

Multi-step method for producing titanium dioxide

Field of the invention

The invention relates to the manufacture of titanium dioxide by oxidation of titanium tetrachloride in a multi-stage method, where both oxygen and titanium tetrachloride are added in several stages.

Technological background of the invention

In one of the commercially used methods for manufacturing titanium dioxide pigment particles, known as the chloride process, titanium tetrachloride (TiCl_4) is reacted with an oxidising gas, such as oxygen, air, etc., and with certain additives in a tubular reactor to form titanium dioxide and chlorine gas:



The TiO_2 particles are subsequently separated from the chlorine gas. Known additives are AlCl_3 as a rutilising agent and steam or alkali salts as a nucleating agent.

The oxidation process is customarily performed in one stage, i.e. the reaction components (educts), oxygen and gaseous titanium tetrachloride, are each added at only one point of the reactor. Owing to the high activation energy of TiCl_4 oxidation, the educts must, before addition, be heated to such a degree that an adiabatic mixed temperature of at least approx. 740 °C is reached. The oxidation reaction is highly exothermal, meaning that an adiabatic reaction temperature of approx. 1,850 °C is reached following complete conversion. Before the pigment produced is separated from the gas mixture in a filter, this mixture has to be cooled to a maximum of 450 °C in order to avoid damage to the filter. This process is energetically unsatisfactory because large amounts of heat are dissipated into the cooling-water system. Single-stage oxidation is also disadvantageous in terms of product quality, since the extensive hot zone for oxidation promotes the formation of hard TiO_2 aggregates.

Consequently, there are various developments in the prior art for operating the process on a multi-stage basis. According to GB 1 064 569, both TiCl_4 and O_2 are added in two stages, in which context the respective quantity of O_2 is sufficient for completely oxidising the

respective quantity of TiCl_4 .

The teaching according to US 4,053,577 provides for a maximum of one of the educts to be introduced into the reactor in two stages.

In the methods according to GB 2 037 266, US 4,803,056 and EP 0 583 063 B1, gaseous TiCl_4 is introduced into a hot oxygen stream in two or more stages.

The method according to EP 0 852 568 B1 provides for not only the TiCl_4 to be added in two stages, but also the oxygen. However, the object of this method is effective control of the mean TiO_2 particle size, and thus of the tone of the TiO_2 pigment base material. In this case, TiCl_4 vapour having a temperature of roughly 400°C is first fed into an oxygen stream with a temperature of roughly 950°C . The TiO_2 particles are formed, and particle growth takes place, in the downstream reaction zone. TiCl_4 vapour heated to a lesser extent (approx. 180°C) is added at a second inlet point. Oxygen having a temperature between 25°C and $1,040^\circ\text{C}$ is introduced at the second inlet point, the temperature of the mixture being sufficient to initiate the reaction.

The multi-stage method according to US 6,387,347 is additionally said to reduce agglomeration. To this end, the previously heated, gaseous TiCl_4 stream is split into two part streams before addition to the reactor. One part stream is oxidised in the first stage of the reactor. The second part stream is cooled by injection of liquid TiCl_4 (de-superheating) and then added to the reactor. De-superheating takes place outside the reactor, the temperature not falling below the condensation temperature of the overall stream.

US 2007/0172414 A1 discloses a multi-stage method for the reaction of TiCl_4 and O_2 in which gaseous TiCl_4 is fed into the reactor in the first stage, and liquid TiCl_4 in the second stage and wherein the oxygen is present in a hyper-stoichiometric amount in the first stage. This method permits energy savings and improvement of the particle size range.

Object and summary of the invention

The object of the present invention is to create a method for manufacturing titanium dioxide by oxidation of titanium tetrachloride that permits further energy savings compared to the methods known from the prior art.

The object is solved by a multi-stage method for manufacturing titanium dioxide by reaction

of titanium tetrachloride with oxygen in a reactor, characterised by the following steps:

a) Introduction of gaseous TiCl_4 into a preheated, oxygen-containing gaseous stream in a first reaction zone of the reactor, where the molar ratio of $\text{TiCl}_4 : \text{O}_2$ in the reaction zone is at least 1, and formation of a gas suspension containing TiO_2 ,

b) Passing of the gas suspension containing TiO_2 into at least one further reaction zone,

c) Introduction of an oxygen-containing gas and liquid TiCl_4 into the at least one further reaction zone and further formation of TiO_2 in the gas suspension.

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

Description of the invention

The method according to the invention differs from the aforementioned multi-stage chloride processes for manufacturing titanium dioxide from the prior art in that the TiCl_4 is added in gaseous form and stoichiometrically or in excess in relation to the oxygen in the first stage (step a)), and in liquid form and sub-stoichiometrically in the second and further stages (step b)).

In step a) TiCl_4 and O_2 react in a first reaction zone of the reactor and form a gas suspension containing TiO_2 (first stage).

In step b) the gas suspension containing TiO_2 is passed into at least one further reaction zone.

In step c) oxygen-containing gas and liquid TiCl_4 is introduced into the at least one further reaction zone and further TiO_2 is formed in the gas suspension (second stage).

The present method can be performed in two stages or more than two stages. In the first stage (step a)) the temperature of the preheated oxygen-containing gas is at least roughly 950°C . In the second or further stages (step c)) in one embodiment of the method the oxygen-containing gas is introduced with a temperature of at least roughly 200°C .

In a special embodiment of the method, the oxygen-containing gas added in the at least one further stage is "cold", i.e. it has a temperature of less than roughly 50°C , for example a temperature of roughly 30°C . This method leads to a further improvement in energy efficiency, since only the portion of the oxygen-containing gas that is required for the first stage needs to be heated in order to provide the activation energy for the reaction. In all other stages, the activation energy is provided by the reaction enthalpy of TiCl_4 oxidation

released in the upstream stages.

In another embodiment of the method in step a) the gaseous TiCl_4 is introduced into the reactor mixed with an oxygen-containing gas. Preferably, the O_2 -content of the gaseous mixture is roughly 20 vol.% maximum. In order to avoid a premature reaction of the components in the gaseous mixture the temperature must not exceed roughly 900 °C. The introduction of the gaseous TiCl_4 mixed with oxygen-containing gas helps to prevent the formation of defects in the TiO_2 structure and leads to improved brightness of the manufactured TiO_2 pigment.

In a special embodiment of the invention the method is performed in a cylindrical plug flow reactor.

Exemplary embodiment of the method

The practical example described below is merely one possible embodiment of the invention and not to be taken as restricting the invention.

The method is performed in two stages, where the TiCl_4 is added in equal quantities in the first and second stages. In the first stage, the temperature of the oxygen-containing gas stream is 1,650 °C, that of the gaseous TiCl_4 introduced being 450 °C. The molar ratio of $\text{TiCl}_4 : \text{O}_2$ in the first reaction zone is roughly 1. Downstream of the first stage, at a point where the reaction of the first stage has taken place completely, an oxygen-containing gas is added first, followed by liquid TiCl_4 . In the second stage, the temperature of the oxygen-containing gas introduced is 30 °C, that of the liquid TiCl_4 introduced likewise being 30 °C.

Compared to the customary, one-stage method, the same temperatures are selected in the first combustion stage in this embodiment of the method according to the invention, but major energy savings result when preheating the educts owing to the substantially smaller quantities of oxygen-containing gas and TiCl_4 to be heated in the first stage. However, in the second stage the educts do not have to be preheated. The total savings achieved correspond roughly to the ratio at which the TiCl_4 is split up over the two stages, i.e. roughly 50% in the present example.

As the practical example described is merely a possible embodiment of the invention, the

present invention optionally also comprises the addition, familiar to the person skilled in the art, of additives for rutilisation (e.g. AlCl_3) and for nucleation (e.g. alkali salts) in the reaction zone.

CLAIMS

- 5 1. Multi-stage method for manufacturing titanium dioxide by reaction of titanium tetrachloride with oxygen in a reactor, characterised by the following steps:
- a) Introduction of gaseous TiCl_4 into a preheated, oxygen-containing gaseous stream in a first reaction zone of the reactor, where the molar ratio of $\text{TiCl}_4 : \text{O}_2$ in the reaction zone is at least 1, and formation of a gas suspension containing TiO_2 ,
- 10 b) Passing of the gas suspension containing TiO_2 into at least one further reaction zone,
- c) Introduction of an oxygen-containing gas and liquid TiCl_4 into the at least one further reaction zone and further formation of TiO_2 in the gas suspension.
- 15 2. Method of Claim 1, characterised in that the oxygen-containing gas is introduced first in Step c), followed by TiCl_4 .
3. Method of Claim 1 or 2, characterised in that the temperature of the oxygen-containing gas is at least roughly 950°C before the reaction in Step a) and less than roughly 50°C before the reaction in Step c).
- 20 4. The method of Claim 1, characterised in that the further reaction zone is located at a point in the reactor where the reaction according to Step a) has taken place completely.
- 25 5. Method of Claim 1 or 2 characterised in that in Step a) gaseous TiCl_4 mixed with an oxygen-containing gas is introduced.
6. Method of Claim 5, characterised in that
- 30 in Step a) the O_2 content of the gaseous mixture is roughly 20 vol.% maximum.
7. Method of Claim 5 or 6, characterised in that the gaseous mixture displays a temperature of roughly 900°C maximum.
- 35 8. Titanium dioxide particles manufactured to any one of Claims 1 to 7.