



(43) International Publication Date
25 August 2011 (25.08.2011)

(10) International Publication Number
WO 2011/102863 A1

(51) International Patent Classification:

C01G 23/07 (2006.01) *C01F 7/56* (2006.01)
C09C 1/36 (2006.01) *C01B 9/02* (2006.01)
C01B 33/107 (2006.01) *C01B 13/20* (2006.01)

(21) International Application Number:

PCT/US2010/055917

(22) International Filing Date:

9 November 2010 (09.11.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/306,673 22 February 2010 (22.02.2010) US

(71) Applicant (for all designated States except US): **E. I. DU PONT DE NEMOURS AND COMPANY** [US/US];
1007 Market Street, Wilmington, Delaware 19898 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **MUSICK, Charles, David** [US/US]; 64 Stephenson Road, Waverly, Tennessee 37185 (US).

(74) Agent: **FICKES, Daphne, P.**; E. I. du Pont de Nemours and Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, Delaware 19805 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PROCESS FOR IN-SITU FORMATION OF CHLORIDES OF SILICON, ALUMINUM AND TITANIUM IN THE PREPARATION OF TITANIUM DIOXIDE

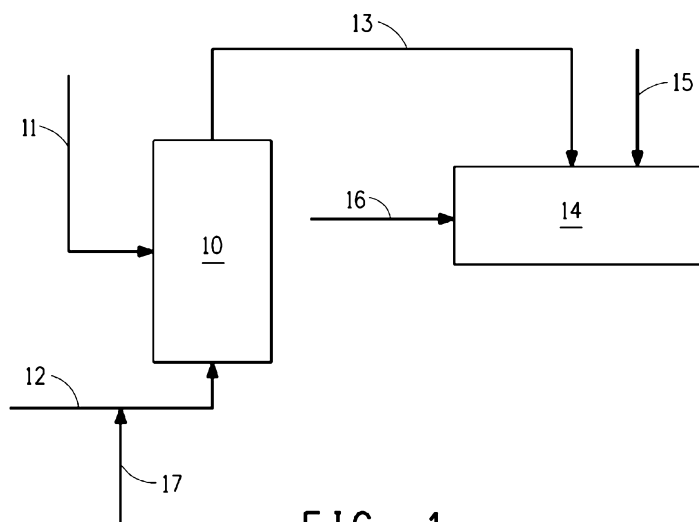


FIG. 1

(57) Abstract: This disclosure relates to a process for producing titanium dioxide, comprising: reacting aluminum and an alloy comprising silicon and titanium having a silicon content of at least 5%, based on the weight of the alloy, with chlorine gas at temperatures above 190 °C to form chlorides of silicon, aluminum and titanium; adding titanium tetrachloride to the chlorides of silicon, aluminum and titanium; oxidizing the chlorides of silicon, aluminum and titanium and titanium tetrachloride; and forming titanium dioxide.

TITLE

PROCESS FOR IN-SITU FORMATION OF CHLORIDES OF SILICON,
ALUMINUM AND TITANIUM IN THE PREPARATION OF TITANIUM DIOXIDE

5

BACKGROUND OF THE DISCLOSURE

Field of the Disclosure:

The present disclosure relates to a process for preparing titanium dioxide, and in particular to the in-situ formation of chlorides of silicon such as silicon tetrachloride and chlorides of aluminum such as aluminum trichloride and chlorides of titanium such as titanium tetrachloride in the preparation of titanium dioxide.

Background of the Disclosure:

Titanium dioxide pigments are prepared using either the chloride process or the sulfate process. In the preparation of titanium dioxide pigments by the vapor phase chloride process, titanium tetrachloride, TiCl_4 , is reacted with an oxygen containing gas at temperatures ranging from about 900 °C to about 1600 °C, the resulting hot gaseous suspension of TiO_2 particles and free chlorine is discharged from the reactor and must be quickly cooled below about 600 °C, for example, by passing it through a conduit, i.e., flue, where growth of the titanium dioxide pigment particles and agglomeration of said particles takes place.

It is known to add various substances, such as silicon compounds and aluminum compounds, to the reactants in order to improve the pigmentary properties of the final product. Aluminum trichloride added during the process has been found to increase rutile in the final product, and silicon tetrachloride that becomes silica in the final product has been found to improve carbon black undertone, CBU, particle size and pigment abrasion.

U.S. patent 3,434,799 discloses the use of silicon metal in the production of TiO_2 ; however, experience of adding silicon metal in the AlCl_3 generator shows poor kinetics for the conversion of silicon to SiCl_4 . For direct addition of silicon metal to the TiO_2 reactor, it would require a very finely divided silicon metal which would be expensive to produce and create a fire or explosion hazard.

U.S. patent 3,642,442 discloses a method for adding aluminum and silicon to the process by generating a gaseous plasma and discharging particles to the process oxygen stream. A shortcoming of this patent is that the electrodes have a limited life and must be replaced on a routine basis requiring the TiO₂ process to be shut down.

The transport, storage and handling of silicon tetrachloride creates issues because the material is highly toxic and silicon tetrachloride handling equipment adds costs to the process.

A need exists for a low cost approach for adding silicon tetrachloride to the process without the need for transportation of a highly toxic material, special processing equipment and expensive silicon tetrachloride facilities. A need also exists for a process wherein the feed to the AlCl₃ generator can be continuous with no shutdown required for maintenance on the electrodes or equipment.

SUMMARY OF THE DISCLOSURE

In a first aspect, the disclosure provides a process for producing titanium dioxide, comprising:

- a) reacting aluminum metal and an alloy comprising silicon and titanium that has a silicon content of at least 5%, based on the weight of the alloy, with chlorine gas at temperatures above 190 °C to form chlorides of silicon, titanium and aluminum;
- (b) adding titanium tetrachloride to the chlorides of silicon, aluminum and titanium of step (a);
- (c) oxidizing the chlorides of silicon, aluminum and titanium, and titanium tetrachloride of step (b); and
- (d) forming titanium dioxide.

By "alloy" we mean a substance made by melting two or more elements together, at least one of them being a metal. An alloy crystallizes upon cooling into a solid solution, a homogeneous mixture, or an intermetallic compound.

In the first aspect, the disclosure provides a process wherein the titanium tetrachloride is present in step (a).

In the first aspect, the disclosure provides a process wherein the steps (a) and (b) are combined.

In the first aspect, the disclosure provides for titanium tetrachloride being present in a major amount in step (c).

In the first aspect, the disclosure provides a process wherein the alloy comprising silicon and titanium is titanium disilicide (TiSi₂).

5 In the first aspect, the disclosure provides titanium dioxide comprising a treatment of silicon dioxide and aluminum dioxide. The silicon dioxide and aluminum dioxide are present on the surface of the titanium dioxide.

BRIEF DESCRIPTION OF THE DRAWING

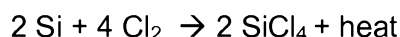
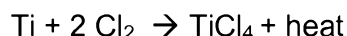
10 Figure 1 is a schematic illustration showing the process for preparing titanium dioxide (TiO₂).

DETAILED DESCRIPTION OF THE DISCLOSURE

In the process of vapor phase oxidation of titanium tetrachloride to form titanium dioxide pigment treated with silicon dioxide and aluminum oxide, chlorides of
15 silicon such as silicon tetrachloride, chlorides of aluminum such as aluminum trichloride and chlorides of titanium such as titanium tetrachloride are formed in-situ by reacting aluminum metal and an alloy comprising silicon and titanium having a minimum of 5% silicon, based on the weight of the alloy, with chlorine gas at temperatures above 190 °C,
20 typically about 300 °C to about 600 °C, optionally in the presence of titanium tetrachloride. Some suitable alloys comprising silicon and titanium include Goodfellow Titanium92/Silicon8 alloy, titanium disilicide (TiSi₂) alloy or any silicon-titanium alloy or silicon-titanium-aluminum alloy that is low in impurities that are detrimental to pigment color. Goodfellow
25 Titanium 92/Silicon 8 Alloy has a melting point of 1330°C and comprises Titanium, Ti: 92.0 %, and Silicon, Si: 8.0 %. Titanium disilicide (TiSi₂) has a melting point of 1470 C and comprises Titanium, Ti: 46.0%, and Silicon, Si: 54.0% Typically, the alloy comprising silicon and aluminum comprises about 5% to about 80% silicon, and more typically about 7% to about 55%
30 silicon.

As shown in Figure 1, the aluminum metal co-fed with the alloy comprising silicon and titanium 11 and chlorine 12 are added to the generator 10. This reaction can occur in fluidized beds, spouting beds,

packed beds, or plug flow reactors. The inert generator bed may comprise materials such as silica sand, glass beads, ceramic beads, TiO₂ particles, or other inert mineral sands. The reaction may occur in the presence of nucleating salts such as potassium chloride, rubidium chloride, or cesium chloride. The alloy comprising silicon and titanium 11 reacts in the generator 10 according to the following equations:



10 The heat of reaction from the chlorination of the titanium metal helps provide sufficient heat to drive the kinetics of the reaction between chlorine and silicon. The heat generated from the chlorination of aluminum and chlorine provides additional heat for the silicon chlorination reaction.

15 Titanium tetrachloride 17 may be present during this reaction to absorb the heat of reaction. The mixture formed in the in-situ step 13 comprises chlorides of silicon such as silicon tetrachloride, and chlorides of aluminum such as aluminum trichloride, and chlorides of titanium such as titanium tetrachloride.

20 The mixture formed in the in-situ step 13 flows into an oxidation reactor 14 and titanium tetrachloride 15 is then added to the mixture, such that titanium tetrachloride is present in a major amount. Vapor phase oxidation of and titanium tetrachloride is disclosed, for example, in U.S. Pat. Nos. 2,488,439, 2,488,440, 2,559,638, 2,833,627, 3,208,866, 3,505,091, and 25 7,476,378.

Such reaction usually takes place in a pipe or conduit, wherein oxygen 16, titanium tetrachloride 15 and the in-situ formed mixture comprising chlorides of silicon such as silicon tetrachloride and chlorides of aluminum such as aluminum trichloride and chlorides of titanium such as titanium 30 tetrachloride 13 are introduced at a suitable temperature and pressure for production of the titanium dioxide. In such a reaction, a flame is generally produced.

Downstream from the flame, the titanium dioxide produced is fed through an additional length of conduit wherein cooling takes place. For the purposes herein, such conduit will be referred to as the flue. The flue should be as long as necessary to accomplish the desired cooling. Typically, the flue is water cooled and can be about
5 50 feet (15.24 m) to about 3000 feet (914.4 m), typically about 100 feet (30.48 m) to about 1500 feet (457.2 m), and most typically about 200 feet (60.96 m) to 1200 feet (365.76 m) long.

CLAIMS

What is claimed is:

1. A process for producing titanium dioxide, comprising:
 - 5 a) reacting aluminum metal and an alloy comprising silicon and titanium that has a silicon content of at least 5%, based on the weight of the alloy, with chlorine gas at temperatures above 190 °C to form chlorides of silicon, titanium and aluminum;
 - (b) adding titanium tetrachloride to the chlorides of silicon,
 - 10 aluminum and titanium of step (a);
 - (c) oxidizing the chlorides of silicon, aluminum and titanium, and titanium tetrachloride of step (b); and
 - (d) forming titanium dioxide.
2. The process of claim 1 wherein titanium tetrachloride is present
- 15 in step (a).
3. The process of claim 1 wherein steps (a) and (b) are combined.
4. The process of claim 1 wherein chlorides of silicon, aluminum and titanium are silicon tetrachloride, aluminum trichloride and titanium tetrachloride.
- 20 5. The process of claim 1 wherein the alloy comprising silicon and titanium is titanium disilicide.
6. The process of claim 1 wherein the alloy comprising silicon and titanium is Titanium 92/Silicon 8
7. The process of claim 1 wherein the alloy comprising silicon and
- 25 titanium comprises about 5% to about 80% silicon, based on the weight of the alloy.
8. The process of claim 1 wherein the alloy comprising silicon and titanium comprises about 7% to about 55% silicon, based on the weight of the alloy. .
- 30 9. The process of claim 1 wherein the alloy comprising silicon and titanium further comprises aluminum.
10. The process of claim 1 wherein the temperature is about 300 °C to about 600 °C.

11. The process of claim 1 wherein the reaction in step (a) occurs in a reactor selected from the group consisting of a fluidized bed reactor, spouting bed reactor, packed bed reactor, and a plug flow reactor.

12. The process of claim 11 wherein the reactor comprises
5 materials selected from the group consisting of silica sand, glass beads, ceramic beads, TiO₂ particles, and other inert mineral sands.

13. The process of claim 11 wherein the reaction in step (a) occurs in the presence of nucleating salts.

14. The process of claim 13 wherein the nucleating salts are
10 selected from the group consisting of potassium chloride, rubidium chloride, and cesium chloride.

15. The process of claim 1 wherein the amount of alloy comprising silicon and titanium is about 0.1% to about 5% by weight, based on the total amount of all reactants.

16. The process of claim 15 wherein the amount of alloy comprising
15 silicon and titanium is about 0.2% to about 1.5% by weight, based on the total amount of all reactants.

17. The process of claim 1 wherein the amount of chlorine is about 0.4% to about 20% by weight, based on the total amount of all reactants.

18. The process of claim 17 wherein the amount of chlorine is
20 about 2% to about 5% by weight, based on the total amount of all reactants.

19. The process of claim 1 wherein the amount of titanium tetrachloride is about 75% to about 99.5% by weight, based on the total
25 amount of all reactants.

20. The process of claim 19 wherein the amount of titanium tetrachloride is about 93% to about 98% by weight, based on the total amount of all reactants.

21. The process of claim 1 wherein the titanium tetrachloride is
30 present in a major amount in step (c).

22. The process of claim 1 wherein the titanium dioxide comprises a treatment of silicon dioxide and aluminum dioxide.

1/1

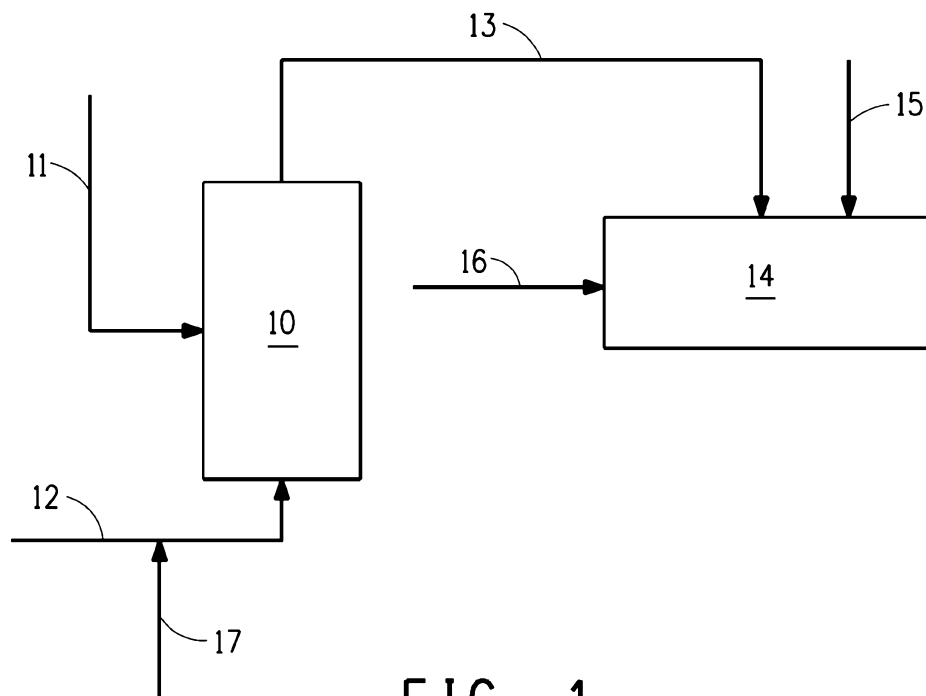


FIG. 1