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FROTH FLOTATION PROCESS FOR OXIDE ORES

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6 Claims. (Cl. 209—166)

This invention relates to an improvement in the process of concentration by flotation of heavy mineral metal oxides and it consists in the treating of such ores while in the state of a pulp with sufficient active acid, together with a saponifiable substance and a water-insoluble liquid ketone.

The heavy mineral metal oxides, among which may be named magnetite, corundum, ilmenite, rutile, chromite, cuprite, zincite, franklinite, and pyrolusite, or some of them, have been treated by flotation heretofore for the purpose of concentrating the ores thereof. In such cases the ratio of concentration has been low and unless the ore was initially sufficiently high grade the concentrate has not been of commercial value, that is, sufficiently free of gangue substances as to permit economical smelting operations. In the case of cassiterite there is no record of a commercial concentrate having been produced by flotation directly from any natural ore. Generally speaking, therefore, concentration of oxide ores by flotation has heretofore been of very little commercial moment because of the low ratio of concentration obtainable thereby.

Heretofore the flotation of heavy mineral oxide ores has been attempted by employing silicates for depressing the gangue materials and frothing and collecting agents for recovering the ore. In this method an extremely critical balance between frothing, collecting, and depressing reagents needed to be maintained if results of any advantage were to be obtained. Even when performing under optimum conditions, such methods have been relatively ineffectual, producing a low ratio of concentration.

The process of this invention, however, is positive in its action. In the case of certain ores the grade of concentrate is roughly independent of the percentage of the ore mineral in the pulp being treated. For example, a grade of concentrate of approximately sixty per cent tin can be obtained effectually from cassiterite pulps containing all the way from two to thirty per cent of tin. In the process of this invention the reagents employed are effective over a substantial range of concentration and there are no critical balances which must be maintained in order to obtain the results desired. The effects of the reagents are striking and easily recognizable and therefore the control of the operation is simplified, due to the fact that visual and other simple observations are all that is necessary in order to keep the process under control.

In this invention neither the amount of saponifiable substance nor ketone need be controlled so long as a sufficient amount of each be used and their action is not based upon the use of starvation amounts thereof. The acid employed is an active acid and its presence in sufficient quantities is very easily determined.

The process of this invention is carried on by reducing the ore to be treated to a proper pulp. This is done by grinding in any usual manner, or in case the particular material is in the form of a slime or other very finely divided state it may be possible to treat the same directly. The pulp is fed into any one of the usual froth flotation machines in which the proper agitation and aeration are provided. There is added to the feed of pulp, or in any other manner desired, a small amount of a saponifiable substance. This substance may be any one of a number of natural fatty acids, from fish, linseed, palm, cocoanut, tung, or red oil, or any high molecular weight, aliphatic or cyclic carboxylic acid, such as oleic acid, or oxidation products of normal or naphthenic petroleum, or naphthenic acids derived from any other source. There is also added a frother consisting of insoluble liquid ketone. For this purpose it has been found that the following will serve the purpose:

Iso-amyl phenyl ketone
Iso-butyl phenyl ketone
Di-iso-amyl ketone
Di-propyl ketone
Di-iso-propyl ketone
Ethyl benzyl ketone
Ethyl butyl ketone
Ethyl-iso-butyl ketone
Ethyl octyl ketone
Ethyl phenyl ketone
Iso-butyl ketone
Hexyl ketone
Nonyl ketone
Octyl ketone
n-propyl iso-butyl ketone
n-propyl phenyl ketone
Iso-propyl phenyl ketone

and homologues and isomers of the same. There is also added an amount of active acid which seems to be somewhat related to the amount of base metal ions exposed upon the surface of the gangue minerals, such ions being chiefly iron, calcium, magnesium, copper, etc. For this purpose I have found that the acids which are ordinarily referred to as "active acids", such as nitric, hydrochloric, hydrofluoric, sulfuric, phosphoric,

acetic, or tartaric are suitable. At any rate, I have discovered that certain ores combine with substantial amounts of acid and that a slight excess thereover is necessary to obtain the successful results of the process of this invention, the quantity not being particularly important so long as an excess is present and the apparatus in which the process is being carried on is reasonably free from attack by the acid.

The process as outlined above is carried on in highly acid condition as compared with flotation heretofore practiced. Under these conditions saponifiable substances, such as described above, are without frothing power and merely produce oiling, and are incapable of supporting any pulp. The discovery of this invention, however, depends to a certain extent upon the important fact that the sparingly soluble liquid ketone produces, with the saponifiable substance, a very strong froth regardless of the acidity of the pulp. Such frothers as have been commonly employed, as pine oil, or cresol, if employed in an acid pulp sufficiently acid to effect gangue mineral to the extent necessary, when used in combination with a fatty acid form drops in the flotation pulp and spread only with long and violent agitation of the pulp. The result is generally over oiling, with no froth, or a poor, small bubble, or brittle froth that fails to produce a concentrate. The sparingly soluble ketones, however, not only produce a good froth when in combination with the fatty acid, but the ketone also serves to spread the fatty acid. It is advantageous at times, therefore, to dissolve a fatty acid in the ketone and to add the combination to the flotation cell. Although the ketone alone will produce a froth, such froth is brittle and ineffective, while the addition of the fatty acid brings about a strong and effective froth.

At times the process of this invention may be practiced as follows: 1000 grams of a cassiterite ore which has been ground in a ball mill are agitated and aerated in a flotation machine together with three grams of hydrochloric acid (concentrated) and one pound of sulfuric acid (concentrated). To this 0.87 of a gram of oleic acid and 0.15 gram of Barrett oil No. 635, which is a fluid coal tar or tarry oil, and 0.20 of a gram of dipropyl ketone. A froth will be formed which will contain probably in excess of fifty per cent of tin, and in one specific case contained fifty-four per cent of tin. In this case the pulp undergoing treatment contained thirty per cent of tin.

The process of this invention at times may also be practiced as follows: The pulp of cassiterite ore is prepared as described above, to which there is added approximately three pounds of concentrated sulfuric acid per ton of dry ore and ten pounds of sodium fluoride per ton of dry ore, which in the presence of sulfuric acid forms hydrofluoric acid. There is also added one-half pound of dipropyl ketone per ton of dry ore and 1.6 pounds of oleic acid per ton of dry ore. The usual aeration and agitation treatment is carried on, producing a froth which may contain approximately sixty per cent of tin, for example, constituting as much as ninety-six per cent of the tin in the ore being treated.

The process may also at times be carried on by treating an ore containing, for example, 2.3 per cent tin, the ore being prepared in the form of a pulp and fed into the usual flotation machine together with three pounds of sulfuric acid per ton of dry ore, together with 2.4 pounds methyl-iso-butyl ketone and three pounds of oleic acid per ton of dry ore. In such case a froth will form which contains a concentrate containing approximately sixty per cent of tin.

The amount of reagents employed and particularly the amount of active acid, may be varied to obtain the desired result. Even a separation of magnetite from andradite garnet may be made and in this case approximately thirty pounds of hydrochloric acid per ton of dry ore was found to give the best results when using a moderate amount of frothing and collecting agents.

The process of this invention makes it possible to recover heavy mineral oxide ores by flotation with results comparable to those obtained with sulfide ores which have heretofore been considered to be much more easily separated by flotation. This invention depends to an extent upon the fact that the oxide minerals when in acid pulps exhibit surface phenomena which distinguish them from the usual gangue materials and which phenomena do not occur in neutral or alkaline solutions, but the invention is also dependent upon the discovery that an effective froth can be maintained in spite of the presence of active acid in substantial amounts. The froth which is removed in the process of this invention may be retreated, if it is desired, to increase the percentage of heavy mineral metal oxide in the concentrate, or the tailings may be retreated, if it is desired, to increase the percentage of mineral recovered.

Herein in the specification and claims the term "active acid" is intended to mean one or more of the group consisting of hydrochloric, hydrofluoric, sulfuric, phosphoric, nitric, acetic, and tartaric acids. The term "water-insoluble liquid ketone" as used herein is intended to mean such ketones as are liquid at ordinary temperatures and which dissolve in water no more than economical operation of the process permits, including those mentioned or referred to above.

The process of this invention has been described in detail above in connection with specific instances in which it may at times be usefully employed. It is not intended, however, that the protection of Letters Patent to be granted hereon be unnecessarily limited thereby, but it is intended that said protection should extend to the full field of the invention as represented by the scope of the claims appended hereto.

What I claim as my invention is:

1. The process of separating the mineral constituents of an ore containing a heavy mineral metal oxide which consists in mixing the ore in a finely divided state with water so as to form a pulp, agitating the pulp in the presence of an active acid, a water-insoluble liquid ketone and a saponifiable substance, supplying the pulp with air to produce a froth containing a concentrate, and removing the froth.

2. The process of separating the mineral constituents of an ore containing heavy mineral metal oxide which consists in mixing the ore in a finely divided state with water so as to form a pulp, agitating the pulp in the presence of over one pound of active acid per ton of dry ore, a water-insoluble liquid ketone, a saponifiable substance, supplying the pulp with air to produce a froth containing a concentrate, and removing the froth.

3. The process of separating the mineral constituents of an ore containing a heavy mineral metal oxide which consists in mixing the ore in a finely divided state with water so as to form a pulp, agitating the pulp in the presence of an

active acid, a water-insoluble liquid ketone and a fatty acid substance, supplying the pulp with air to produce a froth containing a concentrate, and removing the froth.

4. The process of separating the mineral constituents of an ore containing a heavy mineral metal oxide which consists in mixing the ore in a finely divided state with water so as to form a pulp, agitating the pulp in the presence of an active acid, a dipropyl ketone and a saponifiable substance, supplying the pulp with air to produce a froth containing a concentrate, and removing the froth.

5. The process of separating cassiterite from cassiterite ore which consists in mixing the ore in a finely divided state with water so as to form a pulp, agitating the pulp in the presence of an active acid, dipropyl ketone and oleic acid, supplying the pulp with air to produce a froth with the cassiterite floating therein, and removing the froth.

6. The process of separating cassiterite from cassiterite ore which consists in mixing the ore in a finely divided state with water so as to form a pulp, agitating the pulp in the presence of over one pound of sulfuric acid per ton of dry ore, dipropyl ketone and oleic acid, supplying the pulp with air to produce a froth with the cassiterite floating therein, and removing the froth.

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