through the cooling section in a helical flow. The ribs are arranged at an angle of 2° to 6° .

10 US 2006/0133989 A1 discloses a reactor cooling section of helical overall design that is said to achieve improved cleaning of the inner wall by the scrub solids.

DE 1 259 851 discloses a method for manufacturing titanium dioxide by reaction in the gas
15 phase, where part of the gaseous reaction components is introduced tangentially into the reactor. This method is designed, on the one hand, to reduce the formation of deposits on the reactor walls by tangential introduction of one reaction component and, on the other hand, to achieve rapid thorough mixing of the reaction components by generating a back flow (so-called "swirl flow"). The swirl flow is further intensified by the cross-section of the reactor
20 expanding conically in the direction of flow. However, swirl flow leads to residence times of different length for the individual particles in the reactor.

A narrow particle size distribution is important for the quality of a titanium dioxide pigment, particularly for the tinting strength (TS). However, for generating a narrow particle size distribution, not rapid thorough mixing of the reaction components is of primary importance,
25 but a narrow residence time distribution of the TiO_2 particles in the reactor, meaning that any kind of swirl flow in the reactor should be avoided.

Object and summary of the invention

30 The object of the invention is to indicate a method, constituting an improvement compared to the prior art, for, on the one hand, effectively freeing the inner wall of the tubular reactor and the reactor cooling section of TiO_2 deposits with the help of scrub solids, thereby achieving a better cooling performance, and, on the other hand, producing a TiO_2 pigment with a narrow particle size distribution.

35 The object is solved by a method for manufacturing titanium dioxide particles in a cylindrical

tubular reactor by reacting titanium tetrachloride and an axially introduced, oxygen-bearing gas and subsequently cooling the particles, whereby the titanium tetrachloride is introduced into the tubular reactor in the cross-sectional plane of the tubular reactor, but not in the radial direction, and whereby the flow velocity of the oxygen-bearing gas is more than 20 m/s,
5 particularly at least 40 m/s.

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

10 Description of the invention

The invention is explained by means of Figures 1, 2, and 3 without these being intended as a restriction.

Figure 1 is a schematic side view of the tubular reactor. Figure 2 is a cross-sectional view
15 taken along sectional lines 2-2 of Fig. 1 for one embodiment of the invention and Figure 3 is a cross-sectional view taken along sectional lines 2-2 of Fig. 1 for an alternate embodiment of the invention.

Here and below, the term tubular reactor is taken to mean the part of the reactor in which the
20 TiCl_4 oxidation reaction and TiO_2 particle formation take place (see Fig. 1, (10)). The reactor cooling section is taken to be the downstream part of the tubular reactor, where the reaction is arrested by rapid cooling and the gas suspension is further cooled. Various additives and gases, such as aluminium chloride, chlorine, nitrogen, alkali salts, etc., are customarily introduced into the reactor together with the TiCl_4 . Here and below, the term " TiCl_4 " is to be
25 taken to mean the oxygen-free flow consisting essentially of TiCl_4 . The term " O_2 " is to be taken to mean the oxygen-bearing gas flow, here and below.

The invention is based on the knowledge that a major part of the heat is dissipated at the start of the reactor cooling section, where the high temperature of the TiO_2 /gas suspension
30 generates a high, driving temperature gradient towards the inner wall of the tube. The abrasive action of the scrub solids in this area can be substantially improved by causing the scrub solids flow, or the entire flow, to rotate. This rotation and centrifugal force distribute the scrub solids over the entire circumference of the tube, simultaneously pressing them against the wall, as a result of which the latter is cleaned uniformly and intensively.

Referring to Figures 1 to 3, the TiCl_4 is preferably introduced into the reactor (10) through nozzles (12). In the framework of the invention, the term nozzles is taken to mean all kinds of feed lines, such as ducts, pipes, etc., and all kinds of nozzles, such as Venturi tubes or Laval nozzles. The reactor (10) is a cylindrical structure and includes a longitudinal axis (14).

Oxygen is introduced into the reactor (10) in the direction of axis (14). TiCl_4 is introduced into the reactor (10) through nozzles (12) in a tangential direction, but not in radial direction.

Figure 2 illustrates a cross-sectional plane of the reactor (10) having a radius shown by line (16). TiCl_4 is introduced into the reactor (10) in a tangential direction along a path shown by line (18). Line (18) is offset from radius (16) by angle α .

The nozzles (12) can be distributed over the circumference of the reactor (10) in a common axial position (Fig. 2). Alternatively, the nozzles (12) can also be axially offset relative to each other.

In a further embodiment of the invention, the TiCl_4 can also be introduced into the reactor through a slit-like opening (20) (Fig. 3). In this embodiment, the tangential direction of the flow is brought about by baffle plates (22) in the slit-like opening (20) that are set at a corresponding angle α .

According to the invention, the entire flow – reaction mixture and scrub solids – is caused to rotate in the tubular reactor (10) and the reactor cooling section by introducing the added titanium tetrachloride into the tubular reactor (10) tangentially. Owing to its high specific weight, the TiCl_4 introduces substantial tangential momentum into the flow, this being sufficient to generate lasting rotation.

Tangential introduction of the TiCl_4 into the tubular reactor (10) means that introduction takes place in the cross-sectional plane of the tubular reactor (10), but at an angle α of $> 0^\circ$ to $< 90^\circ$, preferably 1° to 15° , and particularly 5° to 10° , relative to the radial direction (Figs. 2 and 3).

Surprisingly, back flow (swirl flow) in the reactor (10) can be largely avoided in the method according to the invention, and a uniform residence time thus achieved for all TiO_2 particles in the reactor (10). In contrast to the teaching in DE 1 259 851, this is achieved by the axially introduced O_2 flow having a flow velocity of more than 20 m/s, particularly at least 40 m/s, and the tubular reactor (10) having a cylindrical form. Under these conditions it is possible to introduce a high tangential momentum to achieve a high cleaning effect without generating of swirl flow. The momentum ratio (ratio of the products of flow velocity and specific weight) of

the tangentially introduced reaction component (TiCl_4) to the axially introduced gaseous component (O_2) is at least about 100.

The improvement of heat transfer to the wall of the cooling section, achieved by introducing the TiCl_4 in accordance with the invention, can be further improved if the scrub solids are extensively scattered when introduced into the tubular reactor (10), this bringing about uniform distribution of the scrub solids and, accordingly, uniform cleaning of the reactor wall. The scattering can be achieved by causing the flow of scrub solids to rotate strongly prior to being introduced into the reactor. This rotation can, for example, be achieved by designing the feed port in a form similar to a cyclone, into which the scrub solids flow is introduced tangentially by means of pneumatic conveying.

Compared to the methods according to US 6,419,893 B1 and US 2006/0133989 A1, the invention is characterised in that, on the one hand, the entire flow is caused to rotate, and cleaning of the inner wall and cooling of the gas suspension are thus optimised. Moreover, no complex design measures downstream of the point of TiCl_4 introduction are necessary, such as wear-susceptible internal fixtures or a helical design of the entire reactor cooling section. Compared to the method according to DE 1 259 851 the invention is furthermore characterised in that, despite the high tangential momentum of the TiCl_4 flow, swirl flow is largely avoided and TiO_2 pigment particles with a narrow particle size distribution, and thus improved tinting strength (TS), can be manufactured.

Example

An example of the invention is explained below, without this being intended as a restriction. 12 t/h TiCl_4 are introduced into a tubular reactor with an inside diameter of approx. 0.3 m by means of 10 circular nozzles, and caused to react with preheated oxygen-bearing gas. The nozzles are located at a common axial position on the tubular reactor and distributed evenly over the circumference. All nozzles are set tangentially in the same direction in the cross-sectional plane, in such a way that they deviate from the radial direction by 6° . Compared to a purely radial layout of the nozzles, this configuration reduces the scrub solids requirement from roughly 2.0 to 1.2 t/h.

CLAIMS

- 5 1. A method for manufacturing titanium dioxide particles in a cylindrical tubular reactor by reacting titanium tetrachloride and an axially introduced, oxygen-bearing gas and subsequently cooling the particles, characterised in that the titanium tetrachloride is introduced into the tubular reactor in the cross-sectional plane of the tubular reactor, but not in the radial direction, and
10 whereby the flow velocity of the oxygen-bearing gas is more than 20 m/s, particularly at least 40 m/s..
- 15 2. The method according to claim 1, characterised in that the titanium tetrachloride is introduced at an angle between $> 0^\circ$ and $< 90^\circ$, preferably at an angle between 1° and 15° , and particularly preferably at an angle between 5° and 10° , relative to the radial direction.
- 20 3. The method according to claim 1, characterised in that the titanium tetrachloride is introduced by means of individual nozzles.
- 25 4. The method according to claim 3, characterised in that the nozzles are axially offset relative to each other.
5. The method according to claim 1 or 2, characterised in that
the titanium tetrachloride is introduced through a slit-like opening displaying baffle plates deviating from the radial direction.
- 30 6. The method according to one or more of the preceding claims characterised in that the scrub solids flow is caused to rotate strongly prior to being introduced into the reactor.
- 35 7. The method according to one or more of the preceding claims characterised in that the product of flow velocity and specific weight of the TiCl_4 flow is at least roughly 100 times the product of flow velocity and specific weight of the O_2 flow.