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FLOTATION OF SILICEOUS ORES

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9 Claims

ABSTRACT OF THE DISCLOSURE

Flotation-separation of a siliceous ore into a floated heavy mineral fraction and a non-floated siliceous fraction using as collector a composition containing acid esters of phosphorus acids in which the state of oxidation of phosphorus corresponds statistically to approximately four.

This is a continuation application of Ser. No. 531,789, filed on Mar. 4, 1966, now abandoned in favor of the present application.

The present invention concerns a process for the flotation-separation of natural siliceous ores into a heavy mineral fraction and a siliceous fraction.

The description "natural siliceous ore" used herein is intended to cover both native ores as well as ore fractions obtained in the course of ore dressing operations.

The mineral composition of most of the siliceous ore deposits throughout the world is generally similar, differing only in percentage of each mineral present according to their origin. These minerals fall generally in the classes of gneisses, granites and pegmatites and there may be mentioned in particular ilmenite, rutile, monazite, zircon, sillimanite, kyanite, andalusite, garnet, spinel, corundum, staurolite, tourmaline and epidote. Among these minerals, ilmenite, rutile, monazite, zircon, garnet and staurolite are the most important.

Where the siliceous ore is in the form of sand and the latter is to be used for the manufacture of glass, the heavy minerals have first to be removed. Moreover, for some of the above minerals such as zircon, monazite and staurolite, beach sands are the most important sources.

It is thus seen that the treatment of natural siliceous ores in accordance with the invention has in many instances for its object the double purpose of recovering various valuable minerals on the one hand and glass sand on the other hand.

There are also cases in which a siliceous gangue is obtained in the course of an ore dressing operation and it is desired to recover some further amounts of the desired ore from the gangue. This is, for example, the case with Florida (U.S.A.) phosphate ores where the bulk of the phosphate is first separated by amine flotation leaving a siliceous gangue still containing about 14% by weight of P_2O_5 .

The flotation-separation of mineral ores with the aid of anionic flotation agents or collectors, as they are termed in the art, is a well-known technique. Among the conventionally used anionic collectors there may be mentioned oleic acid, naphthenic acids, tall oil acids, synthetic fatty acids and various organic sulfonates. It has also been proposed to employ various esters of phosphoric, thiophosphoric and pyrophosphoric acids as anionic collectors.

Known anionic collectors have been found to give unsatisfactory results in the flotation-separation of heavy minerals from natural siliceous ores, particularly where

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valuable minerals are to be recovered from low-grade ores, or where it is necessary to obtain the floated minerals in a concentrated state.

In Israel Patent No. 16686 of Jan. 28, 1962, British Patent No. 1,037,635 and U.S. patent application No. 509,612 of Nov. 24, 1965, there are described compositions containing acid esters of phosphorus acids in which the state of oxidation of the phosphorus corresponds statistically to approximately four and which are obtained by reacting white phosphorus with air or oxygen and at least one hydrocarbon compound containing at least one alcoholic hydroxyl group in the molecule, in the presence of an inert solvent at a temperature of from 0° C. to 45° C. Such a composition of acid esters of phosphorus will be referred to in the following for short as "compositions of acid esters of phosphorus of the kind specified."

The analysis of the composition of acid esters of phosphorus of the kind specified corresponds statistically to that of dialkyl-dihydrogen-hypophosphates with respect to overall oxidation state of the phosphorus, the acid value and the alkyl/phosphorus ratio. The oxidation state of the phosphorus may be expressed by the number of bonds linking a phosphorus atom in a molecule with more electronegative elements, such as oxygen or halogen, less the number of bonds linking it with more electropositive elements, such as hydrogen, an alkali metal or carbon. Thus, the oxidation state of phosphorus in orthophosphoric acid and pyrophosphoric acids is five, in phosphorous acid $-H_3-PO_3-$ three, in phosphine $-PH_3-$ minus three, and in hypophosphoric acid $-H_4P_2O_6-$ and its esters—four. The statistical oxidation state of phosphorus in the composition of acid esters of phosphorus of the kind specified, as determined analytically by the iodine method, is, as mentioned, very close to four. By means of nuclear magnetic resonance measurements it has been shown that said compositions are complex mixtures which may be described as the alcoholysis and hydrolysis products of the theoretical oxide P_4O_8 which may be considered as hypophosphoric acid anhydride. Statistically they may thus be considered as dialkyl-dihydrogen hypophosphates.

In accordance with the present invention it has surprisingly been found that compositions of acid esters of phosphorus of the kind specified are very effective collectors for the flotation-separation of heavy minerals from natural siliceous ores.

The invention thus provides a process for the flotation-separation of a natural siliceous ore into a floated heavy mineral fraction and a non-floated siliceous fraction, which process is characterized by the use of at least one compositions of acid esters of phosphorus of the kind specified as collector.

The preferred collectors in the method according to the invention are those in which the organic radicals consist predominantly of chains having approximately 10 to 18 carbon atoms. Members of this preferred group may, for example, be obtained by employing in the above-mentioned process for the preparation of compositions of acid esters of phosphorus of the kind specified, lauryl alcohol or mixtures of synthetic alcohols known commercially as Alfol 1214 and Alfol 1218.

It has been surprising and unexpected to find in accordance with the present invention that compositions of acid esters of phosphorus of the kind specified are very effective collectors for the flotation-separation of natural siliceous ores, with a high degree of selectivity for floating the heavy mineral fractions, which selectivity is also retained in acidic medium. Such a selectivity could hitherto not be obtained with conventional collectors. As a result of the high selectivity of the collectors used in accordance

with the invention, flotation regulators, such as for example sodium silicate, are not required while they are needed with conventional collectors.

A further advantage is the useful froth produced by the collectors used in accordance with the invention, obviating the necessity of employing special frothing agents.

If desired, activators may be employed in the method according to the invention. A preferred activator is phosphoric acid.

In experiments conducted in accordance with the present invention the following heavy minerals were effectively separated from natural siliceous sand:

- (1) Rutile— TiO_2
- (2) Anatase— TiO_2
- (3) Ilmenite— FeTiO_3
- (4) Leucocoxene—an alteration product of titanium minerals
- (5) Monazite— $(\text{Ce, La, Di})\text{PO}_4$ with ThO_2
- (6) Magnetite— Fe_3O_4
- (7) Chromite— $(\text{FeO} \cdot \text{Cr}_2\text{O}_3)$
- (8) Hematite— Fe_2O_3
- (9) Limonite— $2\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
- (10) Garnet group— $\text{R}^{\text{II}}\text{R}^{\text{III}}(\text{SiO}_2)_3$; ($\text{R}^{\text{II}} = \text{Ca, Mg, Fe, Mn}$); ($\text{R}^{\text{III}} = \text{Al, Fe, Cr, Ti}$)
- (11) Zircon— ZrSiO_4
- (12) Tourmaline— $\text{H}_3\text{Al}_3(\text{B} \cdot \text{OH})_2\text{Si}_4\text{O}_{19}$ (hydrogen may be replaced by alkalis and also the bivalent elements Mg, Fe, Ca)
- (13) Staurolite— $\text{HFeAl}_5\text{Si}_2\text{O}_{13}$
- (14) Cassiterite— SnO_2
- (15) Barite— BaSO_4
- (16) Columbite— $(\text{Fe, Mn})(\text{Nb, Ta})_2\text{O}_6$
- (17) Apatite— $\text{Ca}_{10}\text{P}_6\text{O}_{24}[\text{F}_2, \text{Cl}_2, \text{CO}_3(\text{OH}_2)]$

The invention is illustrated in the following examples without being limited thereto:

EXAMPLE 1

The collector used: A composition of phosphorus acid esters obtained from the reaction of white phosphorus, air and lauryl alcohol.

The purpose: Cleaning of glass sand from iron bearing minerals.

500 grams of glass sand containing 0.05% Fe_2O_3 from the Makhtesh Hatira deposits were mixed with 2000 cc. of water in a Fagergren flotation machine. Then 1 gram of the collector was added and conditioned with mixing for ten minutes. About 1 cc. of H_3PO_4 20% was added, obtained a pH of 3.5, then the flotation was started. After five minutes, the mineral impurities such as schorlite (iron tourmaline), ilmenite and hematite were floated.

The purified glass sand (482 g., 96% recovery) had an iron content of 0.025%.

The above collector was prepared as follows:

A reaction vessel was equipped with an efficient stirrer, a dropping funnel, a thermometer, an inlet tube for air and a reflux condenser the outlet of which was connected by glass-tubing through an empty 10-liter bottle to an efficient cold-trap cooled by means of Dry Ice and acetone, means being provided for measuring the quantity of air passed into the reaction vessel and the quantity of gases leaving through the cold trap. The reaction vessel was charged with 300 g. ethyl acetate and a quantity of 40 g. molten white phosphorus was run in with vigorous stirring, resulting in a fine dispersion of the phosphorus in the ethyl acetate. The reaction vessel was immersed in a water bath through which cold water was passed and a quantity of 240 g. lauryl alcohol was added gradually during 3½ hours, while a steady stream of air of 45 liters/hour (NTP) was bubbled through and the temperature was maintained in the range between 28 to 32° C. by external cooling. Dense white fumes were evolved and the fumes leaving the reaction vessel were precipitated in the ten-liter bottle and in the cold trap. The quantity of the outflowing gas remained steady at 37.5 liters/hour during

three hours and 45 minutes (NTP), at which time the absorption of oxygen ceased and no more fumes were formed. The flow of air was maintained for a further 15 minutes. A clear colourless liquid was obtained. The content of the traps was united with the content of the reaction vessel and the solvent was distilled off under reduced pressure. There was obtained 315 g. of a clear, oily and nearly colourless liquid. The analysis of the reaction product corresponds statistically to the composition of di-lauryl, dihydrogen hypophosphate:

Calculated for $\text{C}_{24}\text{H}_{52}\text{P}_2\text{O}_6$: P, 12.4%; C, 57.7%. Acid number: 225. Found: P, 12.0%; C, 56.8%. Acid number: 216.

Oxygen absorption, calculated for the formation of 15 hypophosphate: 28.9 l. (NTP), oxygen absorption found by flow measurements: 28.5 l. (NTP).

EXAMPLE 2

The collector used: A composition of phosphorus acid ester obtained from reaction of white phosphorus, air and oleyl alcohol.

The purpose: Cleaning of glass sand.

500 grams of glass sand from Makhtesh Hatira containing 0.06% Fe_2O_3 were mixed with 2000 cc. of water and conditioned for ten minutes with 1 gram of the collector. 3 cc. of NaOH 30% were added to obtain a pH of about 10, then some drops of concentrated H_3PO_4 to reduce the pH to 9.5 and to activate the heavy minerals. Then the flotation was started and the mineral impurities separated in the froth. The Fe_2O_3 content of the sand was reduced to 0.025%. The recovery of purified sand was 83% by weight. The collector was prepared similarly as the collector of Example 1, using 340 g. of oleyl alcohol.

EXAMPLE 3

The collector used: The same as in Example 1.

The purpose: Separation of heavy minerals from beach sand.

500 grams of beach sand (from Wabasso, Florida, U.S.A.) containing 4% heavy minerals (including zircon, ilmenite, garnet and staurolite) were mixed with 2000 cc. of water and 2 grams of the collector. About 2 cc. of H_3PO_4 conc. were added as activator obtaining a pH of 4 and the flotation started. The froth was fair and the flotation was continued for five minutes. The float fraction weighed 19 g. assaying 95% heavy minerals by microscopic count.

EXAMPLE 4

The collector used: The same as in Example 1.

The purpose: Recovery of rutile from siliceous ore.

500 grams of silica sand (−48 mesh +200 mesh) containing 10% of rutile were mixed in a Fagergren flotation machine with 2000 cc. of water and 0.5 g. of the collector. About 2 cc. of concentrated H_3PO_4 was added to bring the pH to 4 and the flotation was started and continued for 5 minutes. The float fraction, assaying 96% of rutile by microscopic count, weighed 51 g. corresponding to a 98% recovery.

EXAMPLE 5

The collector used: A composition of phosphorus acid esters obtained from the reaction of white phosphorus, air and 2-ethyl-hexyl alcohol.

The purpose: Recovery of ilmenite from siliceous ore.

500 grams of siliceous ore (−65 mesh +200 mesh) containing 20% ilmenite, were mixed with 2000 cc. of water and conditioned with 1 gram of the collector—then 1–2 cc. of NaOH 30% were added to obtain a pH 10 and some drops of concentrated H_3PO_4 as activator to a pH 9.5. The flotation was continued for five minutes. The float fraction, weighing 98 g., assayed 85% ilmenite by microscopic count. The collector was prepared similarly as the collector of Example 1, using 168 g. of 2-ethyl-hexyl alcohol.

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EXAMPLE 6

The collector used: The same as in Example 1.

The purpose: Recovery of monazite from siliceous ore.

500 grams of beach sand containing 7% monazite (phosphate of cerium, lanthanum and thorium dioxide) were mixed with 2000 cc. of water and 1 g. of the collector. The pH was adjusted to 4 using about 2 cc. of H_3PO_4 30%. The flotation was continued for five minutes. The float fraction, weighing 33 g. assayed 95% monazite by microscopic count.

EXAMPLE 7

The collector used: The same as in Example 1.

The purpose: Recovery of zircon from beach sand.

500 g. of beach sand containing 7% by weight of zircon were flotation-separated as in Example 6. The float fraction, weighing 37 g., assayed 90% of zircon by microscopic count.

EXAMPLE 8

The collector used: The same as in Example 5.

The purpose: Recovery of garnets from beach sand.

500 g. of beach sand containing 15% garnets (mainly pyrope and almandite) and the balance silica, were mixed in a flotation machine with 2000 cc. water and 1 g. of the collector. Then about 2 cc. of NaOH 30% were added obtaining pH 10 and after that 2-3 drops of concentrated H_3PO_4 as activator. The pH of the mixture decreased to 9.5. After a conditioning period of ten minutes, the flotation started and was continued for five minutes. The float fraction, weighing 80 g. assayed 85% garnets by microscopic count.

EXAMPLE 9

The collector used: The same as in Example 1.

The purpose: Recovery of cassiterite from a siliceous tin ore.

500 g. of gravity-preconcentrated tin ore from Geevor, Cornwall, England, 100/200 mesh, containing 2.0% SnO_2 (the remainder being sulfides, iron tourmaline, fluorite and quartz) were mixed with 2000 cc. of water in a Denver flotation machine. 1 g. of the collector and 2 cc. of H_3PO_4 conc. to obtain a pH 3.5, were added. After ten minutes conditioning, the flotation was started and continued for six minutes. The float fraction weighed 107 g., containing 6.6% SnO_2 (recovery 70.6%). Minerals contained in the float fraction, beside cassiterite, were pyrites, arseno-pyrite, chalcopyrite, schorlite and fluorite.

EXAMPLE 10

The collector used: The same as in Example 1.

The purpose: Recovery of cassiterite from a siliceous tin ore.

500 g. of gravity-concentrated Geevor tin ore, 100/200 mesh, containing 2.6% SnO_2 , were mixed with 2000 cc. water in a Denver flotation machine and a prefloat was taken at pH 7, using potassium ethyl xanthate (100 gram/ton ore), to remove sulfide minerals. The non-floated fraction was washed and mixed with 2000 cc. water. Sodium fluoride (200 g./ton ore) as an iron mineral and fluorite depressant, dilute sulphuric acid to obtain pH 2.5, the collector (400 gram/ton ore) and pine oil as a frother (100 gram/ton ore) were added. After ten minutes of conditioning, the flotation was started and the main float fraction was taken. The pH of the residual

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slurry was then adjusted to pH 10 with sodium hydroxide, and a middlings fraction was taken. The following table gives the results:

Fraction	Weight	Percent SnO_2	SnO_2 distrib.
Heads.....	500.0	2.6	100.0
Prefloat.....	10.8	2.5	2.1
Main float.....	53.3	16.2	66.4
Middlings.....	57.7	4.2	18.6
Tails (calc'd).....	378.2	0.44	12.9

EXAMPLE 11

The collector used: The same as in Example 1.

The purpose: Recovery of phosphate mineral from amine flotation tailings (Florida, U.S.A.).

500 g. of tailings (-65 +200 mesh) containing 14% P_2O_5 in a siliceous gangue were mixed with 500 cc. water in a Fagergren flotation machine. The conditioning was performed with 0.5 g. reagent and about 2 cc. H_2SO_4 20%, obtaining a pH of about 4.0. The flotation was started and continued for three minutes. The float fraction, weighing 220 g., assayed 28% P_2O_5 , corresponding to a recovery of 88%.

We claim:

1. Process for the flotation-separation of natural siliceous heavy mineral ores into a floated heavy mineral fraction and a non-floated siliceous fraction, characterized in that as collector there is used at least one composition containing acid esters of phosphorus acids in which the state of oxidation of phosphorus corresponds statistically to approximately four, which composition is obtained by reacting white phosphorus with air or oxygen and at least one aliphatic hydrocarbon compound of 7 to 18 carbon atoms containing an alcoholic hydroxyl group, in the presence of an inert solvent at a temperature of from 0° C. to 45° C.

2. Process according to claim 1, characterized in that the collector is a composition corresponding statistically to a dialkyl-dihydrogen-hypophosphate.

3. Process according to claim 1, characterized in that phosphoric acid is used as activator.

4. Process according to claim 1, characterized in that said heavy mineral is ilmenite.

5. Process according to claim 1, characterized in that said heavy mineral is monazite.

6. Process according to claim 1, characterized in that said heavy mineral is rutile.

7. Process according to claim 1, characterized in that said heavy mineral is zircon.

8. Process according to claim 1, characterized in that said heavy mineral is cassiterite.

9. Process according to claim 1, characterized in that said heavy mineral is apatite.

References Cited

UNITED STATES PATENTS

2,162,494	6/1939	Trotter	209—166
3,037,627	6/1962	Hazen	209—167 X
2,661,634	12/1953	Ernsberger	260—971

FOREIGN PATENTS

978,110	12/1964	Great Britain.
1,175,623	8/1964	Germany.

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