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DISSOLUTION OF TITANIFEROUS ORE CONCENTRATES WITH AMINE ADDITION

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9 Claims. (Cl. 23—117)

This invention relates to the attack of ores. More specifically, it relates to the attack of titaniferous ores such as ilmenite with concentrated sulfuric acid. This invention also relates to the dissolution in strong sulfuric acid of ore concentrates containing small amounts of flotation agents.

In the preparation of ores and minerals for metallurgical treatment it is common practice to remove gangue and foreign material, and concentrate the desired fraction of the ore by any of numerous known procedures. Among the procedures that have been used may be mentioned magnetic separation, wet and dry classification, and flotation concentration. It is with ores that have been concentrated by flotation methods that the present invention is particularly concerned.

The flotation agents used in the flotation concentration of ores and minerals are generally surface active organic compounds capable of preferentially wetting a desired fraction of the ore which may be, for example, fatty acids such as stearic or oleic acid, soaps and similar types of compounds, usually in conjunction with petroleum agents, such as fuel oil and the like. These compounds when used in the flotation process are strongly adsorbed on or absorbed by the ore or possibly react with it to some extent so that it is exceedingly difficult or impossible to remove the last traces of organic flotation agents from the "float" fraction of the ore by normal washing methods and the like.

When ore concentrates containing residual amounts of such flotation agents are further treated by attacking them with strong sulfuric acid, difficulties in operation are frequently encountered by reason of changes in the character of the reaction resulting from the presence of these flotation agents. Such ores foam violently and sometimes uncontrollably, and the difficulties which arise from the excessive foaming and frothing are caused by the flotation agents. In the dissolution of titaniferous ores, such as ilmenite, to produce titanium solutions useful in the preparation of titanium pigment, for example the "digestion" or attack of the ilmenite with concentrated sulfuric acid, is ordinarily a vigorous, rapid reaction which may, however, be controlled by using suitable digestion equipment and appropriate techniques, both of which are well known to the art. When the ilmenite contains flotation agents, the vigorous and copious foaming of the reaction frequently renders it uncontrollable and dangerous.

When excessive foaming takes place during the digestion reaction, an appreciable economic loss is sustained because the foaming carries part of the reaction mixture out of the tank altogether, while an additional portion is removed from the heat of the reaction zone and does not react properly, much of the ore remaining entrapped in the foam and unattacked by the acid.

A severely foaming ore, moreover, will actually be extruded from the tank, and the large quantities of steam and gas evolved during the reaction carry entrained ore, acid and reaction products out through the tank stack. The hot, strongly corrosive froth endangers personnel

and may cause extensive damage to equipment and structural work in the area. Moreover, the violence of the foaming is unpredictable since the precise quantity of residual flotation agent present, and the consequent effects thereof, will vary from batch to batch.

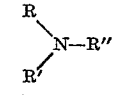
This element of unpredictability renders it difficult or impossible to so vary the digestion conditions as to offset the effect of the flotation agent present. The digestion reaction must be sufficiently strong and vigorous to supply its own heat requirements and, therefore, the reaction conditions cannot be excessively mild; on the other hand, reaction conditions (acid concentration, acid/ore ratio, initial temperature of reactants etc.) if so adjusted as to promote a normal vigorous reaction, may easily render the reaction altogether uncontrollable when flotation agents are present.

While this invention is here described with particular reference to the dissolution of ilmenite ore in concentrated sulfuric acid, it will be obvious that the invention is equally applicable to other reactive titaniferous ores as well as to any other flotation concentrated ore which reacts exothermically with sulfuric acid.

Although foam-producing agents are most commonly introduced during the ore-dressing operations, by flotation processes, they may also occur in the ore for other reasons. For example, it has been suggested to spray ore piles with fuel oil or asphalt in order to cut down wind losses. These agents, which are similar or identical to the fuel oils used as oily collectors in flotation processes, produce the same troublesome foaming at reaction as do the flotation agents used as such, and the process of the present invention is equally applicable to the prevention of foaming from this cause. Moreover, other but less common sources of contamination by these oily materials, including accidental contamination from fuel supplies or the like will produce the same troublesome foaming and may be effectively treated in the same way. The term "flotation agents" as used herein should, therefore, be construed to include materials such as asphalt and fuel oil even when not actually used for flotation purposes.

An object of this invention, therefore, is to provide a method for rendering amenable to digestion in concentrated sulfuric acid an ore concentrate containing organic flotation agents. Another object is to provide a method for treating an ore concentrate which will overcome the tendency of residual flotation agents to render foaming at the digestion reaction violent and uncontrollable. A still further object is to provide an economical method for treatment of an ore concentrate containing an organic flotation agent which will make possible a normal digestion procedure with good digestion efficiencies. An additional object is to provide such a method which produces from a titaniferous ore a reaction product suitable for the manufacture of high-grade titanium pigments and the like. These and other objects will become apparent from the following more complete description of the present invention.

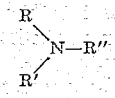
In its broadest aspects, this invention contemplates a method for treating an ore containing organic flotation agents which comprises adding to said ore a small amount of a secondary amine, said amine having the formula:



wherein R and R′ represent saturated alkyl radicals containing from about 12 to about 20 carbon atoms and R″ is selected from the group consisting of hydrogen and saturated alkanoic acyl radicals containing up to about 20 carbon atoms. It has been found that when such a compound is added to the ore in appropriate amount,

which is generally between 0.01% and 0.5%, preferably between 0.05% and 0.2% on an ore weight basis, the flotation agents present are apparently rendered ineffective or their effect is offset, so that the reaction proceeds in a normal, vigorous but controllable manner entirely similar to the type of reaction to be expected from a similar ore not containing residual flotation agents.

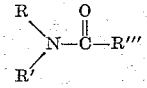
Primary amines of the type H_2NR and tertiary amines of the type NR_3, while in some cases exhibiting a degree of controlling action upon the digestion reaction, are in general not effective, especially when added in economically feasible amounts. Secondary amines (HNR_2) are effective whether added as such or neutralized with mineral or saturated organic acids. If the acid is organic, it should preferably be a saturated fatty acid containing from 12 to 20 carbon atoms. The formula



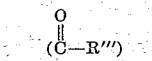
with R, R′ and R″ defined as above, is to be interpreted as including such neutralized secondary amines, whether reacted to form N-alkyl substituted fatty amides or simply associated with the neutralizing acid to form saltlike addition compounds, or both. The formula as given is thus intended here and throughout the specification and claims to include simple secondary amines of the type



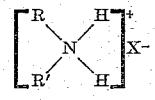
and also dialkylamides of fatty acids, which may be represented by the formula



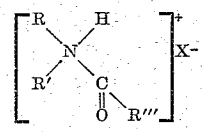
where R and R′ are defined as above and



is the acyl group of a saturated organic acid containing up to 20 carbon atoms, secondary ammonium salts of the type



where X is the anion of a mineral or saturated organic acid, and acyldialkylammonium salts of the type



where X is the anion of a mineral or saturated organic acid.

It is essential that the treating agents of this invention contain substantially only saturated alkyl groups since unsaturated groups, when present in substantial amounts, greatly diminish or destroy entirely the ability of the treating agents to modify and control the course of the reaction, and moreover, actually aggravate the troublesome frothing and foaming encountered in ores which contain flotation agents.

The manner of addition of the agent to the ore appears to be unimportant providing it is distributed in the reaction mixture prior to the actual reaction. The degree of distribution also is not critical and the ordinary mixing employed during such digestion reactions appears to be sufficient adequately to distribute the agent through the reaction mass. The treating agent may, for example, be added to the ore at any convenient stage prior to its introduction into the digestion vessel, or may be added

in solid form to the ore in the digestion vessel itself, or may be added to or dissolved in the sulfuric acid used for the attack of the ore.

The use of larger amounts of treating agent than those above specified is contemplated, but is ordinarily not economically justified. Smaller amounts than those given above are also effective in some cases in controlling the foaming at reaction, depending upon the amount of residual flotation agent present. The amounts of flotation agents present in the ore concentrate are generally extremely small. Normally, from one to five pounds of the flotation agents are employed per ton of ore in flotation methods. The amount present in the ore concentrate is ordinarily somewhat lower than the amount initially employed owing to partial elimination of the flotation agents during subsequent washing, drying, etc., but the major portion of the organic agent usually remains associated with the ore concentrate. Owing to the difficulty of analyzing the ore concentrate for minute amounts of residual flotation agent and the utter impracticality of evaluating the reaction in commercial-scale equipment, which customarily involves reaction of from 10 to 20 tons of ore with from 15 to 30 tons of concentrated sulfuric acid for each batch, it has been found more practical and desirable to evaluate the reactive characteristics of the ore and the quantity of amine treatment agent required by means of an empirical test which is carried out as follows:

A 6″ i. d. cylindrical tank 14″ high and having ¼″ steel walls and a 5/16″ steel plate bottom is provided with an iron sweep agitator having five sweeps, each 5½″ x 9/16″, and adjusted to operate at 200 R. P. M. 1500 grams of the ore to be tested are digested in this tank using the same relative concentration of acid, the same relative acid to ore ratio (based on 100% H_2SO_4) and the same relative quantity of set-off water as are to be employed in the full scale operation. This size charge, in the vessel just described, represents a straight scale model of a typical commercial reaction, having approximately the same shape tank as a typical full-scale installation, and providing the same height freeboard, in proportion to the charge employed. Approximately half of the acid is first introduced into the tank after which the ore is added and washed down with the remainder of the acid to be used. The amine treating agent is then added and finally the set-off water, which has the dual function of diluting the acid to proper strength for reaction and heating up the reaction mixture. The strongly exothermic reaction is initiated and maintained by allowing a Meker burner to play directly on the bottom of the tank throughout the reaction cycle. The course of the reaction is followed by visual observation and may be recognized as complete when copious evolution of steam has taken place and subsided, followed by the setting-up of the reaction mixture to a rigid, porous cake, ordinarily from 15 to 20 minutes after the start of heating. When subjected to this test an ore which does not contain flotation agents will undergo a vigorous but controlled reaction, and the reaction mass will ordinarily stay at least four inches below the top of the tank. An ore which contains flotation agents but is treated with the amine treating agents of this invention will behave in a substantially identical manner. An ore which contains flotation agents and is not so treated will be seen to foam violently and in many cases will overflow and project itself out of the reaction tank. The effectiveness of the quantity of amine treating agent used is gauged by the height to which the reaction mass rises in the tank, and the treatment is considered completely effective if the highest point reached by the reaction mass is four or more inches below the top of the tank. When such is the case, the quantity of treating agent employed is sufficient for the purpose and the same relative amount of treating agents calculated on an ore weight basis may be employed safely in large scale operations.

The employment of the secondary amine treating agents of this invention apparently has no other observable effect upon the course of the reaction than to offset the effect of the residual flotation agent; the reaction proceeds in substantially the same way as would be expected of a similar ore not containing flotation agents, and efficiencies and recoveries are likewise unimpaired. Addition of the amine treating agents of this invention to ores which do not contain flotation agents has no noticeable effect.

In order to more clearly illustrate the process of this invention, the following examples are presented:

Example I

1500 grams of a titaniferous iron concentrate which had been prepared by treating a titaniferous iron ore in a flotation system with 1.5 pounds of fuel oil and 1.0 pound of oleic acid per ton of the unconcentrated feed ore was tested according to the test method described above using 1370 milliliters of 93.2% sulfuric acid and 150 milliliters of water to give an acid strength at reaction of 88%. The reaction was extremely violent and a considerable portion of the reaction mass flowed over the top of the tank. The test was repeated using 0.05% of di octadecylamine, based on the weight of the ore. The reaction in this case was moderately violent and the reaction mass rose to within about four inches from the top of the tank. The test was again repeated using 0.10% of di octadecylamine and the reaction was observed to be vigorous but completely controlled, the reaction mass in this case never rising higher than about five inches from the top of the tank.

On the basis of these preliminary tests, a large scale digestion was carried out using 10 tons of the same titaniferous iron ore concentrate, 16.8 tons of 93.2% sulfuric acid, 20 pounds of di octadecylamine, and 1.1 tons of water. The reaction was rapid, complete and orderly, similar in all respects with reactions produced by ores not containing flotation agents. Better than 95% of the titanium values in the treated ore concentrate were convered to soluble titanium sulfates.

Example II

Another ore concentrate was prepared by flotation concentration of a crude titaniferous ore using 1.0 pound of oleic acid and 1.5 pounds of fuel oil for each ton of raw ore treated. Approximately half of the original ore feed (together with most of the flotation agents) was collected as the flotation concentrate. After subsequent washing and drying the flotation concentrate was tested as described in Example I using di octadecyl stearamide as the treating agent.

On the basis of the preliminary tests another large scale digestion was made according to the procedure described in Example I, but using 0.10% of di octadecyl stearamide as the treating agent. The character of the reaction obtained was substantially similar to that of Example I and resulted in the solubilization of better than 95% of the titanium values.

Example III

An ore concentrate similar to that of Examples I and II was subjected to large scale digestion according to the procedure of Example I, using 0.05% of di hexadecyl ammonium stearate instead of the di octadecylamine as the secondary amine treating agent. Again, a vigorous orderly reaction took place resulting in solubilization of better than 95% of the titanium values.

Example IV

Another ore concentrate similar to that of the preceding examples was subjected to large scale digestion according to the procedure of Example I, using 0.10% of di octadecyl ammonium palmitate instead of the di octadecylamine as the secondary amine treating agent. Results were substantially identical with those of Example I.

Example V

Another portion of the ore concentrate used in Example IV was subjected to large scale digestion according to the procedure of Example I, using 0.10% of di octadecyl stearamide sulfate instead of the di octadecylamine as the secondary amine treating agent. Results were substantially identical with those of Example I.

Example VI

A third portion of the ore concentrate used in Examples IV and V was subjected to large scale digestion according to the procedure of Example I, using 0.2% of di tetradecyl lauramide hydrochloride instead of the di octadecylamine as the secondary amine treating agent. Results were substantially identical with those of Example I.

Example VII

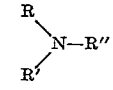
A sample of ore taken from an ore pile which had been sprayed with asphalt to reduce wind losses was tested in the laboratory and was found to have serious foaming characteristics The amount of asphalt present in the ore was not known, but laboratory tests as previously described indicated that foaming at digestion could be prevented by the addition of 0.025% of di octadecylamine. This quantity was added to a plant-scale digestion batch, with results similar to those described in the previous examples.

As shown by the above examples, the present invention provides a method for treatment of ore concentrates containing organic flotation agents, which treatment renders said concentrates amenable to dissolution in strong sulfuric acid according to the normal procedures used for such concentrates. The ordinary effect associated with the presence of organic flotation agents in the ore is to render the reaction with sulfuric acid uncontrollable; by means of the present invention this harmful and dangerous effect of organic flotation agents is prevented and the digestion proceeds as readily and conveniently as when using ore which does not contain flotation agents. The treatment process is simple and easy to employ.

While this invention has been described and illustrated by the examples shown, it is not intended to be strictly limited thereto, and other modifications and variations may be employed within the scope of the following claims.

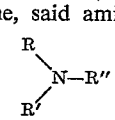
We claim:

1. A method for treatment of titaniferous ores containing organic flotation agents selected from the group consisting of anionic flotation agents, petroleum agents and asphalt materials to render the same amenable to attack by concentrated sulfuric acid which comprises adding to said ore from 0.05 to 0.2% of its weight of an amine having the formula



wherein R and R′ represent saturated alkyl radicals containing from 12 to 20 carbon atoms and R″ is selected from the group consisting of hydrogen and saturated alkanoic acyl radicals containing up to about 20 carbon atoms.

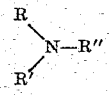
2. In a method for dissolution in sulfuric acid of titaniferous ores containing organic flotation agents selected from the group consisting of anionic flotation agents, petroleum agents and asphalt materials, the improvement which comprises having present during said dissolution from 0.05 to 0.2%, based on the weight of said ore, of an amine, said amine having the formula



wherein R and R′ represent saturated alkyl radicals con-

taining from 12 to 20 carbon atoms and R'' is selected from the group consisting of hydrogen and saturated alkanoic acyl radicals containing up to about 20 carbon atoms.

3. A method of preparing titanium solutions relatively low in iron and gangue from crude ilmenite ore relatively high in iron and gangue which comprises the steps of grinding said ore, concentrating the ilmenite portion of said ore by flotation in the presence of organic flotation agents selected from the group consisting of anionic flotation agents, petroleum agents and asphalt materials, thereby separating said crude ore into a floatable fraction rich in ilmenite and a non-floatable fraction rich in gangue and low in titanium, and subsequently reacting said ilmenite rich fraction with concentrated sulfuric acid in the presence of an amine, said amine having the formula



wherein R and R' represent saturated alkyl radicals containing from about 12 to 20 carbon atoms and R'' is selected from the group consisting of hydrogen and saturated alkanoic acyl radicals containing up to about 20 carbon atoms.

4. Method according to claim 1 wherein said amine is di octadecylamine.

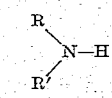
5. Method according to claim 1 wherein said amine is di hexadecyl ammonium stearate.

6. Method according to claim 1 wherein said amine is di octadecyl stearamide.

7. Method according to claim 1 wherein said amine is di octadecyl ammonium palmitate.

8. Method according to claim 1 wherein said amine is di octadecyl ammonium myristate.

9. A method for treatment of titaniferous ores containing organic flotation agents selected from the group consisting of anionic flotation agents, petroleum agents and asphalt material, to render said ores amenable to attack by concentrated sulfuric acid, which comprises adding to said ore from 0.05 to 0.2% of its weight of a substance selected from the group consisting of amines having the formula



wherein R and R' represent saturated alkyl radicals containing from 12 to 20 carbon atoms, and N-acyl derivatives of said amines, said derivatives being characterized in that H in the above formula is replaced by the acyl group of a carboxylic acid containing from 1 to 20 carbon atoms.

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