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2,953,434

PROCESS FOR SULFATING TITANIFEROUS MATERIAL

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This invention relates to the solubilization of titaniferous materials and particularly to the preparation of soluble titanium sulfates suitable for use in the preparation of titanium dioxide pigments by hydrolysis. Still more particularly this invention relates to the preparation of such solutions from slags obtained by smelting iron from titanium bearing ores.

Methods of extracting the major portion of iron from titanium-iron ores, by high temperature electrothermic reduction and the formation of a titanium containing slag material are well known. For example, such methods are disclosed in U.S. Patent No. 2,476,453 issued to W. M. Pierce et al. The slags, thus obtained, are a source of titaniferous materials which are suitable for the preparation of acidic sulfate solutions and the subsequent recovery of titanium dioxide pigments by hydrolytic precipitation.

A particular advantage of this slag material as a titanium source is that it contains a relatively small amount of iron. On the other hand, a large amount of the titanium (i.e., from 5–25% calculated as TiO_2) is contained in the slag in the trivalent state, and this trivalent titanium reductively decomposes the sulfuric acid used in the solubilizing process (also known as the attack) thus resulting in the evolution of obnoxious fumes and the loss of acid.

It is among the objects of this invention to solubilize with the sulfuric acid, titaniferous materials containing titanium in a reduced valence state without appreciable loss of the acid and the resulting evolution of noxious, volatile decomposition products. It is a further object of this invention to provide a simplified process for controlling the impurity content and the evolution of obnoxious fumes during the solubilization of trivalent titaniferous materials with sulfuric acid.

These and other objects of the invention are accomplished by providing an improved process for sulfating a titaniferous material containing titanium in the trivalent state which comprises reacting the titaniferous material with strong sulfuric acid in the presence of a simple ferric iron compound. The amount of ferric iron compound which is used may be equal to or greater than that which is theoretically required for the ferric compound to oxidize the trivalent titanium of the slag to the tetravalent state. Of course, amounts substantially less than theoretical may be used; in fact, it has been unexpectedly found that amounts down to 2–10% of the theoretical are also effective. At the completion of the reaction a solid mass containing soluble titanium compounds is obtained, and this mass is dissolved in an aqueous solvent. It should be noted that the present invention is concerned with the use of simple ferric iron compounds as distinguished from ferric iron compounds which contain metals other than iron in the combined state. These latter materials of which ilmenite and arizonite

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are examples are not within the scope of this invention. The probable function of the simple ferric iron compounds is that of an oxidizing agent.

In a preferred embodiment, our improved process for sulfating titaniferous slag material containing titanium in the trivalent state comprises reacting the titaniferous material with strong sulfuric acid in the presence of a simple ferric iron compound in an amount ranging from about 2–10% of the theoretical amount required to oxidize the trivalent titanium to the tetravalent state. At the completion of the reaction a solid mass containing soluble trivalent and tetravalent titanium compounds is obtained, and this mass is dissolved in an aqueous solvent. In this aspect of the invention, oxidizing agents such as hydrogen peroxide, sodium nitrate and nitric acid are also effective in the same manner as the ferric iron compounds.

In detail, our invention comprises admixing in a reaction vessel suitable for air agitation a finely ground titaniferous slag material, such as that which results from the electrosmelting of titaniferous ore from the Allard Lake Region of Canada, with at least a third of the strong sulfuric acid required for sulfation. Such slag usually contains from about 60–80% total titanium, calculated as titanium dioxide, and of this about 13–19% is in the reduced valence state. 2–10% of the amount of finely divided pigment grade iron oxide which would theoretically oxidize the trivalent titanium to tetravalent titanium is then added. This ferric iron oxide is readily dispersed in the sulfuric acid mixture and dissolves to form ferric sulfate during the period of the attack while the temperature is rising and the sulfuric acid is strong enough and hot enough to readily oxidize trivalent titanium. The sulfation reaction is initiated by raising the temperature of the acid-slag mixture. This can most conveniently be done by dilution, as described in U.S. Patent No. 1,889,027, or by mixing other combinations of sulfuric acid, such as for example 60° Bé. and oleum. After initiation, the temperature rises slowly in a period of about 45 minutes to a temperature in the range of 190–200° C. due to the sulfation reaction. This temperature rise is accompanied by the production of large volumes of steam given off by the reaction, and at the end of the period the sulfation products are set up as a hard porous mass in the reaction vessel. While some improvement in overall yield is usually obtained by holding the reaction mass at this elevated temperature for several hours, the sulfation is essentially complete at this time. This mass will contain a small amount, about 5–10%, of unreacted slag, but otherwise it will be completely soluble. During the reaction substantially no noxious vaporized products (e.g., H_2S and SO_2) from the decomposition of the sulfuric acid are obtained. The titanium sulfate solution obtained by dissolving the mass in dilute acid (usually of about 5–10% strength) will contain about 5–20 grams per liter of trivalent titanium (expressed as TiO_2). This can be oxidized quickly by the addition of sodium nitrate, or allowed to be oxidized by the air used for agitation of the solution. Usually the trivalent titanium concentration is reduced to about 1–2 grams per liter (expressed as TiO_2) for further processing. During the reaction period, air is passed through the reaction mixture for agitation, but under the strong acid conditions of the attack reaction, the air has no appreciable oxidizing effect upon the trivalent titanium as sulfated, and it is completely ineffective in eliminating the formation of the noxious reduction products of sulfuric acid caused by reduced titanium. The solution obtained above can be clarified and hydrolyzed by known means to produce titanium dioxide pigment.

To a clearer understanding of the invention, the following specific examples are given. These are merely illustrative and are not in limitation thereof.

Example 1

Canadian slag obtained by electrosmelting titaniferous iron ore was analyzed as follows:

	Percent
TiO ₂ -----	¹ 69.6
FeO -----	10.0
CaO -----	1.3
MgO -----	4.9
Al ₂ O ₃ -----	6.6
SiO ₂ -----	6.7

¹ 13.9% in the trivalent state; 55.7% in the tetravalent state.

This slag was reacted with the equivalent of 160 pounds of sulfuric acid of 100% H₂SO₄ per 100 pounds of slag by the following procedure. 15,000 pounds of 60° Bé. H₂SO₄ were placed in a 10,000 gallon reaction vessel with a conical bottom and 30,000 pounds of the above slag in finely ground condition were added. While agitating this mixture with air introduced from the bottom of the vessel, 300 pounds of pigment grade ferric oxide (82.5% Fe₂O₃, 10.2% SiO₂), equivalent to about 7.7% of the total requirement for the oxidation of all the trivalent titanium in the slag were then added to the acid-slag mixture. The sulfation reaction was then initiated by the addition of 20,000 pounds of oleum and within about 45 minutes the temperature of the reaction mixture reached 190° C., and a few minutes later a hard porous mass of sulfated slag was obtained. This mass was held at temperature for three hours and then dissolved by adding dilute sulfuric acid and then water. By air agitating the solution for four hours the trivalent titanium content was reduced to about 2 grams per liter. The solution was then ready for clarification and hydrolysis. Analysis of the air-steam mixture evolved from the reaction indicated that less than about 0.4% of the sulfuric acid had been decomposed to form H₂S, SO₂ and other decomposition products of H₂SO₄.

A similar reaction made without the addition of Fe₂O₃ to the acid-slag mixture resulted in a loss by reduction of sulfuric acid to H₂S, SO₂ and other products of about 8% of the total H₂SO₄ added.

Example 2

Using the same slag and the same amount of sulfuric acid and slag as used in Example 1, 150 pounds of finely ground iron oxide (equivalent to about 3% of the total oxidation requirement of the trivalent titanium of the slag) were added just before the reaction started. The loss of sulfuric acid to reduction decomposition products including H₂S and SO₂ was less than about 1.5% of the total sulfuric acid used. The porous reaction mass, when dissolved in dilute sulfuric acid using air agitation produced a solution containing about 160 grams per liter of titanium (expressed as TiO₂) about 20 grams per liter of which was in the trivalent state.

Methods of sulfation of titanium ores are well known. A convenient method, and one that has been generally utilized in performing of the present invention, is described in U.S. Patent No. 1,889,027. The sulfation reaction for the solubilization of the titanium content of slags may be carried out in the same type of equipment used previously for the sulfation of ilmenite, and for mixtures of slag and ilmenite. The reaction is analogous and only slight adjustments of the strength of acid used need be made. In general, the final acid strength should be within the range of about 85-95% H₂SO₄, usually between 89 and 93%, and it is obvious that one may use 96-100% H₂SO₄, or oleum with water or steam or weaker

acid to obtain optimum acid strength for the slag material being sulfated.

After being sulfated the slag reaction mass is dissolved in dilute sulfuric acid or water, and the solution may be adjusted to any final degree of reduction by further addition of oxidizing agents. This solution after suitable clarification can be hydrolyzed by usual methods. Satisfactory methods have been described in U.S. Patents Nos. 2,511,218 and 2,479,637 and Reissues 18,590, and 18,854.

Many simple ferric iron compounds can be utilized for the elimination of the noxious fumes evolved during sulfation of titaniferous slag containing trivalent titanium. The preferred material for such use is ferric oxide which can be obtained in a finely divided state free from unwanted contaminating impurities. Examples of other satisfactory simple ferric iron compounds include ferric sulfate, ferric sulfate dissolved in dilute sulfuric acid, oxidized copperas or basic ferric sulfate, magnetite, hematite, limonite, and ferric ammonium sulfate.

The present invention offers several distinct advantages. As the examples show, the loss of sulfuric acid is reduced to a minimum thereby eliminating the presence of obnoxious fumes in the air and steam mixture which is evolved from the sulfation reaction. The absence of these fumes in the latter mixture overcomes the necessity for costly processes of scrubbing to prevent air pollution. A further advantage resides in the fact that minor amounts of relatively pure oxidizing agents are used in the process, thus improving the quality of the final pigment product.

We claim:

1. An improved process for sulfating a titaniferous material containing titanium in the trivalent state which comprises reacting said titaniferous material with strong sulfuric acid in the presence of an oxidizing agent selected from the group consisting of ferric iron oxides, ferric iron sulfates, hydrogen peroxide, sodium nitrate, and nitric acid, said oxidizing agent being present in an amount ranging from about 2 to 10% of the theoretical quantity required to oxidize the trivalent titanium to the tetravalent state, obtaining a solid mass containing soluble titanium compounds, and dissolving said mass in an aqueous solvent.

2. An improved process for sulfating a titaniferous material containing titanium in the trivalent state which comprises reacting said titaniferous material with strong sulfuric acid in the presence of a ferric iron oxide in an amount ranging from about 2-10% of the theoretical quantity required to oxidize the trivalent titanium to the tetravalent state, obtaining a solid mass containing soluble titanium compounds and dissolving said mass in an aqueous solvent.

3. The process of claim 2 in which the ferric iron oxide is substantially pure ferric oxide.

4. The process of claim 2 in which the ferric iron oxide is hematite.

5. The process of claim 2 in which the ferric iron oxide is limonite.

6. The process of claim 1 in which the oxidizing agent is ferric sulfate.

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