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PHOSPHATE MINERAL BENEFICIATION PROCESS

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This invention relates to the concentration of phosphate minerals by froth flotation. More specifically, the invention relates to a froth flotation process effective, inter alia, to separate silica from phosphate minerals.

Phosphate rock normally occurs in association with silica as a major gangue constituent. The phosphate industry has devoted substantial effort to devise efficient and economical methods for the production of a phosphate rock concentrate having a minimum silica content, preferably not more than about 3% or 4% by weight.

Conventional practice, particularly in the Florida phosphate industry, employs a phosphate mineral concentration process pursuant to which a rough concentration is effected by washing or desliming and the final concentration is achieved by two stages of froth flotation. In the first flotation stage, deslimed raw rock feed is conditioned with caustic soda, a hydrocarbon such as fuel oil, or kerosene, and a fatty acid reagent such as tall oil and thereafter subjected to froth flotation in conventional manner to yield a phosphate product commonly called a rougher concentrate. The rougher concentrate normally contains from about 8% to about 20% by weight of silica and hence is a low grade phosphate material of limited value. Accordingly, the rougher concentrate is conventionally freed of reagents or "deoiled" by scrubbing with a mineral acid such as sulfuric acid and deslimed in preparation for a second stage of froth flotation concentration. The de-oiled, deslimed rougher concentrate is frequently designated as "amine flotation feed" by reason of the strong cationic amine collecting agents which are conventionally employed in the second froth flotation stage in which the silica is floated and discharged to waste. The underflow from the second stage is high phosphate concentrate which is transferred to storage.

The amine collecting agents useful in the second or amine flotation stage are efficient and yield a satisfactory phosphate concentrate of satisfactory grade; however, the cost of such amine collecting agents constitutes a significant portion of the cost of phosphate mineral beneficiation. Accordingly, the art is continuously seeking more economical collecting agents which may be employed in lieu of the relatively expensive amines with at least equivalent results.

It is therefore a primary object of the invention to provide a process for the concentration of phosphate minerals by froth flotation which is substantially more economical than conventional procedures.

It is an additional object of the invention to provide a process for the concentration of phosphate minerals by the two-stage flotation technique which is at least as efficient and substantially less expensive then similar processes now commercially employed.

It is a more specific object of the invention to provide a novel collector for use in the second or amine stage of a conventional two stage froth flotation procedure for the concentration of phosphate minerals.

Amines conventionally used as collectors in froth flotation processes for the concentration of phosphate minerals are aliphatic in character and contain from about 8 to about 20 carbon atoms. Such amine collectors are synthesized by standard procedures which yield a crude synthesis reaction mixture which is fractionated to provide a relatively lower boiling amine material for use, inter alia, as a froth flotation collector and a relatively higher boiling bottoms fraction or residue. Various well known methods of synthesis are employed including reduction of the corresponding fatty acids, amination of the corresponding halogenated hydrocarbons, and the like. Regardless of the method of synthesis employed, it has generally been considered necessary to separate a comparatively lower boiling amine product fraction for use as a flotation collector from a relatively higher boiling residue portion of the amine synthesis reaction mixture.

Now, in accordance with this invention, it has been discovered that silica containing phosphate minerals can be efficiently concentrated by froth flotation in the presence of a collecting agent comprising the residue normally resulting from the separation, from a crude product of the synthesis of an aliphatic amine containing from about eight to about twenty carbon atoms, of a fraction having a boiling point lower than that of said residue and containing a substantial portion of at least one aliphatic amine having from about eight to about twenty carbon atoms, and recovering a phosphate concentrate. It will be appreciated that the amine residues are useful as collection agents regardless of the primary purpose for which the lower boiling amine fraction is prepared or utilized.

The invention generically embraces utilization of collectors comprising amine residues of all types in the froth flotation of phosphate minerals. It will be appreciated that the composition of such amine residues will vary, for example, with the particular method of amine synthesis utilized, the starting materials employed, the end point of the lower boiling fraction which may be removed, and the like. The utility of the amine residues in the invention changes only in degree with such variations and materials and conditions and the invention therefore contemplates utilization of all residues from the synthesis of aliphatic amines containing from about eight to about twenty carbon atoms and mixtures thereof. The preferred amine residues are formed by the reduction of about eight to about twenty carbon atom fatty acids followed by the separation of an amine fraction containing not more than about eighteen carbon atoms. Particularly appropriate starting materials which yield the preferred amine residues comprise natural mixtures of fatty acids such as coconut oil fatty acids, tallow fatty acids and soy bean oil fatty acids.

The invention further contemplates utilization of the amine residues in combination with conventional amine collectors. Indeed, in some cases it may be appropriate to blend the various amine residues which may be available with conventional aliphatic amine collectors to produce a reagent of more uniform characteristics. Optimum results in certain cases have been achieved by utilization of a mixture of the residues resulting from the commercial preparation of amines derived from natural fatty acid mixtures with from about 20% to about 40% by weight of the corresponding lower boiling amine fraction. The invention in its generic embodiment embraces a utilization of all collectors comprising amine residues and hence includes the utilization in the froth flotation concentration of phosphate minerals of the entire crude product of the synthesis of aliphatic amines containing from about eight to about twenty carbon atoms.

The amine residue containing flotation collectors of this invention are employed in conventional manner and in conventional proportions known to the art and de-

scribed inter alia in U.S. Patents 2,293,640 and 2,724,501. In general, and in accordance with conventional practice, the amine residue collection agents of this invention are partially neutralized by the addition of an appropriate mineral or organic acid such as hydrochloric acid or acetic to facilitate solution in water and to provide a pulp having a pH of from about 7 to about 8. The amine residue reagents of the invention are employed in proportions requisite to provide from about 0.4 pound to about 1.5 pound of reagent per ton of ore treated. The particular proportions utilized do not constitute the essence of the invention. The optimum quantity of amine will vary to a minor degree with the specific reagent utilized and can readily be determined by expedients well known to those skilled in the art.

It will be appreciated by those skilled in the art that the froth flotation concentration of phosphate minerals entails problems different from those which attend concentration of metallic ores by the same physical process. Hence reagents useful in metallic ore concentration may prove quite inappropriate for phosphate mineral beneficiation.

The following examples illustrate the best mode presently known for the practice of the invention.

EXAMPLE I

A sample of rougher concentrate formed by the fatty acid beneficiation of deslimed Florida phosphate rock in a commercial phosphate rock concentration plant was scrubbed with sulfuric acid in conventional manner to yield a substantially reagent free feed appropriate for second stage froth flotation concentration with an amine collector. The sample was divided into eleven aliquot portions for comparative testing.

Five percent by volume water emulsions of the following amine reagents were prepared using two parts by weight of kerosene for each part by weight of amine reagent.

(1) A commercial amine collector composed of a mixture of equal parts by volume of a butyl amine and "Alamine 26," a commercial amine product formed by the reduction of tallow acids followed by fractionation of the crude reduction product to yield a material containing approximately 30% by weight hexadecyl amines, 45% by weight octadecyl amine and 25% by weight octadecenyl amine.

(2) A product similar to 1, supplied by the Harshaw Chemical Company under the trade name "Uvermene 38."

(3) A residue remaining after the separation of a lower boiling amine fraction similar to "Alamine 26" from an amine product formed by the reduction of tallow acids, and supplied by Armour and Company under the trade name "Armeen Residue (Tallow)."

(4) A residue remaining after the separation of a lower boiling amine fraction from an amine product formed by the reduction of coconut oil fatty acids and supplied by Armour and Company under the trade name "Armeen Residue (Cocoa)."

(5) A residue remaining after the separation of a lower boiling amine fraction from an amine product formed by the reduction of soy bean oil fatty acids and supplied by Armour and Company under the trade name "Armeen Residue (Soy bean)."

(6) A mixed residue believed to be generally comparable to a mixture of equal parts of reagent "3" and reagent "5" and supplied by General Mills under the trade name "Alamine 60."

(7) A mixed amine residue comparable to reagent No. 6 supplied by Armour and Company under the trade name "Armeen Residue."

(8) A mixture comprised of 80% by weight of reagent No. 7 and 20% by weight of tallow amines supplied by Armour and Company under the trade name of "Armeen T."

(9) A reagent similar to reagent No. 8 but containing 60% by weight of amine residue and 40% by weight of "Armeen T."

(10) A mixture similar to reagent No. 8 but containing 40% by weight of amine residue and 60% by weight of "Armeen T," and supplied by Armour and Company.

(11) A reagent believed to be similar to reagent No. 8 but containing about equal parts by weight of amine residue and "Armeen T" and supplied by Armour and Company under the trade name "Mixed Crude Armeen Lot 5593."

All emulsions are neutralized to a pH of 7.0 which corresponds to approximately 75% neutralization of the total amine. The feed was conditioned at about 25% solids and subjected to froth flotation in a 500 gram Denver laboratory flotation cell in which the phosphate concentrate was recovered from the underflow and the silica tail was floated, in conventional manner with the results as indicated in Table I.

Table I.—Approximate amine reagent cost for optimum flotation with various amines

Amine Reagent No.	Approximate Cost/Lb. FOB In Tank Cars, Cents	Lbs./Ton Feed Required	Cost/T. Amine Feed, Cents	Grade and Recovery in Conc.		
				BPL	Insol.	BPL Rec., Percent
1	28	0.6	16.8	74.4	2.71	90.2
2	33	1.5	49.5	73.4	5.06	98.2
3	6	0.7	4.2	74.7	3.06	94.0
4	6	0.9	5.4	75.0	2.75	97.7
5	6	1.1	6.6	75.6	2.6	96.9
6	6	0.9	5.4	74.4	2.83	97.7
7	6	1.1	6.6	72.7	2.6	96.6
8	11.4	0.7	8.0	73.1	2.8	97.2
9	16.8	0.5	8.4	73.4	2.8	97.8
10	22.2	0.5	11.1	72.3	3.6	97.8
11	20.0	0.5	10.0	73.1	3.2	98.4

The present invention provides a process which is effective materially to reduce the cost of the froth flotation concentration of phosphate minerals and accordingly constitutes a significant contribution to the art.

It will be appreciated that the specific amine synthesis reaction mixtures from which the amine residue flotation agents are derived does not constitute an essential or critical feature of the invention which extends to the utilization of residues from the synthesis of all saturated and unsaturated, straight and branched chain aliphatic amines containing from about eight to about twenty carbon atoms. Representative amines include octyl, nonyl, decyl, decenyl, isodecyl, dodecyl, isododecyl, dodecenyl, tetradecyl, hexadecyl, hexadecenyl, isohexadecenyl, and octadecyl amine; and mixtures thereof.

I claim:

1. A process for the beneficiation of a silica containing phosphate ore which comprises subjecting said ore to froth flotation in the presence of a collector consisting of a high boiling amine residue produced by (*a*) synthesis of mixed amines by reduction of a natural fatty acid mixture selected from the group consisting of the coconut oil fatty acids, the tallow fatty acids, and the soy bean fatty acids; and (*b*) removing from the crude synthesis reaction mixture the amines containing not more than about eighteen carbon atoms; the residue of said reaction mixture remaining after the removal of said fraction constituting said collector and consisting essentially of mixed amines containing more than eighteen carbon atoms together with materials present in said crude reaction mixture which have a boiling point in excess of the terminal boiling point of said removed fraction.

2. The process of claim 1 wherein said crude synthesis product is produced by the reduction of tallow fatty acids.

3. The process of claim 1 wherein said crude synthesis product is produced by the reduction of soy bean oil fatty acids.

4. The process of claim 1 wherein said crude synthesis product is produced by the reduction of coconut oil fatty acids.

5. In a process for the concentration of phosphate minerals by a two-stage froth flotation procedure in which a rougher concentrate is produced in the first flotation stage, and a final concentrate produced in the second flotation stage, the improvement which comprises utilizing as a collector in said second flotation stage a residue consisting of a high boiling amine residue produced by (*a*) synthesis of mixed amines by reduction of a natural fatty acid mixture selected from the group consisting of the coconut oil fatty acids, the tallow fatty acids, and the soy bean fatty acids; and (*b*) removing from the crude synthesis reaction mixture the amines containing not more than about eighteen carbon atoms; the residue of said reaction mixture remaining after the removal of said fraction constituting said collector and consisting

essentially of mixed amines containing more than eighteen carbon atoms together with materials present in said crude reaction mixture which have a boiling point in excess of the terminal boiling point of said removed fraction, and recovering a phosphate concentrate.

6. The process of claim 5 wherein said natural mixture of fatty acids comprises tallow acid.

7. The process of claim 5 wherein said natural mixture of fatty acids comprises coconut oil fatty acids.

8. The process of claim 5 wherein said natural mixture of fatty acids comprises soy bean oil fatty acids.

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