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BENEFICIATING TITANIFEROUS ORES

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This invention relates to methods of beneficiating titaniferous ores by treating such ores with sulfuric acid. Its object includes means for obtaining improved yields of the recoverable titanium values contained in such ores.

Processes for the manufacture of titanium compounds, particularly titanium dioxide pigments, in commercial use at the present time, depend almost exclusively upon the beneficiating or reducing of ilmenite with sulfuric acid. Ilmenite is a mineral composed principally of titanium dioxide and ferrous oxide in the proportion of ferrous titanate, $FeTiO_3$, together with minor amounts of other metallic or metallic oxide impurities. Whether or not the titanium dioxide and ferrous oxide are actually combined as ferrous titanate or merely intimately associated physically, as in solid solution, has not been established. This mineral, as such, is found in many widely-scattered parts of the world, for instance, in Norway, India, and the United States. It is also found in physical association with other minerals, such as apatite, a calcium phosphate ore. Processes have been developed for separating the ilmenite from its association with these other minerals. Regardless of its source, i. e., whether it was obtained as native ilmenite or by separation from associated contaminating minerals, and because it yields to attack by concentrated sulfuric acid, as distinguished from most other forms of titaniferous ores, such as rutile, sphene, etc., ilmenite constitutes the raw material for the present-day processes for manufacturing titanium compounds.

In beneficiating ilmenite with sulfuric acid, the ore is first ground to a fine particle size, usually about 200 mesh. This finely-ground ilmenite is then mixed with concentrated sulfuric acid, usually over 90 percent strength, and the resulting mixture is then heated either by the application of external heat or by injecting live steam into the mass. When the temperature of the mass is raised sufficiently, a reaction between the ilmenite and sulfuric acid sets in which, because of its exothermic character, requires no further added heat. It has been observed that the yields of recoverable titanium values obtainable from ilmenite secured from different sources by treating such ores with sulfuric acid varies considerably. Having addressed ourselves to this problem, we have developed means of increasing the yield values obtainable from ilmenite, regardless of its source, which means constitute the basis for our invention.

We have found that the yield of recoverable titanium values obtained from ground ilmenite when beneficiating this ore with sulfuric acid may vary to a certain degree directly to the extent that the particles of the ground ore are wet by the sulfuric acid. In general, when nearly all the particles are wet by the acid, the yields are high; when only a portion of the particles is wet, the yields are correspondingly lower. This is so because the particles which are not wet by the sulfuric acid cling together and form agglomerates whose outside surface is the only portion attacked by the sulfuric acid.

Our present invention comprises heating a mixture of ground titaniferous ore, concentrated sulfuric acid, and a phosphate compound in suitable proportions which, we believe will enable the sulfuric acid to wet and adhere to each individual particle of the ground ore. Such a wetting agent functions, in our opinion, to reduce the surface tension at the liquid-solid interphase between the individual particles of ore and the sulfuric acid.

Phosphate compounds functioning as wetting agents are preferred for the practice of our invention. Thus, when the P_2O_5-content of a mixture of ground titaniferous ore and sulfuric acid is maintained between about 0.1 percent and about 2.0 percent, preferably between about 0.5 percent and about 1.0 percent during the heat-treatment, which causes the reaction between the ore and acid to take place, improved yields of the titanium values are obtained. For example, phosphoric acid may conveniently be added to the ore-sulfuric acid mixture in amounts sufficient to give the desired content of P_2O_5. Although phosphoric acid, because of its availability is preferred, it will be understood that any phosphate material, such as a phosphate-bearing ore, e. g. apatite, or a phosphate compound, e. g. trisodium phosphate, Na_3PO_4, which by reacting with the sulfuric acid of the reaction mixture yields phosphoric acid, may be employed in the practice of our invention. By the expression "phosphate compounds", as used in the claims attached hereto, we mean to designate those substances, such as phosphate minerals and phosphate compounds, which by interaction with sulfuric acid yield phosphoric acid. The phosphoric acid is added in any convenient manner, either to the ground ilmenite or concentrated sulfuric acid, or to the mixture of the two; or the three are mixed together simultaneously. The phosphoric acid is employed preferably as concentrated acid because, as will be understood, the concentration of the sulfuric acid will be reduced by the water

added with the phosphoric acid. The relative proportions of ore and concentrated sulfuric acid need not be varied in any way from the common practice when practicing our invention, but the sulfuric acid may be employed in amounts sufficient to form normal salts with all base-forming elements present in the ore or, if desired, in amounts less than, or in excess of this chemically equivalent quantity. It is, however, economical to use as little sulfuric acid as possible and to obtain a more or less solid reaction cake. The heat-treatment is then carried out in any suitable manner, for example, according to the method set forth in U. S. Patent No. 1,889,027 of November 29, 1932, to W. F. Washburn. After the reaction is completed, the reaction mass is taken up in water in the usual way, and the resulting solution subjected to the usual treatments, such as clarification, etc., in order to obtain finally a sulfuric acid solution of the titanium originally present in the ore.

The improved results of our invention are readily perceived by examination of the following tabulated data:

Table A.—Wetting of ilmenite ore

[The extent that a ground titaniferous ore is wet by sulfuric acid may be evaluated by determining the degree of settling of ore particles suspended in sulfuric acid. The data were obtained by thoroughly and uniformly mixing ilmenite (ground about 200 mesh) with 90 percent sulfuric acid and measuring the amount settled out of suspension after various time intervals.]

Test No.	1	2	3	4	5
Percent P_2O_5 added (based on weight of ore)	None	.10	.20	.40	.80
Percent settled after—					
½ hour	8.4	6.4	4.0	3.2	2.0
1 hour	16.0	12.8	11.2	8.0	5.2
1½ hours	19.2	15.2	14.4	11.6	7.6
2 hours	19.6	16.8	15.6	13.6	9.2
2½ hours	20.4	17.6	16.8	14.8	10.8
3 hours	21.2	18.4	18.0	16.4	12.4

These figures indicate a progressive decrease in the rate of settling, and thereby an increase in the extent the ore is wet by sulfuric acid as the P_2O_5-content is increased.

Table B.—Comparative yields—varying P_2O_5-contents

[When the five reaction mixtures—Tests Nos. 1-5, Table A, were heated in the above-described manner, and the reaction products analyzed for titanium dioxide recovery, the following figures were obtained:]

Test No.	Percent P_2O_5 added to reaction mixture (based on ore content)	Percent of TiO_2-content of ore recovered
1	None	77.39
2	.10	88.53
3	.20	86.80
4	.40	92.35
5	.80	86.40

The highest yields were obtained in this series of tests when adding but 0.40 percent P_2O_5, but the results are based on pilot plant tests and it is known that commercial operations always give higher yields than pilot plant tests.

Table C.—Use of apatite (phosphate mineral)

[Ground ilmenite was mixed with sulfuric acid and varying amounts of pulverized apatite mineral, containing 6.20 percent P_2O_5, were added. After heating the mixture to cause a reaction to take place between the ore and the sulfuric acid, analysis of the reaction products gave the following results:]

Test No.	1	2	3	4	5
Percent P_2O_5 added as apatite (based on weight of ore)	None	.13	.20	.393	.82
Yield—percent TiO_2 recovered	76.17	78.45	80.46	84.4	80.65

It will be understood that in determining the amount of phosphate to be added to the ore it may be desirable to determine first whether the titaniferous ore itself contains P_2O_6, and if so, to take this into account.

The reaction masses obtained from the practice of our invention are especially useful in the preparation of titanium dioxide pigments, titanium salts, and the like.

This description of our invention has been given for clearness of understanding and no undue limitations should be deduced therefrom, but the appended claims should be construed as broadly as possible in view of the prior art.

We claim:

1. Method of beneficiating titaniferous ores, which comprises mixing together ground titaniferous ore, concentrated sulfuric acid and a phosphate compound, the latter in such amounts that the resulting mixture will have a P_2O_5 content, based on the weight of ore in the mixture of between about 0.1 per cent and about 2.0 per cent and heating the said mixture to cause a reaction to take place between the ore and the sulfuric acid.

2. Method of beneficiating titaniferous ores, which comprises mixing together ground titaniferous ore, concentrated sulfuric acid and phosphoric acid, the latter in such amounts that the resulting mixture will have a P_2O_5 content, based on the weight of ore in the mixture of between about 0.1 per cent and about 2.0 per cent and heating the said mixture to cause a reaction to take place between the ore and the sulfuric acid.

3. Method of beneficiating titaniferous ores, which comprises mixing together ground titaniferous ore, concentrated sulfuric acid and ground apatite mineral, the latter in such amounts that the resulting mixture will have a P_2O_5 content, based on the weight of ore in the mixture of between about 0.1 per cent and about 2.0 per cent and heating the said mixture to cause a reaction to take place between the ore and the sulfuric acid.

4. In a method of beneficiating a titaniferous ore which includes a heat-treatment of a mixture of ground titaniferous ore and concentrated sulfuric acid, the step which consists in adding to a mixture of ground titaniferous ore and concentrated sulfuric acid an amount of a phosphate compound such that the mixture will have a P_2O_5 content, based on the weight of ore in the said mixture, of between about 0.1 per cent and about 2.0 per cent.

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