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PROCESSING OF TITANIUM ORES

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1

This invention relates to an improvement in the processing of titanium ores and more particularly to the comminution of ilmenite to promote its reactivity with acids in the extraction of titanium values therefrom.

In the production of titanium oxide pigments from titanium ores such as ilmenite, the ore is converted to soluble titanium and iron salts by acid attack, followed by extraction of such salts with the aid of water or dilute acid solutions. Titanium ores most generally used in such pigment manufacture comprise beach sand Indian ilmenite, analyzing around 60% TiO_2 and 25% of iron. As is known, this ilmenite sand may be reacted with sulfuric acid to form iron and titanium sulfates, either before or after grinding of the ore to a fine condition. The unground ore is less easily attacked by the acid and accordingly excess quantities of acid must be used to obtain satisfactory acid conversion. The acid is the more expensive reagent and any excess H_2SO_4 cannot be separated from the soluble salts, while any excess of ilmenite can be readily removed due to its solid character. Hence, the industry has endeavored to obtain high conversion of acid even though a sacrifice in conversion of ilmenite has resulted. This is justified by both economical and chemical considerations. The acid content of the resulting solutions may be increased when the solutions are found deficient, but it is impractical to remove any excess of acid. The industry takes advantage of this by normally carrying out the sulfating operation in the presence of a slight excess of ilmenite in order that the acidity of the sulfate mixed will be slightly lower than is desirable in the solution which is later to be prepared for hydrolysis. The extent of the excess of ilmenite has been found to depend largely on the fineness of the ore.

The sulfate reaction is most easily carried out when the ilmenite is in finely-ground condition and suspension difficulties are not encountered during the course of the reaction. Finely-divided ilmenite is readily suspended in sulfuric acid and only a minimum of agitation is required to maintain a uniform suspension up to and during the course of the reaction to form the soluble iron and titanium sulfates. This decrease of agitation requirements has reduced plant installation costs for the acid attack and the saving effected has justified the installation of grinding equipment for the ore. The increased conversion of the ilmenite also has been a strong contributing factor in restoring to ilmenite grinding.

The effect of ore fineness on conversion of its

2

titanium content to soluble titanium sulfate is well known. Thus, whereas only about ⅔ of Indian ilmenite becomes solubilized when treated in the unground state with sulfuric acid, about 95% is solubilized when the ore has been previously ground to a fineness in excess of 90% through 325 mesh screen. Further increases in the conversion result upon decrease in the 325 mesh screen residue. An increase amounting to about 2% is obtained when the fineness has been increased from 91 to 97% through a 325 mesh screen.

When ground ilmenite is sulfated, it is usually ground in the dry condition and with the aid of air-separating equipment. The reduction mill may comprise a tube mill, ring-roll mill, or a ball mill type. These mills are ordinarily swept with air to draw off the fines while the coarse material remains to be retreated and further comminuted in the mill. The associated air separation is not satisfactorily efficient because the ground product flocculates. Addition of ordinary air-dispersing agent use has not been resorted to because of the danger of subsequent solution or final product contamination. Good dispersion of the ground product in air is essential to highest efficiency and the recovered product must be easily dispersed in sulfuric acid, without any impairment of its reactivity or contamination of the solution resulting from the sulfation. In other words, the grinding efficiency has been somewhat low and undesirably impaired by reason of the flocculation of the finely-ground material which occurs during air separation. This has caused a heavy load upon the mill by virtue of poor separation of the fines.

It is among the objects of this invention to overcome the above and other disadvantages which characterize prior titaniferous ore grinding operations, and to provide a novel method for attaining such objects. A salient object is to overcome the flocculation of ilmenite during its particle size reduction and to increase the efficiency of ilmenite dry grinding and air separation operations. Further objects are to decrease costs, especially power consumption in the preparation of a finely-ground ilmenite of a given fineness specification; to increase the capacity of a given plant by increasing the efficiency of grinding and separation equipment employed therein through the addition of a dispersing agent which will have no bad or undesired effect upon the subsequent processing operations, nor contaminate the solutions or final TiO_2 pigment resulting therefrom. Other objects and advantages will be evident from the ensuing description of the invention.

The above and other objects are attainable in this invention which broadly comprises effecting the particle size reduction and subsequent separation of the ground particles of a titaniferous ore in the presence of a small amount of naphthenic acid.

In a more specific and preferred embodiment, the invention comprises adding to beach sand Indian ilmenite from about .02% to .2%, on the ore basis, of naphthenic acid during the introduction of the ilmenite into a dry grinding mill equipped with an air separator together with means for recirculating the coarser ore fractions, and effecting the subsequent ore reduction and air separation of the ground particles in the presence of the naphthenic acid so added.

In practically adapting the invention, the basic ore, Indian ilmenite, in the form of small pebbles or a sand consisting of particles in excess of about 40 mesh is fed to a conical ball mill equipped with an air classifier system, e. g., is air swept to remove finely-ground material and this air-borne dust is removed to a separator system of the usual type where the fines are collected as by use of a cyclone, the coarse materials being returned to the mill for further grinding. In order to improve and promote the grinding or classification, or both, a small amount of naphthenic acid, say, about .05 to .15%, is added to the ore as it is fed to the mill. By reason of such treatment, the production rate becomes increased without any sacrifice in fineness, and, if desired, the fineness can be increased without any sacrifice in the production rate.

Naphthenic acid use in this system has been found to be unique in its behavior since it fulfills the requirements of an air dispersing agent and yet is not injurious to and does not impair the preparation of hydrolyzable titanium sulfate solutions nor affect the final TiO_2 product from the finely-ground ore containing the reagent. As already mentioned, the treated ore must readily disperse in air and also in sulfuric acid. Other reagents such as those of the oleic acid type when used in the system, though useful in promoting grinding efficiency, provide a treated ore which cannot be readily wetted with the sulfuric acid and hence an undesired impairment of conversion results. This decreased conversion nullifies the effect of the increased fineness and accordingly the objects of this invention are not realized when such other agents are used as dispersing or grinding aids.

The term "naphthenic acid," as used herein, refers to cycloparaffinic carboxylic acids as found particularly in various petroleum oils. They may be extracted from these oils or distillates thereof by processes well known in the art, such as by treatment of the oils or their distillates with aqueous sodium hydroxide solutions in which the acids dissolve yielding sodium salts. The lyes from this treatment are acidified, thereby yielding considerable amounts of free cycloparaffinic carboxylic acids. It is understood, however, that this method of recovery of the naphthenic acid material is not essential to the present process and is given only as a method for its recovery and to identify the material.

To a clearer understanding of the invention, the following specific examples are given, none of which is to be considered as limiting the invention:

Example I

Indian beach sand ilmenite was ground in a conical ball mill containing steel balls and equipped with a superfine air classifier at a rate of 5.5 tons per hour and with classifier and fine damper sets adjusted to give a top product size of 93% through 325 mesh. Experience had shown that such conditions gave the optimum mill load, which in this case was 250–260 kilowatts on the motor.

Naphthenc acid, to the extent of 2 pounds per ton of ore going to the mill, was added to the mill feed with no other change being made in the system. The throughput of the mill was then found to be 8.2 tons per hour or an increase in mill capacity of about 50%. The resulting naphthenic acid-treated ilmenite was then tested for attackability with sulfuric acid. It was found to be readily wetted by the acid and that the titanium content of the ore converted readily to soluble titanium sulfate when treated in the usual manner of attack.

Example II

Indian beach sand ilmenite was ground in a conical ball mill containing steel balls and equipped with a superfine air classifier at a rate of 8.0 tons/hour and with a classifier and fine damper sets adjusted to give a top product size of 87% through 325 mesh.

Naphthenic acid, to the extent of $\frac{1}{10}$% of the ore, was added to the mill feed. In addition the mill was adjusted to give increased fineness by means of a change in the air damper setting to give a fineness of 93% through a 325 mesh screen while maintaining the optimum mill load. The grinding rate under these conditions was found to be 8.2 tons an hour which is slightly better than that found using no naphthenic acid. This production gave increased conversion of the ilmenite upon treatment with sulphuric acid as compared with the untreated production. This increased conversion to the soluble condition amounts to about 2%.

Example III

To the mill of Example I was fed the same ilmenite, together with 1# naphthenic acid/ton of ore. In addition the mill was adjusted to give increased fineness by means of a change in the air damper setting to give a fineness of 97.2% through a 325 mesh screen while maintaining the optimum mill load. The grinding rate under these conditions was found to be 6 tons/hour which is approximately a 10% increase in capacity over that found when using no naphthenic acid. This increase in fineness along with a considerable increase in capacity shows the effectiveness of naphthenic acid even in amounts as low as 1#/ton of ore.

While the invention has been described as applied to certain specific embodiments thereof, obviously it is not limited thereto. For example, while particularly adaptable to Indian ilmenite treatment, it is also applicable to the treatment of all types of titaniferous ores, including the various ilmenite, rutile and brookite forms.

Similarly, though especially useful in the treatment of titaniferous ores preparatory to their sulfuric acid attack and sulfation, the contemplated naphthenic acid treatment is also effective and beneficial prior to the attacking or digesting of the ore with other mineral acids (hydrochloric, nitric) to obtain titanium chloride or nitrate solutions, etc.

I claim as my invention:

1. A process for converting a titaniferous ore to water-soluble state, comprising subjecting said ore to comminution, air classification, and reaction with a mineral acid, in the presence of a small amount of a naphthenic acid dispersing agent consisting of naphthenic acids derived from petroleum oils, said agent being adapted to disperse said ore in air and said mineral acid.

2. A process for converting a titaniferous ore to water-soluble state, comprising subjecting said ore to comminution, air classification, and reaction with a mineral acid, in the presence of from .02% to .2%, on the ore basis, of a naphthenic acid dispersing agent consisting of naphthenic acids derived from petroleum oils, said agent being adapted to disperse said ore in air and said mineral acid.

3. A process for converting beach sand Indian ilmenite to water-soluble state which comprises subjecting said ilmenite to comminution, air classification, and reaction with a mineral acid, in the presence of from .02% to .2%, on the ilmenite basis, of a naphthenic acid dispersing agent consisting of naphthenic acids derived from petroleum oils, said agent being adapted to disperse said ilmenite in air and said mineral acid.

4. A process for improving the grinding and air classification of beach sand Indian ilmenite preparatory to its acid attack to form soluble titanium compounds therefrom, which comprises mixing on the ilmenite basis about .02% to .2% of naphthenic acid with said ilmenite while the latter is being fed to a dry grinding mill equipped with an air separator, effecting the comminution and air separation of said ilmenite in the presence of said naphthenic acid consisting of naphthenic acids derived from petroleum oils, and thereafter reacting the comminuted naphthenic acid-containing ilmenite with sulfuric acid to convert said ilmenite to water-soluble titanium and iron sulfates.

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