United States Patent Office 2,794,702 Patented June 4, 1957

2,794,702

PREPARATION OF HYDROLYZABLE TITANIUM SULFATE SOLUTIONS FROM TITANIFEROUS SLAGS

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No Drawing. Application July 6, 1954, Serial No. 441,632

3 Claims. (Cl. 23—117)

This invention relates to the solubilization of titaniferous slags, and particularly to the preparation of soluble titanium salts from the latter while avoiding fume nuisance and other difficulties attending the solubilization and utilization of such slags.

A recent development in the titanium industry stems from the availability of enormous titanium ore deposits of eastern Canada plus the idea of combining the separation of titanium values therefrom with the production of metallic iron. These ores of Canada contain 20–40% of titanium oxide with the remainder largely being iron oxide. The ores are being smelted in an electric furnace in admixture with carbon to produce molten iron and a high titanium slag. The latter contains titanium oxides, analyzing from about 60% to 80% as TiO_2 with the remainder being primarily iron, calcium, magnesium, aluminum and silicon which are largely contributed by the ore and the reducing agent used in the furnacing operation. This slag is reactive to sulfuric acid, and sulfate solutions of titanium can be prepared therefrom by an operation similar to that used in preparing titanium sulfate solutions from ilmenite ores. The slag is ground so that about 90%–95% will pass through a 325 mesh screen, and the reaction with sulfuric acid is carried out by methods already well understood in the titanium pigment industry. The slags contain a minor amount of ferrous oxide and no ferric oxide. In addition the slags contain 10–20% of titanium in a reduced state; consequently, the attack mass gives a product which upon dissolution may contain considerable trivalent titanium. During the sulfation or attack operation the reduced (trivalent) titanium content of the slag acts as a reducing agent on the strong sulfuric acid, and part of the acid is lost in the form of SO_2, H_2S and/or S. As a result there is not only an undesirable loss of sulfuric acid but also a fume nuisance of considerable magnitude. Moreover, the resulting solution, if it contains appreciable reduced titanium, is unsatisfactory for the subsequent hydrolysis since the trivalent titanium content of the liquor must be oxidized to be effectively hydrolyzed. U. S. Patents 2,589,909 and 2,589,910 relate to the oxidation of the reduced titanium of such liquors.

We have now found that the loss of sulfuric acid, the fume nuisance and the subsequent necessity of oxidizing the liquors mentioned last above can be readily avoided in part or entirely by subjecting the slag to an oxidizing roast designed to oxidize most if not all of the trivalent titanium to TiO_2.

Accordingly, it is an object of this invention to subject titanium slag to an oxidizing roast in advance of the sulfating attack thereon.

It is a further object to eliminate in part or entirely the loss of sulfuric acid and the fume nuisance encountered in the sulfation attack on titaniferous slags as a result of the presence of trivalent titanium in said slags.

It is still another object to overcome in part or entirely the disadvantages attending the presence of trivalent titanium in the solutions derived from titaniferous slags by sulfating attacks thereon.

Another object is to render titaniferous slags more amenable to the attack methods and the use of equipment previously employed in connection with ilmenite ores.

These and other objects will be apparent from the following description of the invention.

Our invention broadly comprises the preparation of titanium sulfate solutions suitable for the recovery of pigmentary titanium dioxide therefrom by well known hydrolysis methods, by reacting on roasted titaniferous slag with strong sulfuric acid and thereby producing a solid mass containing soluble titanium sulfate which is subsequently dissolved in an aqueous solvent to obtain the titanium sulfate solution.

As noted above, we have discovered that by subjecting titaniferous slags such as are currently available to the titanium pigment industry to an oxidizing roast, the slag can be beneficiated sufficiently to permit it to be handled in much the same manner as ilmenite ores. The roast can be conducted so as to convert as much of the trivalent titanium as is desired, or all, to quadrivalent titanium, thereby to bring the slag to any desired standard in that respect, and at the same time can convert as much as is desired of the ferrous oxide to ferric oxide without at the same time insolubilizing any appreciable amount of the titanium values, thereby to avoid the disadvantages discussed above. To this end, the slag is preferably ground to the finenesses suitable for attack purposes and then is passed through roasting equipment in such manner as to be exposed to an oxidizing atmosphere while in a heated state. By controlling the temperature of the ground slag and the duration and effectiveness of its exposure to air or other oxidizing gases, the extent of oxidation can be adjusted as desired. Such an oxidizing roast can be carried out in various forms of equipment well known to those skilled in the art, as in a rotary calciner, a Wedge- or Herreshoff-type furnace, a fluidized bed, a stationary- or rabbled-hearth furnace, etc. The use of such conventional equipment permits the roasting to be done economically and with a minimum of contamination with undesired impurities.

The following examples illustrate the principles of our invention. In these examples smelted titaniferous slag derived from the titanium ore deposits of eastern Canada was ball-milled in a dry state to a fineness as follows:

	Percent
+200 mesh	0.10
−200 mesh+400 mesh	5.8
−400 mesh	94.1

The slag analyzed as follows:

Total Fe	8.17
Metallic Fe	0.06
Ti_2O_3	14.1
Total TiO_2	72.0

In Examples I and II, the roasting was conducted in a laboratory furnace in a static bed. In Examples III and IV, the roasting was carried out in a rotary calciner.

EXAMPLE I

Atmosphere of oxygen

The slag was oxidized by passing oxygen over the bed of slag while the temperature of the laboratory furnace

was controlled carefully at 400°, 500° and 600° C. The products were analyzed.

	Percent Total Fe	Percent Met. Fe	Percent Ti_2O_3	Excess oxidation expressed as Fe+++, percent
1 hr. at 400° C	8.1	0	2.20	0.0
1 hr. at 500° C	8.0	0	0.0	3.2
1 hr. at 600° C	7.9	0	0.0	5.3

It is to be noted that the slags in the runs made at temperatures 500° and 600° C. were excessively oxidized, giving rise to the formation of some ferric iron.

EXAMPLE II

Air atmosphere

1 hr. at 400° C.....percent	8.1	0	0.92	0.0
1 hr. at 500° C.....do	7.8	0	0.0	3.7

EXAMPLE III

Oxygen atmosphere

A portion of the same ground slag used in Examples I and II was placed in a rotary calciner and subjected to oxidation by oxygen.

¾ hr. at 400° C.....percent	8.1	0	1.2	0.0
¾ hr. at 500° C.....do	8.0	0	0.0	3.5

EXAMPLE IV

Air atmosphere

A charge similar to that of Example III was treated in a similar manner, but the oxidizing gas was air rather than oxygen.

¾ hr. at 400° C.....percent	8.1	0	2.0	0.0
¾ hr. at 500° C.....do	8.0	0	0.0	3.8

From the foregoing examples it is evident that the roasting treatment whether carried out in oxygen or in air, or in a static bed or a turbulent bed, is selective in that trivalent titanium is oxidized almost exclusively to TiO_2 before ferric oxide begins to form. Hence, by controlling the temperature and duration of the treatment, one can oxidize the trivalent titanium to TiO_2 without forming more than a small amount of ferric oxide, or if desired, one can continue the oxidation beyond that stage and form any desired amount of ferric oxide. While it would usually be undesirable to secure excessive oxidation in the form of ferric oxide, particularly where a plant is operating on the basis of roasting all of its slag, it is nevertheless possible to conduct the plant operations on the basis of roasting only a part of the slag sufficiently to give moderate amounts of ferric oxide and then mixing such roasted slag with appropriate amounts of unroasted slag. The principles on which such a mixture would be utilized are fully explained in the copending application of Allan, Rummery and Appel, Serial No. 367,734, filed July 13, 1953.

The roasted slag can be sulfatized and solubilized by conventional attack methods using strong sulfuric acid. The following example is illustrative.

EXAMPLE V

The oxidized slag was analyzed.

Chemical analysis:

72.0% TiO_2
8.0% Fe (total)
0.0% Ti_2O_3
0.1% Fe_2O_3

Fineness:

+200 mesh=0.1%
−200+325 mesh=13.5%
−325+400 mesh=14.4%
−400 mesh=72.0%

45.5 gallons of 98% sulfuric acid was placed in the attack vessel. With agitation sufficient to prevent lumping, 380 pounds of the above slag was added, and 5.4 gallons of water. Finally, raw, dry steam was introduced and the reaction between the acid and slag proceeded vigorously to a climax, at which point a solid mass of sulfated titanium values resulted which was readily soluble in water and dilute acid.

During this attack there were evolved some sulfuric acid vapors with no more than a trace of SO_2 or H_2S. When a similar attack was made using the unoxidized slag there were evolved considerable amounts of SO_2 and H_2S vapors. In this instance of the oxidized slag the acid loss was 0.15%. The recovery of TiO_2 from the oxidized slag, upon dissolution of the attack mass, was 95.5%.

EXAMPLE VI

An attack was made upon unoxidized slag and used for comparison with Example V.

The raw material employed was TiO_2 slag produced at Sorel, Quebec. In this example, no ilmenite ore or other oxidizing material was added to the slag.

Chemical analysis of slag:

TiO_2 ..... 72.2%.
Fe ..... 8.33% (0.6% metallic iron) (No ferric iron).
SiO_2 ..... 5.99%.
Al_2O_3 ..... 6.30%.
CaO ..... 0.48%.
MgO ..... 3.59%.
Ti_2O_3 ..... Appr. 16% (equivalent to 18% of TiO_2).

Screen analysis:

	Percent
+200	0.02
+325	1.42
+400	9.25
−400	89.31

Attack conditions:

Weight of slag ..... 750 lbs.
Weight of H_2SO_4 (96.5%) ..... 1200 lbs. at 100%.
Conc. of acid used ..... 96.5%.

No scrap iron was added, nor required, for the reduction of the solution.

The 96.5% H_2SO_4 was placed in the empty attack tank and agitated with air. The slag was added gradually, then agitated for 15 minutes longer. Steam was introduced to initiate the attack from a ¾" line at 45 p. s. i. gauge pressure. The temperature rose in 9 minutes from ambient temperature to 178° C., at which time the steam was turned off. The temperature continued to rise gradually to 222° C. and then receded to 210° C. after a total elapsed time of 30 minutes from the first introduction of the steam. There was a 2.52% acid loss in the attack giving rise to obnoxious fumes, or an acid weight loss of about 4 pounds per 100 pounds of slag.

The attack-mass was aged 2 hours, then dissolved by gradually adding cold water.

96% of the TiO_2 in the slag was sulfated and dissolved.

EXAMPLE VII

In this example no titanium slag was used. Quilon ilmenite was attacked under conditions similar to those of the preceding examples.

Quilon ilmenite analysis:

TiO_2 ..... 57.2%.
Total Fe ..... 25.4%.
Fineness ..... 97.4% −200 mesh.

Attack conditions:

Weight of ore	1000 lbs.
Weight of H_2SO_4 at 100%	1675 lbs. (118 gals. at 93.3%).
Conc. of acid	93.3%.
100% acid/ore ratio	1.675.

The ground Quilon ilmenite was added to the acid gradually with air agitation over a period of 10 minutes, and agitation was continued 10 minutes longer.

The reaction was initiated by the introduction of raw steam from a 50 p. s. i. line through a ¾" valve wide open. The initial acid-ore temperature was 20° C. After 19 minutes of steam the temperature was 162° C. The steam was turned off and the batch solidified immediately. The maximum temperature was 203° C. After 2 hours aging, the mass was at 165° C. and was soft and porous. Eighty-three pounds of scrap iron was added to reduce the ferric iron. The acid loss was 0.15% or about .25 pound per 100 pounds ore.

The recovery of TiO_2 in solution form was 93.6%.

The sulfation of the roasted slag can be carried out in the same type of equipment heretofore used in the sulfation of ilmenite. The reaction is analogous and only slight adjustments need be made in the strength of acid used. In general, the acid should be within the range of about 85–95% H_2SO_4, usually between 89% and 93%, and it is obvious that one can use mixtures of 96–100% H_2SO_4 and/or oleum with water, steam and/or weaker acid to obtain the acid strength which one finds best for the particular slag which he is treating.

It will be understood that the low total-iron content of slags is desirable since it results in titanium sulfate solutions of low iron content. Solutions having an iron content of 18–35 grams of iron per 100 grams of TiO_2, upon being hydrolyzed conventionally, provide hydrolysates which yield high-grade TiO_2 pigments upon calcination at temperatures ranging from, say, 900–1050° C. Such solutions are readily prepared, as already noted, by dissolving the sulfatized slag or attack mass in water or other suitable aqueous media such as

dilute acid or other forms of liquors obtained in other stages of the TiO_2-producing system. Obviously, the trivalent titanium content of the solutions can be suitably adjusted, if desired, immediately prior to hydrolysis and in the same manner as is well known in present-day titanium pigment producing operations utilizing ilmenite.

Having now described our invention, what we claim is:

1. In a process for preparing a hydrolyzable titanium sulfate solution from smelted titaniferous slag containing titanium in a lower state of oxidation than corresponds to TiO_2 and containing iron in a lower state of oxidation than corresponds to ferric oxide, wherein the slag in a finely-divided condition is reacted with concentrated sulfuric acid until a solid reaction mixture has been formed having substantially all of the reactive titanium of this slag in the form of soluble titanium sulfate, and wherein said solid reaction product is treated with aqueous solvent to extract said soluble titanium sulfate, the improvement which consists of initially roasting said slag in a finely-divided state under oxidizing conditions at temperatures between about 400° C. and 600° C. until at least a major part of the lower state titanium has been oxidized to TiO_2.

2. The improvement as claimed in claim 1 wherein the roasting of said slag is continued until all of said lower state titanium has been oxidized to TiO_2 and a small part of the iron content has been oxidized to ferric oxide.

3. The improvement as claimed in claim 2 wherein the roasting of said slag is carried out at temperatures between about 400° and 500° C. in air for about one hour.

References Cited in the file of this patent

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2,589,909	Weikel	Mar. 18, 1952

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