(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)
(19) World Intellectual Property Organization
(43) International Publication Date
3 August 2017 (03.08.2017)

(51) International Patent Classification:
C09C 1/36 (2006.01) B02C 21/00 (2006.01)
C09G 23/08 (2006.01) B02C 17/16 (2006.01)
B02C 17/20 (2006.01)

(21) International Application Number:
PCT/EP2017/000077

(22) International Filing Date:
24 January 2017 (24.01.2017)

(25) Filing Language:
English

(26) Publication Language:
English

(30) Priority Data:
16000192.1 27 January 2016 (27.01.2016) EP

(71) Applicant: KRONOS INTERNATIONAL, INC.
[DE/DE]; Patents & Literature, Peschstr. 5, 51373 Leverkusen (DE).

(72) Inventors: JURGENS, Volker; Heinsberger Str. 44, 57399 Kirchhundem (DE). BLUMEL, Siegfried; An der Deckersweide 24, 40883 Ratingen-Eggerscheid (DE).
FRIEDRICH, Jorg; Unterbuscherhof 66, 42799 Leichlingen (DE). SCHMITT, Volker; von Herrn Dr. Schmitt, Kradenpuehl 42, 42799 Leichlingen (DE). ABDIN, Achim; Herrn Abdin, Edwin-Lilienthal-Str. 7, Nordenham (DE).

(74) Agent: KRONOS INTERNATIONAL, INC.; Patents & Literature, Peschstr. 5, 51373 Leverkusen (DE).

(81) Designated States (unless otherwise indicated, for every kind of regional protection available):

(84) Designated States (unless otherwise indicated, for every kind of national protection available):

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

(54) Title: PRODUCTION OF TITANIUM DIOXIDE PIGMENT OBTAINED BY THE SULFATE PROCESS WITH A NARROW PARTICLE SIZE DISTRIBUTION

(57) Abstract: The invention relates to a process for producing a titanium dioxide pigment obtainable by the sulfate process with a narrow particle size distribution, the pigment itself, and the use of said pigments in coatings and printing inks.
Production of titanium dioxide pigment obtainable by the sulfate process with a narrow particle size distribution.

Field of the invention

The invention relates to a process for producing a titanium dioxide pigment obtainable by the sulfate process with a narrow particle size distribution, the pigment itself, and the use of said pigments in coatings and printing inks.

Technological background of the invention

Titanium dioxide pigment in the rutile crystal modification usually produced by either the chloride process or the sulfate process. Rutile titanium dioxide pigment particles obtainable by the sulfate process generally have a lower hardness as compared to rutile titanium dioxide pigment particles produced by the chloride process. Therefore, the latter are more suitable for use in printing inks.

In the production by the chloride process, the raw material containing iron and titanium is reacted with chlorine, and the titanium tetrachloride formed is subsequently oxidized to titanium dioxide which is the so-called titanium dioxide base pigment. In the production by the sulfate process, the raw material containing iron and titanium is liberated in concentrated sulfuric acid in order to form titanyl sulfate. The titanyl sulfate is hydrolyzed and calcined in a rotary kiln to form titanium dioxide, the titanium dioxide base pigment. The titanium dioxide base pigment largely consists of agglomerates of primary particles, which must be deagglomerated as much as possible before further processing. The titanium dioxide base pigment obtained by the sulfate process usually has a broader particle size distribution in comparison to the titanium dioxide base pigment obtainable by the chloride process. For the deagglomeration, the titanium dioxide base pigment particles are subsequently slurried to form a suspension, and subjected to wet milling, for example, in an agitator ball mill. Subsequently, the particles are subjected to an inorganic and/or organic aftertreatment depending on the field of application.
For the general use in printing inks and coatings, in particular optical properties, such as opacity and gloss, are of a critical importance. Said properties are essentially determined by the broadness of the particle size distribution. Too fine fractions in the particle size distribution adversely affect opacity, whereas coarse particles reduce the gloss. Thus, a particle size distribution being as narrow as possible, as well as an optimized particle size are desired. The mean particle size and the broadness of the particle size distribution can be influenced by the type of wet milling. Usually, wet milling is performed by conveying the particle suspension through the agitator ball mill in one passage, which produced a relatively broad particle size distribution. In addition, however, it is known that multiple conveying through the agitator ball mill either in a cycle, the so-called circuit grinding, or in the form of several batches, the so-called multi-passage grinding, results in a narrower particle size distribution.

Summary of the invention

It is the problem of the invention to provide a process by which titanium dioxide particles derived from the sulfate process can be provided with a narrow particle size distribution and a particular suitability for use in coatings and, in particular, in printing inks.

The problem is solved by a process for producing a titanium dioxide pigment, in which titanium dioxide particles obtained by the sulfate process are ground in an aqueous suspension before aftertreatment, characterized in, that the wet milling is performed as a passage milling in a cascade of at least three agitator ball mills and that the grinding media of the first agitator ball mill have a larger diameter and/or a higher density than that of the grinding media of the second or subsequent agitator ball mill.

Therefore, in a first aspect, the present invention relates to a process for producing a titanium dioxide pigment, in which titanium dioxide particles obtained by the sulfate process are ground in an aqueous suspension prior to aftertreatment, characterized in, that the wet milling is conducted as a passage milling in a cascade of at least three agitator ball mills and that the grinding media of the first agitator ball mill have a larger diameter and/or a higher density than that of the grinding media of the second or subsequent agitator ball mill.

In another aspect the present invention relates to a titanium dioxide pigment obtainable by the process disclosed herein.
Finally, in a further aspect, the present invention refers to the use of a titanium dioxide pigment described herein in coatings and printing inks.

Further advantageous embodiments of the invention are contained in the dependent claims.

Description of the invention

These and further aspects, features and advantages of the invention become apparent to the skilled person from a study of the following detailed description and claims. Each feature from one aspect of the invention may also be used in any other aspect of the invention. Numerical ranges stated in the form "from x to y" include the values mentioned and those values that lie within the range of the respective measurement accuracy as known to the skilled person. If several preferred numerical ranges are stated in this form, of course, all the ranges formed by a combination of the different end points are also included.

According to experience, during the wet milling of a suspension of titanium dioxide particles in an agitator ball mill (hereinafter also referred to as a sand mill), the particle agglomerates are largely deagglomerated, and the primary particles are further comminuted to a certain extent. There is a difference between titanium dioxide particles obtained by the sulfate process and titanium dioxide particles obtained by the chloride process, the former particles being more readily comminuted. In the following, the processing in an agitator ball mill is referred to as "milling" or "wet milling".

The present invention proceeds from the experience that multi-passage grinding provides a narrower dwelling time distribution for the particles and thus a narrower particle size distribution as compared to circuit grinding in an agitator ball mill. The invention is further based on the recognition that the kinetic energy of the grinding media acting on the particles during the milling is a function of the size of the grinding media and of the density of the grinding media. At the same time, the comminuting progress is a function of the number of grinding media/particle contacts, which increases as the size of the grinding media is reduced.

According to the invention, a suspension of unground titanium dioxide particles obtained by a sulfate process is subjected, in the first passage, to wet milling in an agitator ball mill with grinding media having a larger diameter and/or a higher density as compared to the grinding media employed in the second or subsequent passages. In this way, the grinding media in
the agitator mill of the second and subsequent passages are adapted to the comminuting progress and the consequently decreasing viscosity of the particle suspension, and thus optimization of the input amount of energy is achieved. At the same time, excess grinding of the particles and the production of an undesirable fine fraction (< 0.2 µm) are minimized.

The multi-passage milling offers the opportunity to employ either horizontally or vertically mounted mills. Horizontally mounted closed agitator ball mills can also be operated at an increased viscosity of the suspension with relatively high throughput volumes, for example, with 15 to 18 m³/h, in contrast to vertically mounted open mills. In contrast, vertical open mills can usually be operated only at a throughput of up to about 8 m³/h.

According to the invention, a suspension of titanium dioxide base pigment particles derived from the sulfate process that have not yet been aftertreated is employed. In the unground state, the particle suspension has a higher fraction of agglomerates and a higher viscosity.

In a particular embodiment of the invention, a titanium dioxide base pigment is employed that has an SC value of < 4.5 before the wet milling according to the invention. According to the invention, an "SC value" designates the negative b* value measured according to DIN 53165 as a blue cast of a paint composition consisting of titanium dioxide and black paste (so-called MAB test). Usually, the SC value for titanium dioxide base pigments obtained by a sulfate process is > 4.5, preferably from 5 to 7. The lower SC value of < 4.5 is associated with an increased hardness of the particles and an increased particle size. An SC value of < 4.5 can be achieved in the sulfate process, for example, by longer calcination times or higher calcination temperatures.

The grinding media employed in the first passage are larger and/or have a higher density than those used in the second and subsequent passages. Preferably, the grinding media are larger and have a higher density than those used in the subsequent passages. For example, ceramic grinding media, such as grinding media of aluminum oxide, zirconium silicate or zirconium oxide, are employed in the first passage in the agitator ball mill. Preferably, the grinding media have a diameter within the range of from 0.6 to 1.2 mm. The grinding of the first passage is also referred to as pre-grinding.

In a preferred embodiment of the invention, the grinding of the first passage is performed in a closed and optionally horizontally mounted agitator ball mill (hereinafter also referred to as a
sand mill). Preferably, a usual dispersant, especially hexametaphosphate, is additionally added to the suspension. Usual dispersants are known in the art.

In a further step (further passage), preferably subsequent to the first step (first passage), grinding media having a smaller size and/or lower density are employed. For example, sand has a lower density as compared to ceramic grinding media. In particular, Ottawa sand is suitable, for example, with a diameter of from 0.6 to 0.8 mm, or from 0.4 to 0.6 mm.

The second and further passage grinding can take place in a horizontal or vertical sand mill. When Ottawa sand is employed, the vertically mounted sand mill is preferred, because there is increased sand breakage in the horizontally mounted mill, and the discharge system of the sand mill will clog.

A vertically mounted sand mill for the second passage can have an open construction. According to the invention, the third passage grinding may also be performed in a vertical sand mill.

In a preferred embodiment of the invention, the grinding is performed under such conditions that the first agitator ball mill is filled with zirconium silicate or zirconium oxide beads of a size of 0.6 to 0.8 mm, the second agitator ball mill is filled with Ottawa sand of a size of 0.6 to 0.8 mm, and the third agitator ball mill is filled with Ottawa sand of a size of 0.4 to 0.6 mm.

The procedure according to the invention enables large throughput volumes in each of the preferred three grinding passages, so that the dwelling time within the mills is shortened, and thus excess grinding of the particles is prevented. Preferably, the process according to the invention is performed under such conditions that the throughput in the first passage per hour is more than 15-fold, especially more than 20-fold and more preferably about 30- to 35-fold, the mill volume.

Moreover, further dispersant can be added between the grinding passages. Further, NaOH can be used to adjust an optimum pH and thus an optimum viscosity of from 50 to 500 mPas, preferably from 100 to 200 mPas.

Subsequently to the wet milling, the titanium dioxide pigment particles are subjected to well established inorganic and/or organic aftertreatment. Inorganic aftertreatment usually includes coating with inorganic oxides or water-containing oxides, such as SiO$_2$, Al$_2$O$_3$, ZrO$_2$, etc. These
may be compact or rather loose coatings. In a particular embodiment, the pigment particles are treated with aluminum oxide, preferably in a multistage process. The skilled person is familiar with the aftertreatment processes used in TiO2 process technology.

Finally, the aftertreated TiO2 pigment particles are usually micronized in a steam jet mill. In the meantime, a hydrophilic organic compound, such as 1,1,1-trimethylolpropane (TMP), may optionally be added as a grinding aid to the steam jet mill. Further known suitable organic additives can also be used. The amount of added grinding aid, calculated as carbon, should preferably be within a range of from 0.05 to 0.50% by weight, preferably from 0.18 to 0.35% by weight, carbon, based on TiO2.

In another embodiment of the invention, the titanium dioxide particles are subjected to dry milling, preferably in a pendulum mill or high compression roller mill, before the wet milling. The dry milling enables the cracking of hard particle agglomerates that cannot be deagglomerated during the wet milling in the agitator ball mill. During the dry milling, a grinding aid, such as 1,1,1-trimethylolpropane (TMP) or trimethylolethane (TME) or related substances, may be added. The preferred amount is around 0.03 to 0.3% by weight, especially from 0.04 to 0.1% by weight, calculated as carbon and based on TiO2.

The process according to the invention enables the production of titanium dioxide pigment that is suitable, in particular, for coatings in general and especially for printing inks.
CLAIMS:

1. A process for producing a titanium dioxide pigment, in which titanium dioxide particles obtained by the sulfate process are ground in an aqueous suspension prior to after-treatment, characterized in that the wet milling is conducted as a passage milling in a cascade of at least three agitator ball mills and that the grinding media of the first agitator ball mill have a larger diameter and/or a higher density than that of the grinding media of the second or subsequent agitator ball mill.

2. The process according to claim 1, characterized in that at least the first agitator ball mill is operated at a throughput per hour of more than 15-fold, especially more than 20-fold and more preferably about 30- to 35-fold, the mill volume.

3. The process according to claim 1 or 2, characterized in that at least the first agitator ball mill is horizontally mounted, and at least one of the further agitator ball mills is vertically mounted.

4. The process according to one or more of claims 1 to 3, characterized in that the first agitator ball mill is horizontally mounted, and the second and third agitator ball mills are vertically mounted.

5. The process according to one or more of claims 1 to 4, characterized in that the first agitator ball mill is filled with ceramic grinding media having a size within a range of from 0.6 to 1.2 mm.

6. The process according to one or more of claims 1 to 5, characterized in that the first agitator ball mill is filled with zirconium silicate beads of a size of 0.6 to 0.8 mm, the second agitator ball mill is filled with Ottawa sand of a size of 0.6 to 0.8 mm, and the third agitator ball mill is filled with Ottawa sand of a size of 0.4 to 0.6 mm.

7. The process according to one or more of claims 1 to 6, characterized in that the dispersant contains a dispersant, especially hexametaphosphate.

8. The process according to one or more of claims 1 to 7, characterized in that the titanium dioxide particles have an SC value (MAB test) of < 4.5 before the wet milling.
9. The process according to one or more of claims 1 to 8, characterized in that the titanium dioxide particles are subjected to dry milling in a pendulum mill or high compression roller mill before the wet milling.

10. The process according to claim 9, characterized in that a grinding aid, especially 1,1,1-trimethylolpropane (TMP), is added in the dry milling.

11. The process according to claim 10, characterized in that from 0.03 to 0.3% by weight, especially from 0.04 to 0.1% by weight, TMP is added, calculated as carbon and based on TiO₂.

12. The process according to one or more of claims 1 to 11, characterized in that the titanium dioxide particles are aftertreated with aluminum oxide subsequently to the wet milling, preferably in a multistage process.

13. The process according to claim 12, characterized in that the titanium dioxide particles are subsequently micronized in a steam jet mill, and in the meantime, a hydrophilic or organically compound, especially 1,1,1-trimethylolpropane (TMP), is added.

14. A titanium dioxide pigment obtainable by the process according to one or more of claims 1 to 13.

15. Use of the titanium dioxide pigment obtainable according to claim 14 in coatings and printing inks.
## A. CLASSIFICATION OF SUBJECT MATTER

INV. C09C1/36 C01G23/08 B02C17/20 B02C21/00 B02C17/16

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

- C09C
- C01G
- B02C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

- EPO-Internal
- BIOSIS
- CHEM ABS Data
- COMPENDEX
- EMBASE
- INSPEC
- WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>ine 12 - line 24 col umn 5, line 65 - col umn 6, line 26 -----</td>
<td>7,9,10, 12,13</td>
</tr>
<tr>
<td>X</td>
<td>US 3 220 867 A (O‘SHAUNNESSY JAMES M) 30 November 1965 (1965-11-30) col umn 2,</td>
<td>14,15</td>
</tr>
<tr>
<td>Y</td>
<td>l ine 18 - line 42 col umn 3, line 9 - line 15 -----</td>
<td>12</td>
</tr>
<tr>
<td>Y</td>
<td>DE 10 2010 053164 Al (KRONOS INT INC [DE]) 6 June 2012 (2012-06-06) paragraphs</td>
<td>7,12,13</td>
</tr>
<tr>
<td></td>
<td>[0027], [0029] -----</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>DE 10 2011 015856 Al (KRONOS INT INC [DE]) 4 October 2012 (2012-10-04) paragraphs</td>
<td>12,13</td>
</tr>
<tr>
<td></td>
<td>[0018], [0019], [0030] -----</td>
<td></td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

See patent family annex.

### * Special categories of cited documents :

- **A** document defining the general state of the art which is not considered to be of particular relevance
- **B** earlier application or patent but published on or after the international filing date
- **L** document which may throw doubts on priority claim(s) on which the document is cited to establish the publication date of another citation or other special reason (as specified)
- **O** document referring to an oral disclosure, use, exhibition or other means
- **P** document published prior to the international filing date but later than the priority date claimed

### **T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

### **X** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

### **Y** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

### **A** document member of the same patent family

### Date of the actual completion of the international search

7 April 2017

### Date of mailing of the international search report

18/04/2017

**Form PCT/ISA/210 (second sheet) (April 2005)**
<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>DE 195 36 657 A1 (METALLGESELLSCHAFT AG [DE]) 10 April 1997 (1997-04-10) column 2, line 21 - line 29 column 2, line 27 - column 3, line 25 column 3, line 45 - line 60</td>
<td>12,13</td>
</tr>
<tr>
<td>Y</td>
<td>DE 10 2006 049495 A1 (TRONOX PIGMENTS INTERNAT GMBH [CH]) 13 September 2007 (2007-09-13) paragraphs [0005], [0010], [0011], [0020], [0021]</td>
<td>7,9,10</td>
</tr>
</tbody>
</table>
### Patent document Publication

<table>
<thead>
<tr>
<th>Patent document cited in search report</th>
<th>Publication date</th>
<th>Patent family member(s)</th>
<th>Publication date</th>
</tr>
</thead>
<tbody>
<tr>
<td>US 5407464 A 18-04-1995</td>
<td>AU 1306595 A</td>
<td>01-08-1995</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CA 2181063 Al</td>
<td>20-07-1995</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EP 0739242 Al</td>
<td>30-10-1996</td>
<td></td>
</tr>
<tr>
<td></td>
<td>US 5407464 A</td>
<td>18-04-1995</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wo 9519223 Al</td>
<td>20-07-1995</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>US 3220867 A 30-11-1965</td>
<td>AT 253642 B</td>
<td>10-04-1967</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BE 642161 A</td>
<td>04-05-1964</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DE 1467489 Al</td>
<td>09-01-1969</td>
<td></td>
</tr>
<tr>
<td></td>
<td>FI 42737 B</td>
<td>30-06-1970</td>
<td></td>
</tr>
<tr>
<td></td>
<td>GB 1073491 A</td>
<td>28-06-1967</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LU 45170 Al</td>
<td>07-03-1964</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NL 136820 C</td>
<td>07-04-2017</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NL 302269 A</td>
<td>07-04-2017</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SE 309643 B</td>
<td>31-03-1969</td>
<td></td>
</tr>
<tr>
<td></td>
<td>US 3220867 A</td>
<td>30-11-1965</td>
<td></td>
</tr>
<tr>
<td>DE 102010053164 AI 06-06-2012</td>
<td>NONE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DE 102011015856 AI 04-10-2012</td>
<td>AU 2012237486 AI</td>
<td>19-09-2013</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CN 103476877 A</td>
<td>25-12-2013</td>
<td></td>
</tr>
<tr>
<td></td>
<td>DE 102011015856 AI</td>
<td>04-10-2012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EP 2694599 AI</td>
<td>12-02-2014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>JP 5931172 B2</td>
<td>08-06-2016</td>
<td></td>
</tr>
<tr>
<td></td>
<td>JP 2014514391 A</td>
<td>19-06-2014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>KR 2014003360 A</td>
<td>18-03-2014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>RU 2013148886 A</td>
<td>10-05-2015</td>
<td></td>
</tr>
<tr>
<td></td>
<td>TW 201247790 A</td>
<td>01-12-2012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UA 113054 C2</td>
<td>12-12-2016</td>
<td></td>
</tr>
<tr>
<td></td>
<td>US 2012247702 AI</td>
<td>04-10-2012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wo 2012130408 AI</td>
<td>04-10-2012</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EP 0869994 AI</td>
<td>14-10-1998</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ES 2148794 T3</td>
<td>16-10-2000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wo 9712943 Al</td>
<td>10-04-1997</td>
<td></td>
</tr>
<tr>
<td>DE 102006049495 AI 13-09-2007</td>
<td>NONE</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>