

1

3,428,427

**PROCESS FOR PRODUCING A PRODUCT HIGH IN TITANIUM DIOXIDE CONTENT**

Dusan Raicevic, Beloeil, Quebec, Canada, assignor to Quebec Iron and Titanium Corporation, New York, N.Y., a corporation of Canada

No Drawing. Filed June 24, 1965, Ser. No. 466,859  
U.S. Cl. 23-202 10 Claims  
Int. Cl. C01g 23/04

**ABSTRACT OF THE DISCLOSURE**

This invention relates to a process for producing a product rich in titanium dioxide and relatively low in other materials from titaniferous material that is first leached with dilute sulfuric acid to produce a solid residue which is subsequently leached with a dilute aqueous alkaline solution to obtain a titanium dioxide product.

This invention relates to a process for producing a product high in titanium dioxide from iron-bearing titaniferous materials. More particularly, this invention relates to a process for producing a product that is rich in titanium dioxide, and that can be regarded as a synthetic rutile, from ilmenite ore, titanium-bearing slag, and the like.

The word "ilmenite" refers to a specific chemical, that is generally accepted as having the formula  $\text{FeO} \cdot \text{TiO}_2$ . The precise form in which this mineral occurs varies from deposit to deposit. One of the important deposits is the Allard Lake deposit in Quebec, Canada. The ilmenite ore there is a mechanical mixture of ilmenite and hematite. Most ores of ilmenite are mixtures of ilmenite and hematite or magnetite.

The Allard Lake ore is smelted at Sorel, Quebec, by the Quebec Iron and Titanium Corporation, to produce iron and a slag that is rich in titanium dioxide. A general description of the smelting operation at Sorel and its products can be found in United States Patent 2,476,453, granted July 19, 1949.

Typical analyses of Allard Lake ilmenite ore, and of the slag that is produced therefrom, appear below in Table I.

TABLE I.—TYPICAL ORES AND SLAGS

| Item                                 | Percentages by Weight |                          |        |        |        |
|--------------------------------------|-----------------------|--------------------------|--------|--------|--------|
|                                      | An Ilmenite Ore       | An Upgraded Ilmenite Ore | Slag 1 | Slag 2 | Slag 3 |
| TiO <sub>2</sub> .....               | 34.8                  | 35.6                     | 77.3   | 69.4   | 70.3   |
| Cr <sub>2</sub> O <sub>3</sub> ..... | 0.1                   | 0.11                     | 0.20   | 0.20   | 0.16   |
| V <sub>2</sub> O <sub>5</sub> .....  | 0.2                   | 0.30                     | 0.60   | 0.55   | 0.54   |
| FeO.....                             | 30.0                  | 27.90                    | 10.6   | 17.3   | 12.62  |
| Fe <sub>2</sub> O <sub>3</sub> ..... | 25.1                  | 27.81                    | 0      | 0      | 0      |
| MnO.....                             | 0.1                   | 0.14                     | 0.2    | 0.3    | 0.25   |
| SiO <sub>2</sub> .....               | 3.5                   | 2.26                     | 3.8    | 3.8    | 4.8    |
| Al <sub>2</sub> O <sub>3</sub> ..... | 2.8                   | 1.72                     | 4.6    | 4.7    | 4.4    |
| MgO.....                             | 2.9                   | 2.86                     | 4.9    | 4.8    | 4.8    |
| CaO.....                             | 0.5                   | 0.46                     | 0.6    | 0.6    | 0.7    |

In Table I, above, the term "upgraded ilmenite ore" is employed to refer to an ore that has been upgraded by physical methods. Such methods would include conventional mineral dressing techniques. For example, to produce the upgraded ilmenite ore, whose analysis is presented in Table I, ore as received from the mine was crushed, ground, screened, and subjected to magnetic separation. These operations remove gangue materials.

2

Leaching is a well-known technique for removing impurities from ilmenite ore and other titaniferous materials. It is possible to leach ilmenite ore with dilute sulfuric acid, such as, for example, sulfuric acid having a concentration from about 10% to about 60%, at temperatures from about 100° C. to about 250° C. or higher, and under pressures up to about 500 p.s.i., to produce a residue containing a high proportion of titanium dioxide and a much smaller proportion of impurities than would be found in the ore. The presence of a reducing agent, or the use of reducing conditions, has a beneficial effect upon the removal of impurities.

Attempts to leach titanium-bearing slag, in similar fashion, for the purpose of reducing impurities and upgrading the content of titanium dioxide, have encountered considerable difficulty. A practical and successful process for leaching slag is described in the copending patent application of Dr. Peter J. Ensio, Ser. No. 319,312, filed Oct. 28, 1963 now abandoned. The process that is described in this application recognizes that ferric ions are normally present in the leach liquor during the leaching of ilmenite ore, and that removal of the chromium and vanadium is therefore facilitated while removal of the iron is hindered; and that when leaching slag, however, ferric ions are absent, and trivalent titanium ions are normally present, so that the removal of iron is facilitated whereas the removal of chromium and vanadium is hindered.

The leaching technique described in the Ensio application is based upon the discovery that the presence of ferric ions in the leaching solution has a pronounced beneficial effect upon the removal of chromium and vanadium from the slag. The ferric ions can be introduced in various ways, such as, for example, by the addition of oxidants during leaching. Preferably, however, the ferric ions are provided by mixing the slag with an ilmenite ore, such as, for example, the Allard Lake ilmenite ore, that provides ferric ions.

Typical leaching conditions, according to the Ensio process, are those where the mixture of slag and ore comprises at least 50% to about 60% of slag; the acid strength is from about 35% up to about 60%; the temperature is at least 400° F.; the pressure is about 200 p.s.i. but may be higher, for example, up to about 500 p.s.i.; and the leaching time is at least about 2 hours. The quality of the titanium dioxide residue that is obtained may be adjusted by controlling the leaching process variables, including acid concentration, temperature, pressure, time, and amount of excess acid employed. The term "excess acid" is used to refer to the amount of acid that is employed above that which is needed for the removal of iron, titanium, vanadium, calcium, magnesium, and other non-titaniferous impurities.

In a typical demonstration of leaching in accordance with the Ensio patent application, a mixture was prepared that contained 60% by weight of slag and 40% by weight of a beneficiated, 92 grade Allard Lake ore concentrate. (The grade number refers to the sum of the percentages of iron and titanium oxides present.) The slag contained 70% titanium dioxide and 11%  $\text{Ti}_2\text{O}_3$ . The slag and the ore each were ground, prior to leaching and mixing together, so that at least 85% of the particles passed through a 325 mesh. A 45% fresh sulfuric acid was used for leaching, in 100% excess, at a temperature of 400° F., under a pressure of about 200 p.s.i., for two hours.

After leaching, over-all titanium dioxide recovery in

the residue was at least 98%. Repeated demonstrations of the process indicate that a product having the following specifications may be consistently produced:

Table II.—Leached product specifications

| Chemical specifications:               | Percentage by weight |
|----------------------------------------|----------------------|
| Fe -----                               | max-- 1.5            |
| Cr <sub>2</sub> O <sub>3</sub> -----   | max-- 0.1            |
| V <sub>2</sub> O <sub>5</sub> -----    | 0.5-0.10             |
| CaO+MgO -----                          | max-- 0.5            |
| Loss on ignition -----                 | max-- 0.2            |
| TiO <sub>2</sub> (natural basis) ----- | 90-94                |

The leached product is in the form of a slurry containing solid particles all of which pass through a 20 mesh screen, and of which at most about 3% pass through a 200 mesh screen. The solid particles vary in color from light to dark brown, depending upon the particular reaction conditions to which the mixture has been subjected.

While leached products that fall within the specifications stated in Table II represent a substantial upgrading of the ilmenite ore, these products must compete technically with rutile that is obtained from natural rutile deposits of grades that are as high and sometimes higher than those of the leached products. Accordingly, there is a demand for a product having specifications higher than those that may be obtained by the best leaching techniques previously known.

One object of the present invention is to provide a practical process for treating an iron-bearing titaniferous material, to produce a product having a high content of titanium dioxide and relatively low contents of other materials.

A more specific object of the invention is to provide an improved leaching process for iron-bearing titaniferous material, that can produce products that are comparable to and competitive with products obtained from natural rutile deposits.

Another object of the invention is to provide a practical process that can be used with an ilmenite ore, for producing products that are comparable to and competitive with products obtained from natural rutile deposits and that are rich in titanium dioxide.

Another specific object of the invention is to provide a practical process for the production of a pigment material from an ilmenite ore.

A further specific object of the invention is to provide a practical process for the production, from an ilmenite ore, of a material that is rich in titanium dioxide and that is suitable for use as a feed material for the chlorination process for the production of titanium dioxide.

Still another specific object of the invention is to provide a practical process for the production, from ilmenite ore, of a material that is rich in titanium dioxide and that is usable as a coating for welding rods.

A more general object of the invention is to provide practical processes for producing products rich in titanium dioxide, and relatively low in other materials, including, for example, chromium, vanadium, iron, silica, and materials that are lost on ignition, from iron-bearing titaniferous materials such as, for example, ilmenite ore, upgraded ilmenite ore, and titanium-bearing slag.

Other objects of the invention will be apparent hereinafter from the specification and from the recital of the appended claims.

I have now found that a valuable product, that has a high content of titanium dioxide and a relatively low content of other, undesirable materials, may be produced by a process that comprises leaching an iron-bearing titaniferous material, in finely-divided form, with a dilute sulfuric acid solution, to obtain an iron-bearing solution and a solid residue; separating the iron-bearing solution and the solid residue; and then leaching the solid residue with a dilute aqueous alkaline solution, to obtain a solid residue that is high in titanium dioxide content. As compared to products prepared by previously known processes, this

product is relatively high in titanium dioxide content, and desirably low in its content of iron, chromium, vanadium, silica, and materials that are lost on ignition.

The product that is thus obtained can be further processed, if desired, by calcining, at an elevated temperature such as, for example, a temperature in the range between about 800° C. and 900° C., to produce a pigment material of a natural light beige color. Alternatively, the product may be mixed with a carbonaceous material and sintered at a temperature in the range from about 1000° C. to about 1400° C., to produce a synthetic rutile in porous form, that is suitable for use as a feed material for the chlorination process for the production of titanium dioxide, or that is suitable for the preparation of a coating for welding rods.

In one preferred embodiment of the process in accordance with this invention, the iron-bearing titaniferous material is ground to an extremely small particle size, at which approximately 85% of the particles will pass through a 325 mesh screen. The finely-divided material is then mixed with a dilute sulfuric acid, having a concentration in the range from about 10% to about 60%, and the mixture is heated in an autoclave at a temperature in the range from about 100° C. to about 250° C., at a pressure up to about 300 p.s.i., for a sufficiently long time to permit substantially complete reaction between the sulfuric acid and the titaniferous material. The material is then discharged from the autoclave, and the liquid material is separated from the solid residue. The residue preferably is then washed, and then is subjected to a physical separation, preferably in a hydrocyclone, to separate the material under 325 mesh size from the larger material. The coarse material preferably is then subjected to a second leaching process with dilute sulfuric acid, to insure complete reaction. The fine material is passed on to the next step in the process.

The fine material is then further leached with a dilute aqueous alkaline solution, preferably a solution containing at least one member selected from the group consisting of alkali metal hydroxides and alkali metal carbonates. The term "alkali metal" is employed herein to describe the hydroxides and carbonates of potassium, sodium, lithium, and ammonia. This leaching step is preferably carried out with a solution of the character described having a concentration in the range from about 5% to about 25%, at atmospheric pressure, and at a temperature in the range from about 100° C. to about 110° C., for a period of time in the range from about one and a half hours to about three hours. The solid material is then separated from the leaching liquid, and may be washed to remove any residual traces of the alkaline leach liquid.

The solid material may then be further processed to produce a variety of products for desired applications. Calcining in the presence of a suitable modifier is the technique that is preferred for the production of materials for use as colored pigments. For the production of chlorination process feed materials or welding rod coatings, calcining is ordinarily preferred, after mixing with a carbonaceous material such as, for example, one of the soluble starches, a fuel oil, a low ash coke, sawdust, or some combination of these or equivalent materials. Ordinarily, such a mixture is pelletized for sintering, and water is used if necessary to assist in pelletizing.

In the calcining of these materials, among the many suitable modifiers that can be employed, to speed up the conversion of the leached residue to the form of rutile, antimony oxide and zinc oxide are two preferred materials. However, other modifiers may be employed, if desired, particularly if different colors are desired.

The invention is further explained in detail, below, by the description of several demonstrations thereof.

#### EXAMPLE 1

To demonstrate the invention on a small scale, 45 kgs. of a titanium-bearing slag, produced in electric furnace,

smelting of an ilmenite ore, and having a 70.3% content of titanium dioxide, was placed in a 50 gallon autoclave with 107.5 liters of 35% sulfuric acid. The mixture was then heated to a temperature of about 200° C. under autogenous pressure, for four hours.

The materials were then removed from the autoclave, settled, and decanted. The solids were repulped several times with fresh water, to remove residual acid.

The acid-leached residue had the following partial analysis:

Table III.—Partial analysis of acid-leached residue

| Item:                                | Percentage by weight |
|--------------------------------------|----------------------|
| TiO <sub>2</sub> .....               | 82.1                 |
| Fe .....                             | 0.85                 |
| Cr <sub>2</sub> O <sub>3</sub> ..... | 0.08                 |
| V <sub>2</sub> O <sub>5</sub> .....  | 0.10                 |
| Loss on ignition .....               | 6.52                 |

The acid-leached residue, after washing, was separated in a hydrocyclone into an overflow fraction of fines, consisting essentially of materials having a particle size that will pass through a 325 mesh screen, and into an underflow fraction of coarse materials, of larger size. The coarse material was set aside for subsequent repetition of the acid-leaching step.

The comparative analyses of these two fractions appears in Table IV, below:

TABLE IV.—PARTIAL ANALYSES OF FRACTIONS

|                                      | Fines, Overflow,<br>Percent | Coarse, Underflow,<br>Percent |
|--------------------------------------|-----------------------------|-------------------------------|
| TiO <sub>2</sub> .....               | 89.0                        | 67.8                          |
| Fe .....                             | 0.16                        | 0.9                           |
| Cr <sub>2</sub> O <sub>3</sub> ..... | 0.08                        | 0.08                          |
| V <sub>2</sub> O <sub>5</sub> .....  | 0.10                        | 0.12                          |
| Loss on Ignition .....               | 5.98                        | 4.4                           |
| SiO <sub>2</sub> .....               | 3.91                        | 9.0                           |

The fines fraction was then divided into two parts. One part was mixed with a 10% solution of potassium hydroxide. The second part was mixed with a 25% solution of potassium hydroxide. Both solutions were then heated in open reactors, and were maintained at temperatures in the range from about 90° to about 105° C. for two hours.

Thereafter, the solid residues were each repulped three times, then dried. The analyses of these fractions was as follows:

TABLE V.—ANALYSES OF ALKALINE-LEACHED RESIDUES

| Item                                 | Material Leached with<br>10% Potassium Hy-<br>droxide, percent | Material Leached with<br>25% Potassium Hy-<br>droxide, percent |
|--------------------------------------|----------------------------------------------------------------|----------------------------------------------------------------|
| TiO <sub>2</sub> .....               | 91.9                                                           | 93.25                                                          |
| Fe .....                             | 0.16                                                           | 0.16                                                           |
| Cr <sub>2</sub> O <sub>3</sub> ..... | 0.08                                                           | 0.08                                                           |
| V <sub>2</sub> O <sub>5</sub> .....  | 0.10                                                           | 0.11                                                           |
| Loss on Ignition .....               | 4.0                                                            | 3.5                                                            |
| SiO <sub>2</sub> .....               | 2.67                                                           | 0.92                                                           |

The alkaline-leached residue, that had been treated with 25% potassium hydroxide, was calcined at 950° C. for two hours. The product was a synthetic rutile material that contained 96.7% titanium dioxide and about 0.2% iron, as determined by colorimetric analysis.

The process of the present invention, as demonstrated in this example, effected a substantial enrichment of the titanium dioxide content of the solid material, namely, from 70.3% to 96.7%, after calcining. Moreover, the impurities were substantially reduced. In the case of silica in particular, the reduction was from an initial content of about 4.8% down to 0.92%.

#### EXAMPLE 2

Another demonstration of the invention was made, following the same general procedure as was employed in Example 1, but using sodium hydroxide as the alkaline leaching material. The results are summarized below in Table VI:

TABLE VI

| H <sub>2</sub> SO <sub>4</sub> Leach Residue—Fines |                |                               | Alkaline Atmospheric Leach<br>Residue |                |                               |
|----------------------------------------------------|----------------|-------------------------------|---------------------------------------|----------------|-------------------------------|
| TiO <sub>2</sub> ,<br>percent                      | Fe,<br>percent | SiO <sub>2</sub> ,<br>percent | TiO <sub>2</sub> ,<br>percent         | Fe,<br>percent | SiO <sub>2</sub> ,<br>percent |
| 89.0                                               | 0.4            | 4.0                           | 92.8                                  | 0.4            | 0.6                           |

The alkaline-leached residue above was mixed with substantially equal amounts, in admixture, of antimony oxide, Sb<sub>2</sub>O<sub>3</sub>, and zinc oxide ZnO, in total amount of the admixture of about 0.5%, as a modifier, and was then calcined in a rotary drum at temperatures in the range from about 800° C. to about 900° C. The resulting product was suitable for use as pigment material and was characterized by a natural light beige color.

Another portion of material, that had been acid-leached and alkaline-leached as just described, was mixed with sawdust while in the form of a pulp. The mixture was then filtered, with the observation that filtration was substantially facilitated by the presence of the sawdust. The moist material was then pelletized in a rotary drum, and the pellets were then sintered at temperatures up to 1400° C., for two hours. The synthetic rutile produced had a porous, spongy texture, and was eminently suitable for use as a feed material for the chlorination process for the manufacture of titanium dioxide.

#### EXAMPLES 3-8

Further to demonstrate the invention, the process was repeated, substantially in accordance with the procedures described in Example 1, but using as feed materials for the process slag alone, a mixture of slag and ilmenite ore, and ilmenite ore alone. The leached residues were calcined, following generally the procedure outlined in Example 2. In the case of Examples 3, 5, and 7, the alkaline leaching step was omitted, to provide comparative data to permit an evaluation of the effectiveness of alkaline leaching. The results are tabulated below in Table VII:

TABLE VII

| Material<br>Leached                         | H <sub>2</sub> SO <sub>4</sub> Leached Residue |                |                               | NaOH Leached Residue          |                |                               | Synthetic<br>Rutile Product   |                |
|---------------------------------------------|------------------------------------------------|----------------|-------------------------------|-------------------------------|----------------|-------------------------------|-------------------------------|----------------|
|                                             | TiO <sub>2</sub> ,<br>percent                  | Fe,<br>percent | SiO <sub>2</sub> ,<br>percent | TiO <sub>2</sub> ,<br>percent | Fe,<br>percent | SiO <sub>2</sub> ,<br>percent | TiO <sub>2</sub> ,<br>percent | Fe,<br>percent |
| Example 3..... Slag Alone...                | 90.1                                           | 0.3            | 4.0                           |                               | Not Leached    |                               | 94.2                          | 0.3            |
| Example 4..... do .....                     | 89.0                                           | 0.4            | 4.0                           | 92.8                          | 0.4            | 0.6                           | 93.7                          | 0.4            |
| Example 5..... Slag/ore <sup>1</sup> .....  | 88.8                                           | 1.5            | 2.8                           |                               | Not Leached    |                               | 92.6                          | 1.55           |
| Example 6..... do <sup>2</sup> .....        | 88.8                                           | 1.5            | 2.8                           | 91.2                          | 1.6            | 0.9                           | 93.1                          | 1.6            |
| Example 7..... Ore Alone <sup>2</sup> ..... | 85.2                                           | 2.7            | 4.5                           |                               | Not Leached    |                               | 90.1                          | 2.8            |
| Example 8..... do <sup>2</sup> .....        | 85.2                                           | 2.7            | 4.5                           | 88.0                          | 2.7            | 1.5                           | 93.4                          | 3.0            |

<sup>1</sup> The mixture of slag and ore in each case included 70 parts slag to 30 parts of ore, by weight. <sup>2</sup> The acid leaching step was repeated twice, without hydrocyclone separation between the first and second acid leaching steps.

As the data in Table VII demonstrates, the process of the present invention is highly effective in producing a high quality synthetic rutile product that is unusually rich in its content of titanium dioxide, and unusually low in its content of iron and silica.

#### EXAMPLES 9-18

Further to demonstrate the invention, the data from several additional performances of the process, using different alkaline leaching conditions, are summarized below in Table VIII, as follows:

TABLE VIII

| Example No.: | H <sub>2</sub> SO <sub>4</sub> , Pressure Leach |              |                            |             |                            | Alkaline Atmospheric Leach              |                            |             |                            | Synthetic Rutile           |             |
|--------------|-------------------------------------------------|--------------|----------------------------|-------------|----------------------------|-----------------------------------------|----------------------------|-------------|----------------------------|----------------------------|-------------|
|              | Feed                                            |              | Residue—Fines              |             |                            | Kind and percent sol'n                  | Residue                    |             |                            | TiO <sub>2</sub> , percent | Fe, percent |
|              | Slag, percent                                   | Ore, percent | TiO <sub>2</sub> , percent | Fe, percent | SiO <sub>2</sub> , percent |                                         | TiO <sub>2</sub> , percent | Fe, percent | SiO <sub>2</sub> , percent |                            |             |
| 9.....       | 100                                             | -----        | 89.0                       | 0.4         | 3.91                       | 10% KOH.....                            | 91.9                       | 0.4         | 2.6                        | 95.7                       | 0.44        |
| 10.....      | 100                                             | -----        | 89.0                       | 0.4         | 3.91                       | 25% KOH.....                            | 93.3                       | 0.4         | 1.0                        | 98.0                       | 0.45        |
| 11.....      | 100                                             | -----        | 89.0                       | 0.4         | 4.0                        | 10% NaOH.....                           | 92.9                       | 0.4         | 1.5                        | 97.2                       | 0.4         |
| 12.....      | 100                                             | -----        | 90.1                       | 0.3         | 4.0                        | 25% NaOH.....                           | 92.9                       | 0.3         | 0.8                        | 96.7                       | 0.3         |
| 13.....      | 100                                             | -----        | 89.0                       | 0.4         | 4.0                        | 25% NaOH.....                           | 92.8                       | 0.4         | 0.6                        | 98.7                       | 0.4         |
| 14.....      | 70                                              | 30           | 88.8                       | 1.5         | 2.8                        | 10% NaOH.....                           | 91.6                       | 1.6         | 1.0                        | 94.7                       | 1.6         |
| 15.....      | 70                                              | 30           | 88.8                       | 1.5         | 2.8                        | 25% NaOH.....                           | 91.2                       | 1.6         | 0.9                        | 96.1                       | 1.6         |
| 16.....      | 70                                              | 30           | 88.8                       | 1.5         | 2.8                        | 25% Na <sub>2</sub> CO <sub>3</sub> ... | 89.8                       | 1.6         | 2.1                        | 93.4                       | 1.6         |
| 17.....      | 100                                             | -----        | 85.2                       | 2.7         | 4.48                       | Nil.....                                | -----                      | -----       | -----                      | 90.1                       | 3.0         |
| 18.....      | 100                                             | -----        | 85.2                       | 2.7         | 4.48                       | 25% NaOH.....                           | 88.0                       | 2.7         | 1.5                        | 93.4                       | 3.5         |

In the performance of the invention as summarized above in Table VIII, the acid leaching conditions were generally the same as those described previously, with the exception that in Examples 17 and 18, the acid leaching step was repeated twice on the same feed material, in view of the fact that ore was being used.

As the foregoing demonstrations of the invention amply demonstrate, the process of the present invention permits a significant increase in the titanium dioxide content of products, such as synthetic rutiles, that can be produced from ilmenite ores and titanium-bearing slags.

To carry out the acid leaching step, the use of pure acid is not necessary. Sulfuric acid waste acids from several industries, particularly from the manufacture of TiO<sub>2</sub> pigments, can be used advantageously. A typical pigment plant waste acid may have the following analysis, for example:

Table IX.—Pigment plant waste acid analysis

| Item:                                | Content, g.p.l. |
|--------------------------------------|-----------------|
| TiO <sub>2</sub> .....               | 6               |
| Cr <sub>2</sub> O <sub>3</sub> ..... | 0.4             |
| V <sub>2</sub> O <sub>5</sub> .....  | 1.3             |
| Ferrous iron .....                   | 25              |
| Sulfuric acid .....                  | 300             |

From the economic standpoint, the process of the present invention presently has greatest attraction where the feed material is an ilmenite ore. However, for applications where the end product must have low contents of iron, chromium, vanadium, silica, and other gangue materials, technical considerations will require the selection of a slag-ilmenite ore mixture as the raw material for the process. Similarly, leaching with pigment plant waste acid is economically attractive where such acid is available at relatively low cost. Its performance is almost as good as that of fresh acid of equal strength. However, where the end product must meet high specifications, improved end product analyses can be obtained either by increasing the strength of the waste acid, either by evaporation or fortification, or by increasing the severity of the leaching conditions, or by using fresh acid.

In general, time and temperature in leaching have a common effect, such that longer times at lower temperatures are equivalent to shorter times at higher temperatures. This is true of both the acid and alkaline leaching operations.

When a synthetic rutile product is made by mixing the residue from alkaline leaching with a carbonaceous material, and firing at a temperature that may be in the range, for example, from about 1100° C. to about 1300° C., the carbonaceous material is fugitive, and substantially no carbon content appears in the final product. In the case of finely ground coke, oil, starch or the like, the primary purpose served is to assist in pelletizing. Sawdust serves the additional function of facilitating filtration and in evolving gases during sintering that yield an unusually porous product.

An additional advantage of the present process is that the liquors from the acid and alkaline leaching operations can be used, partially to neutralize each other. This facilitates disposal of the liquid effluent from the process.

While the invention has been disclosed herein by reference to the details of preferred embodiments thereof, it is to be understood that such disclosure is intended in an illustrative, rather than a limiting sense, and it is contemplated that various modifications will readily occur to those skilled in the art, within the spirit of the invention and the scope of the appended claims.

I claim:

1. A process for leaching an iron-bearing titaniferous material that comprises:

leaching the material in finely divided form with a dilute sulfuric acid solution, to obtain an iron-bearing solution and a solid residue;

separating the iron-bearing solution and the solid residue, and

leaching the solid residue with a dilute aqueous alkaline solution, to obtain a solid residue that is high in TiO<sub>2</sub> content.

2. A process in accordance with claim 1 wherein the acid leaching step is carried out with a sulfuric acid solution having a concentration in the range from about 10% to about 60%, at a temperature in the range from about 100° C. to about 250° C., and under a pressure up to about 300 p.s.i.

3. A process in accordance with claim 1 wherein the dilute aqueous alkaline solution is a solution containing at least one member selected from the group consisting of an alkali metal hydroxide and an alkali metal carbonate.

4. A process in accordance with claim 3 wherein the alkaline leach is conducted at an elevated temperature up to about 150° C.

5. A process in accordance with claim 1 including the additional step of firing the solid residue from the alkaline leaching step at an elevated temperature in excess of 800° C. to reduce the moisture content of said residue.

6. A process in accordance with claim 1 including the additional step of mixing the solid residue from the alkaline leaching with a carbonaceous material, then sintering the mixture at a temperature of at least about 1000° C. to reduce the moisture content of said residue and to thereby produce a synthetic rutile product in porous form.

7. A process for leaching an iron-bearing titaniferous material that comprises:

leaching the material in a particle size at which at least 85% of the particles are minus 325 mesh, with a dilute sulfuric acid solution to obtain an iron-bearing solution and a solid residue;

separating the residue into a first fraction that is reacted sufficiently with the acid so that the iron content, expressed as metallic iron, has been reduced to a content of about less than 4% and to a second fraction that is not as completely reacted as the first fraction; and

leaching said first fraction with a dilute aqueous alkaline solution, to obtain a solid residue that is high in  $\text{TiO}_2$  content.

8. A process in accordance with claim 7 including the additional step of reprocessing the second fraction of the acid-leached residue through a second, similar acid leaching step, to react it more completely, then reprocessing it through a second, similar alkaline leaching step.

9. A process in accordance with claim 8 including the additional step of firing the solid residue from the acid leaching and alkaline leaching steps to reduce the moisture content of said residue.

10. A process in accordance with claim 8 including the additional step of recovering the residual liquors from the acid leaching and alkaline leaching steps, and mixing them to provide a more nearly neutral liquid effluent from the process.

#### References Cited

##### UNITED STATES PATENTS

|           |         |                       |           |
|-----------|---------|-----------------------|-----------|
| 2,731,327 | 1/1956  | Anderson et al. ....  | 23—202    |
| 2,804,375 | 8/1957  | Kamlet .....          | 23—202    |
| 2,875,107 | 2/1959  | Daiger .....          | 23—202 XR |
| 2,961,298 | 11/1960 | Tikkanen .....        | 23—202    |
| 3,001,854 | 9/1961  | Kenworthy .....       | 23—117    |
| 3,018,170 | 1/1962  | Soloducha .....       | 23—202 XR |
| 3,069,235 | 12/1962 | Schechter et al. .... | 23—202    |
| 2,815,272 | 12/1957 | Armant et al. ....    | 75—1      |
| 2,974,014 | 3/1961  | Hoekje et al. ....    | 75—1 XR   |

EDWARD STERN, *Primary Examiner.*

U.S. Cl. X.R.

23—87, 312; 75—1