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(54) Title: PROCESS FOR PRODUCING AND COOLING TITANIUM DIOXIDE

(57) Abstract: An improved process for producing titanium dioxide wherein gaseous titanium tetrachloride and oxygen are reacted at a high temperature to produce particulate solid titanium dioxide and gaseous reaction products is provided. The titanium dioxide and gaseous reaction products are cooled by passing them through a tubular heat exchanger along with a scouring medium for removing deposits from the inside surfaces of the tubular heat exchange. By this invention, the particulate scouring medium, the particulate titanium dioxide and the gaseous reaction products are caused to follow a spiral path as they flow through the tubular heat exchanger whereby the scouring medium more thoroughly removes the deposits and the titanium dioxide and gaseous reaction products are cooled more efficiently.



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PROCESS FOR PRODUCING AND COOLING TITANIUM DIOXIDE

The present invention relates to processes for producing and cooling titanium dioxide, and more particularly, to such processes wherein the cooling of the titanium dioxide and gaseous reaction products produced is more efficiently carried out.

In the conventional production of titanium dioxide utilizing the chloride process, heated gaseous titanium tetrachloride and heated oxygen are combined in a tubular reactor at high flow rates. A high temperature oxidation reaction takes place in the reactor whereby particulate solid titanium dioxide and gaseous reaction products are produced. The titanium dioxide and gaseous reaction products are cooled by passing them through a tubular heat exchanger along with a scouring medium for removing deposits from the inside surfaces of the heat exchanger. The scouring medium is a particulate solid such as sand, sintered or compressed titanium dioxide, rock salt or the like. In spite of the use of a scouring medium, the solid titanium dioxide and other deposits on the inside surfaces of the tubular heat exchanger have only been partially removed in the known processes, thereby leaving deposits which reduce the heat transfer efficiency of the heat exchanger.

A first aspect of the present invention provides a process for producing titanium dioxide wherein gaseous titanium tetrachloride and oxygen are reacted at a high temperature to produce particulate solid titanium dioxide and gaseous reaction products and the titanium dioxide and gaseous reaction products are cooled by passing them through a tubular heat exchanger along with a scouring medium for removing deposits from the inside surface of the tubular heat exchanger, the improvement in removing said deposits and thereby increasing the cooling of said titanium dioxide and gaseous reaction products which comprises causing said scouring medium, said particulate titanium dioxide and said gaseous reaction products to follow a spiral path as they flow through said tubular heat exchanger whereby said scouring medium thoroughly removes said deposits.

The present invention is more clearly understood by reference to the accompanying drawings, in which:

FIG. 1 is a side cross-sectional view of a tubular heat exchanger section which includes spiraling vanes and recesses in accordance with this invention; and

FIG. 2 is an end view taken along line 2--2 of FIG. 1.

Titanium dioxide pigment may be produced according to the chloride route by reacting heated gaseous titanium tetrachloride and heated oxygen in a tubular reactor at high temperatures. The titanium tetrachloride can include aluminum chloride in an amount sufficient to produce a rutile pigment containing between 0.3% to 3% by weight of aluminum oxide. Typically, the titanium tetrachloride can be preheated to a temperature in the range of from 343 °C (650 °F) to 982 °C (1800 °F) depending upon the particular preheater apparatus utilized. The oxygen may be typically preheated to a temperature in the range of from 954 °C (1750 °F) to 1871 °C (3400 °F). The oxidation reaction temperature at a pressure of 1 kg/sg.cm. (one atmosphere) may be typically in the range of from 1260 °C (2300 °F) to 1371 °C (2500 °F). The reaction can produce particulate solid titanium dioxide and gaseous reaction products.

The reaction products may conventionally immediately be introduced into an elongated tubular heat exchanger, wherein the reaction products may be cooled by heat exchange with a cooling medium such as cooling water. The elongated tubular heat exchanger may be made up of a plurality of individual heat exchanger sections which can be sealingly bolted together. The heat exchanger sections and overall length of the heat exchanger can vary widely depending on factors such as the titanium dioxide production rate, the desired discharge temperature and the diameter of the heat exchanger among other factors. Consequently, commercial producers of titanium dioxide that utilize the chloride process, that is, the process of oxidizing titanium tetrachloride, may use heat exchangers of varying diameters and lengths to cool the reaction products. In known examples, the heat exchanger sections have an internal diameter of 18 cm (7 inches) and are from 2.1 m (7 feet) to 4.9 m (16 feet) long. The elongated tubular heat exchanger may often also include an adapter section which can be from 0.3 m (1 foot) to 1.2 m (4 feet) long. While passing through the elongated tubular heat

exchanger, the titanium dioxide and gaseous reaction products can be cooled to a temperature of 704 °C (1300 °F) or less.

5 In order to prevent the build-up of deposits formed of titanium dioxide and other materials produced in the oxidation reaction, a scouring medium may be injected into the tubular heat exchanger along with the reaction products. Examples of scouring media which can be used include, but are not limited to, sand, mixtures of titanium dioxide and water which are pelletized, dried and sintered, compressed titanium dioxide, rock salt, fused alumina, titanium dioxide and salt mixtures and the like. The salt mixed with titanium dioxide can be potassium chloride, sodium chloride and the like.

15 The scouring medium can impinge on the inside surfaces of the heat exchanger and removes deposits therefrom. While the scouring medium removes some of the deposits, it often does not remove all of the deposits and as a result, a layer of the deposits on the inside surfaces of the heat exchanger remains. The remaining layer of deposited material decreases the heat transfer rate from the reaction products being cooled through the walls of the heat exchanger and into the cooling medium. This in turn may significantly decrease the efficiency of the heat exchanger and increases the overall costs of producing the titanium dioxide, by requiring the installation and maintenance of a longer heat exchanger and requiring a greater amount of the scouring medium. After the reaction products are cooled, the particulate solid titanium dioxide may be separated from the gaseous reaction products and the scouring medium.

25 The present invention is based on the discovery that the removal of the deposits from the inside surfaces of the heat exchanger can be improved by causing the scouring medium to follow a spiral path through the heat exchanger. While various techniques can be utilized for causing the scouring medium to follow a spiral path through the heat exchanger, a presently preferred technique is to provide one or more spiraling vanes on the inside surfaces of at least a portion of one or more of the individual heat exchanger sections. Preferably, for 18 cm (7 inch) to 28 cm (11 inch) internal diameter heat exchanger sections, two or more spiraling vanes having spiraling recesses therebetween are provided in 2.4 m (8 foot) portions of two or more of the

individual heat exchanger sections. Most preferably from, four to six spiraling vanes with four to six spiraling recesses therebetween are provided in the spiraled portions of the sections.

Referring now to the drawings, one of the individual 18 cm (7 inch) internal diameter by 4.8 m (16 feet) long heat exchanger sections making up an elongated heat exchanger for cooling the reaction products is illustrated and generally designated by the numeral 10. The heat exchanger section 10 includes four spiraling vanes 12 with four recesses 14 therebetween extending over an 2.4 m (8 foot) internal portion thereof. As shown in FIG. 1, the vanes 12 and recesses 14 rotate over the initial 2.4 m (8 foot) internal surface length of the heat exchanger 10. The rate of rotation of the spiraling vanes and recesses is constant and is generally in the range of from 0.79 degrees per cm (2 degrees per inch) to 2.4 degrees per cm (6 degrees per inch), preferably 1.8 degrees per cm (4.5 degrees per inch). As shown in FIG. 2, the spiraling vanes 12 and recesses 14 have curved rectangular cross-sectional shapes. Generally, the heights, widths and rate of rotation of the spiraling vanes are such that for an individual heat exchanger section containing the vanes over its initial 2.4 m (8 feet) of internal surface length, the maximum pressure drop at the maximum reaction products flow rate through the section is 14.1 g/sq. cm. (0.2 pounds per square inch). A further requirement is that the scouring medium completely scours the inside surfaces of the heat exchanger section including the surfaces of the spiraling recesses. These criteria are met, for example, by a heat exchanger section having a length of 4.8 m (16 feet), an internal surface diameter of 18 cm (7 inches) and having four curved rectangular vanes equally spaced over the initial 2.4 m (8 feet) of internal surface therein when the vanes are 1.3 cm (0.5 inch) high, 3.8 cm (1.5 inches) wide and have a rate of rotation of 1.7 degrees per cm (4.3 degrees per inch) and when a scouring medium having a specific gravity of 2 and a particle size of 0.7 mm (0.028 inch) is utilized with an inlet gaseous reaction product flow rate of 3 kg (6.6 pounds) per second at a temperature of 954 °C (1750 °F).

As mentioned, all of the heat exchanger sections utilized to make up the elongated tubular heat exchanger can include spiraling vanes and recesses. Generally, however, the heat exchanger sections which include spiraling vanes and recesses in

the elongated heat exchanger can be separated by several heat exchanger sections which do not include spiraling vanes and recesses. The number of heat exchanger sections which do not include vanes and recesses depends on whether those heat exchanger sections are thoroughly cleaned by the scouring medium under the
5 operating conditions involved.

The vanes can be formed of a corrosion resistant alloy such as an alloy of nickel and chromium or they can be formed of a ceramic wear resistant material such as alumina, silicon carbide or the like. Also, the vanes can be hollow so that the cooling
10 medium will keep them cooler, heat transfer will be increased and pigment deposits will be reduced.

A second aspect of the present invention provides an improved process for producing particulate solid titanium dioxide comprising the steps of:

15 (a) reacting gaseous titanium tetrachloride and oxygen at a temperature of at least 1149 °C (2100 °F) to produce particulate solid titanium dioxide and gaseous reaction products;

(b) cooling said produced particulate solid titanium dioxide and gaseous reaction products with a cooling medium in a tubular heat exchanger to a
20 temperature of 704 °C (1300 °F) or less;

(c) injecting a scouring medium into said heat exchanger for removing deposits from the inside surfaces thereof;

(d) causing said scouring medium to follow a spiral path through said heat exchanger and thereby increase the removal of deposits from said surfaces; and
25

(e) separating said particulate solid titanium dioxide from said scouring medium and said gaseous reaction products.

A more specific process for producing particulate solid titanium dioxide may comprise the steps of: (a) reacting gaseous titanium tetrachloride and
30 oxygen at a temperature in the range of at least 1204 °C (2200 °F) to produce particulate solid titanium dioxide and gaseous reaction products; (b) cooling the produced particulate solid titanium dioxide and gaseous reaction products with a cooling medium in a tubular heat exchanger to a temperature 704 °C (1300 °F) or less;

(c) injecting a scouring medium into the heat exchanger for removing deposits from the inside surfaces thereof; (d) causing the scouring medium to follow a spiral path through the heat exchanger and thereby increase the removal of deposits from the surfaces by providing one or more spiraling vanes on the inside surface of all or a portion of the tubular heat exchanger; and (e) separating the particulate solid titanium dioxide from the scouring medium and the gaseous reaction products.

In order to further illustrate the improved process of the present invention, the following example is given.

Example

A series of tests were performed to increase the efficiency of an elongated tubular heat exchanger used for cooling the titanium dioxide and gaseous reaction products produced in the chloride process. The heat exchanger was instrumented to determine the effectiveness of heat transfer and consisted of a number of sections of water jacketed pipe. Cooling water flowed through the jacket and reaction products from the reactor consisting of a mixture of Cl_2 , TiO_2 pigment, and 5 to 10 percent O_2 flowed through the interior of the pipe. The heat exchanger sections were 4.8 m (16 feet) long and were connected together by flanges. An external water pipe called a jumper connected the water jacket of one section to the water jacket of the adjacent section. A thermocouple was placed in each jumper and total water flow through the heat exchanger sections was measured at the inlet to the sections. The amount of heat that was transferred from the reaction products stream to the water in each heat exchanger section was determined from the difference in temperature between the water inlet and outlet and the water flow rate. The gas temperature for the heat exchanger sections was calculated from a mass balance for the reactor, the amount of heat fed to the reactor with the reactant feed streams and the total heat lost from the reactor upstream of the sections. A heat transfer coefficient was calculated for each heat exchanger section from the temperature of the product stream and the amount of heat that was transferred to the cooling water in that section.

The calculated heat transfer coefficients were then compared to the heat transfer coefficients calculated from empirical heat transfer correlations available in the open literature for particulate free gases. It was anticipated that the correlations for

particulate loaded gases would be different than for clean gases, but it seemed probable that there would be a relatively constant ratio between the coefficient measured for the heat exchanger sections and the coefficients calculated for clean gas. The results indicated that the deviation between the values calculated from empirical correlations and those determined experimentally were much greater for the sections near the exit of the elongated heat exchanger than for those at the inlet. It seemed likely that the difference could be due to deposits in the sections. Tests were then initiated to develop methods for improving heat transfer near the exit of the elongated heat exchanger. The tests were performed using the last 8 sections of the elongated heat exchanger. All of the sections were 0.18 m (7-inches) in diameter and approximately 4.8 m (16-feet) in length except for the last section which was an adapter for attaching the elongated heat exchanger to the product collection section. The adapter section was 1.2 m (4-feet) in length and slightly larger in diameter than the other sections. The results of all of the tests are given in the Table below.

Test 1

A control test was performed using silica sand as the scouring medium. The product rate for the reactor was set at a level that could be maintained even if heat transfer rates were to change significantly. The ratios of the measured heat transfer coefficients to theoretical heat transfer coefficients were determined. The results indicate that the difference between the actual coefficients and the theoretical coefficients increases as the gases move down the elongated heat exchanger.

Test 2

In the second test, a device was placed in the middle of a heat exchanger section to introduce N_2 tangentially into the section. The reactor produced TiO_2 pigment at a rate of 59 to 68 kg per minute (130 to 150 pounds per minute). Approximately 5.7 cubic metre (200 standard cubic feet) of N_2 was introduced into the section over a period of several minutes. The result was that the heat transfer improved measurably over the entire product cooler downstream of the point of injection. The increase in heat transfer was attributed to more efficient scouring rather than increased turbulence

for two reasons. The first was that the increase in heat transfer was observed as far as 100 section diameters downstream from the point of N₂ injection. Calculations and published data indicated that any increase in heat transfer due to turbulence decreases rapidly and disappears completely within 20 pipe diameters downstream^{1, 2}. The second reason that the increase was due to better scouring was that the increase in heat transfer was observed to continue for sometime after the N₂ flow had stopped.

Test 3

A scouring medium of TiO₂ was prepared by agglomerating unfinished pigment, heat treating the material to produce a suitably hard material and then screening the material to provide a particle size distribution similar to that of the silica sand that had been used. The TiO₂ scouring medium was fed at the front of the reactor. The results of this test were similar to the results of Test 1.

Test 4

A heat exchanger section having spiraling vanes and recesses as shown in FIGS. 1 and 2 was installed in place of heat exchanger section No. 6. The portion of the heat exchanger section which included the spiraling vanes and recesses was the first 2.4 m (8 feet) of the section. The scouring medium was the same as used in Test 3, and the product rate was approximately the same as in Tests 1 and 3. The results indicate that the average heat transfer coefficient for section No. 7 immediately downstream of section No. 6 was significantly higher than the average heat transfer coefficient for section No. 7 in Test 3. The average heat transfer coefficient for section No. 8 that was 9.8 m (32 feet) or 55 pipe diameters from the end of the spiraling vanes and recesses was slightly higher than the average heat transfer coefficient for section No. 8 in Test 3.

Test 5

The heat exchange section including the spiraling vanes and recesses was installed in place of section No. 11 and a test similar to Test 4 was performed. The

results indicate that a significant improvement was obtained even for section No. 13 that was 7.9 m (26 feet) or more than 47 pipe diameters from the end of section No. 11.

5 Additional Tests

A test similar to Test 5 was performed using spiraling vanes with a ceramic material. The heat transfer results for sections No. 12 and No. 13 with the ceramic vanes were the same as for Test No. 5. The heat transfer within the section containing the vanes was dependent on the conductivity of the material used for the vanes and the design of the vanes. In another set of tests, the temperature of the gases exiting the bag filter was determined when the heat exchanger was operated without spiraling vanes. Vanes were then installed in place of section No. 11 and the production rate increased until the temperature of the gases exiting the bag filters had reached that same temperature. The results were that without the vanes, a production rate of 97 tons per day resulted in an exit temperature of 187 °C (369 °F) and with vanes, a production rate of 119 tons per day resulted at an exit temperature of 184 °C (363 °F). "INCONEL™" vanes were operated for over 30 hours. No measurable wear was found on the vanes and raw pigment quality was excellent. No deposits were found on the vanes.

The results of the tests indicate that the spiraling vanes and recesses increase the effectiveness of the scouring medium. It is believed that the decrease in the ratio of the actual to theoretical heat transfer coefficients as the gases approach the end of the elongated heat exchanger is due to increased deposits near the end of the heat exchanger. This is consistent with the vanes being more effective in the No. 11 position than in the No. 6 position. Calculations indicate that at the production rates used in the tests described, the increase in pressure drop through 45.7 m (150 feet) of spiraling vanes as compared to smooth pipe would be in the order of only a few pounds per square inch. For this reason, two to four heat exchanger sections including 2.4 m (8-foot) spiraling vane portions can be spaced at various distances apart in the elongated heat exchanger. Continuous spiraling vanes in the elongated heat exchanger can also be utilized if the cost of the vanes permits. The results also indicate the spiraling vanes

can be made of an alloy such as "INCONELTM" 600 or ceramic materials such as silicon carbide ceramic, alumina, or a composite ceramic. The use of ceramics is advantageous if wear or chemical attack becomes a problem.

5 References

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TABLE

15 Ratios Of Measured To Theoretical Heat Transfer Coefficients

Test Number	1	2	3	4	5
20 TiO ₂ Production Rate, tons per day	104	-	108	105	108
Location of Spiraling Vaness and Recesses (8' portions)	None	None -N ₂ injected at No.8	None	No.6	No.11
25 Heat Exchange Section No. 6 Ratio	0.8	-	0.81	-	0.81
Heat Exchange Section No. 7 Ratio	0.73	-	0.75	0.86	0.72
Heat Exchange Section No. 8 Ratio	0.57	-	0.61	0.64	0.57
30 Heat Exchange Section No. 9 Ratio	0.58	-	0.62	0.62	0.55
Heat Exchange Section No. 10 Ratio	0.52	-	0.58	0.56	0.56
35 Heat Exchange Section No. 11 Ratio	0.50	-	0.58	0.49	-
Heat Exchange Section No. 12 Ratio	0.39	-	0.46	0.44	0.61
Heat Exchange Section No. 13 Ratio	0.42	-	0.53	0.40	0.67

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Thus, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those which are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit of this invention as defined by the appended claims.

1. In a process for producing titanium dioxide wherein gaseous titanium tetrachloride and oxygen are reacted at a high temperature to produce particulate solid titanium dioxide and gaseous reaction products and the titanium dioxide and gaseous reaction products are cooled by passing them through a tubular heat exchanger along
5 with a scouring medium for removing deposits from the inside surface of the tubular heat exchanger, the improvement in removing said deposits and thereby increasing the cooling of said titanium dioxide and gaseous reaction products which comprises causing said scouring medium, said particulate titanium dioxide and said gaseous
10 reaction products to follow a spiral path as they flow through said tubular heat exchanger whereby said scouring medium thoroughly removes said deposits.
2. The process of claim 1 wherein said scouring medium is selected from the group consisting of mixtures of titanium dioxide and water which are pelletized, dried and sintered, compressed titanium dioxide, rock salt, fused alumina and titanium
15 dioxide and salt mixtures.
3. The process of claim 2 wherein said scouring medium is a mixture of titanium dioxide and water which is pelletized, dried and sintered.
4. The process of claim 1 wherein said scouring medium, said particulate titanium dioxide and said gaseous reaction products are caused to follow a spiral path
20 through said heat exchanger by providing one or more spiraling vanes on the inside surfaces of all or a portion of said tubular heat exchanger.
5. The process of claim 4 wherein all or a portion of said inside surfaces of said tubular heat exchanger includes from four to six spiraling vanes with four to six spiraling recesses therebetween.
6. The process of claim 5 wherein the rate of rotation of said spiraling
25 vanes and recesses is in the range of from 0.79 degrees per cm (2 degrees per inch) to 2.4 degrees per cm (6 degrees per inch).
7. The process of claim 5 wherein said spiraling vanes and recesses have curved rectangular cross-sectional shapes.
8. The process of claim 1 wherein the heat exchange medium utilized in
30 said tubular heat exchanger to cool said particulate titanium dioxide and gaseous reaction products is water.

9. The process of claim 4 wherein said tubular heat exchanger is made up of a plurality of connected together heat exchanger sections.

10. The process of claim 9 wherein less than all of said heat exchanger sections include said spiraling vanes.

5 11. An improved process for producing particulate solid titanium dioxide comprising the steps of:

(a) reacting gaseous titanium tetrachloride and oxygen at a temperature of at least 1149 °C (2100 °F) to produce particulate solid titanium dioxide and gaseous reaction products;

10 (b) cooling said produced particulate solid titanium dioxide and gaseous reaction products with a cooling medium in a tubular heat exchanger to a temperature of 704 °C (1300 °F) or less;

(c) injecting a scouring medium into said heat exchanger for removing deposits from the inside surfaces thereof;

15 (d) causing said scouring medium to follow a spiral path through said heat exchanger and thereby increase the removal of deposits from said surfaces; and

(e) separating said particulate solid titanium dioxide from said scouring medium and said gaseous reaction products.

20 12. The process of claim 11 wherein said scouring medium is selected from the group consisting of mixtures of titanium dioxide and water which are pelletized, dried and sintered, compressed titanium dioxide, rock salt, fused alumina and titanium dioxide and salt mixtures.

13. The process of claim 12 wherein said scouring medium is a mixture of titanium dioxide and water which is pelletized, dried and sintered.

25 14. The process of claim 11 wherein said scouring medium, said particulate titanium dioxide and said gaseous reaction products are caused to follow a spiral path through said heat exchanger by providing one or more spiraling vanes on the inside surfaces of all or a portion of said tubular heat exchanger.

30 15. The process of claim 14 wherein all or a portion of said inside surfaces of said tubular heat exchanger includes four spiraling vanes with four spiraling recesses therebetween.

16. The process of claim 15 wherein the rate of rotation of said spiraling vanes and recesses is in the range of from 0.79 degrees per cm (2 degrees per inch) to 2.4 degrees per cm (6 degrees per inch).

17. The process of claim 15 wherein said spiraling vanes and recesses have
5 curved rectangular cross-sectional shapes.

18. The process of claim 11 wherein said cooling medium is cooling water.

19. The process of claim 14 wherein said tubular heat exchanger is made
up of a plurality of connected together heat exchanger sections.

20. The process of claim 19 wherein less than all of said heat exchanger
10 sections include said spiraling vanes.