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METHOD OF BENEFICIATING SULFIDE AND OXIDE ORES OF COPPER, MANGANESE, LEAD AND ZINC

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This invention relates to the concentration of metal values. Particularly, it relates to the use of new and novel flotation agents to effect a separation of metal values in ores from gangue. More particularly, it relates to the use of organic phosphates and pyrophosphates as flotation agents for sulfide and oxide type ores. Among such ores and minerals, to the beneficiation of which this invention is particularly adapted, are the ores of manganese and copper.

In the flotation art, ores are generally classified as being of three types. These types are sulfide, oxidized and silicate ores. Also, these different types may be floated by many collectors but in commercial practice certain collectors are preferred. For instance, the sulfide ores are generally floated in commercial practice with either the xanthate type collectors or the organic thiophosphates, sometimes referred to as "Aerofloats." The oxidized ores are normally floated by effecting a sulfidizing treatment followed by the usual sulfide collector treatment or by an unsaturated or a saturated fatty acid type collector treatment.

In general, it may be said that the flotation of oxidized ores is not entirely satisfactory although it is widely practiced in connection with a prior sulfidizing treatment or with the fatty acid collectors. This inadequateness of the present collectors for flotation of oxidized ores is particularly apparent in view of the difficulties experienced in floating manganese and copper oxidized ores by present practices.

The flotation of the oxidized ores per se normally present special problems but these problems are frequently encountered with the sulfide ores. For instance, most sulfide ores such as the pyrites have oxidized coatings and they are substantially less readily floated than freshly prepared synthetic sulfide ores. In fact, some authors have attributed from ⅓ to ¾ of the total copper loss in sulfide copper ore flotation to the presence of these oxidized surfaces. If desired, sulfidization may be used to convert the oxidized ore to the sulfide by treating the ore with sodium sulfide or related sulfides and thus achieve a reduction in the loss of metal values to tailings. This treatment is not only expensive and troublesome but frequently an excessive amount of metal values are lost to tailings.

In addition to the aforesaid limitations of the flotation agents and methods of use with oxidized ores, it should be emphasized that, as far as applicant knows, there is presently no method of selectively floating manganese ores to free them of gangue.

To further illustrate the state of the flotation art and to supply the definitions of certain terms common to this field, reference is made to Section 12, Flotation Handbook of Mineral Dressing by Arthur F. Taggert (John Wiley and Sons, Inc., fourth printing, September 1950).

The use of certain classes of phosphorous derivatives or compounds as flotation agents or flotation aids is well

known. The organic thiophosphates are used extensively as collectors in the flotation of copper sulfide ores. The organic phosphites find some use as collectors but it is frequently necessary to use them in combination with frothing agents such as pine oil to obtain a froth having the desired properties.

Besides the use of the organic phosphorous derivatives as collectors, the inorganic phosphates and phosphites have been used as flotation aids to enhance the collecting action of a collector or to suppress the collection of gangue, etc.

Although some classes of organic and inorganic phosphorous compounds are known to be helpful in the recovery of metal values by flotation, applicant has not been able to find a teaching that the organic phosphates and the organic hydrogen phosphates are capable of acting as a flotation collector. However, applicant has found them to be remarkably well suited to flotation of certain types of ores. In fact, applicant has discovered that the organic phosphates and hydrogen phosphates are capable of collecting certain ores without a preflotation treatment, for instance sulfidization.

Accordingly, a principal object of this invention is to provide a new class of flotation agents.

A further object of this invention is to provide flotation agents for collecting oxidized ore.

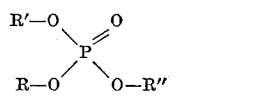
A still further object is to disclose novel agents for handling ores wherein the use of activation steps, for instance sulfidization, is unnecessary.

Another object of this invention is to provide a method and flotation agents for collecting the oxidized ores of manganese and copper as well as the sulfide ores of copper.

Still another object is to provide an economical method for collecting manganese ores from gangue by flotation.

In accordance with the aforesaid objects, I have discovered that the organic phosphates, the organic pyrophosphates, organic hydrogen phosphoric acids and the organic hydrogen pyrophosphoric acids are collectors for certain sulfide and oxidized ores and furthermore these collectors are able to float maganese ores. To the best of applicant's knowledge this has not been successfully accomplished in the past on a commercial scale. In addition to the aforesaid discovery, I have discovered that it is possible by using mixtures of the mono- and/or di-organic phosphoric acid and the tri-organophosphates to float simultaneously the sulfide and oxidized ores while depressing the gangue. Hence a method for obtaining a highly selective concentration of the desired metal values is provided.

The organic phosphates may be considered as derivatives of phosphoric acid and, in some cases, of pyrophosphoric acid, since some of the organic pyrophosphoric acids are known to undergo rearrangement to give organic orthophosphoric acid under the conditions found in the flotation cell. Accordingly, the organic phosphates or hydrogen phosphoric acids may be considered as having the following formula:



in which R is selected from the radicals consisting of alkyl, aryl, alkyl aryl or aryl alkyl and R' and R" are selected from the radicals consisting of alkyl, alkyl aryl,

aryl alkyl, aryl and hydrogen. Hence, the derivative having the formula RH_2PO_4 would be derived theoretically by replacing one of the hydrogens of phosphoric acid with an alkyl radical, for instance, and is known as an alkyl phosphoric acid. The di-substituted derivative is called a dialkyl phosphoric acid or, in the event, the substitute is aryl, it is called diaryl phosphoric acid. Likewise, the tri-substituted phosphoric acid is called trialkyl or aryl phosphate. The nature of the organic radical may vary from a methyl radical to one of twenty or more carbon atoms, or it may be paraffinic, aromatic, or mixtures of both, i.e., alkyl aryl and aryl alkyl. The exact nature of the radicals usable in my invention will be developed hereinafter.

Those collectors which function by chemical reaction with the ore have a very low but definite solubility in water and are organic compounds of the acidic, basic and salt types. These collectors are further characterized by being capable of ionizing in aqueous solutions to produce organic ions. These organic ions are capable of attaching to the mineral surface of a particle of ore. It is obvious that the polar part of these organic ions is orientated toward the ore particle while the hydrocarbon part is orientated outward from said particle. Thus, the attachment of these organic ions to the ore particle forms a water repellent surface or barrier around at least a part of the surface of the ore particle and thereby facilitates the formation of froths when the ore slurry is agitated in the presence of air.

In view of the above outlined necessary characteristics of a good collector, it would appear that it is necessary for the organic radical of applicant's collector to be of a particular size, i.e., have an upper and a lower size limit or chain length. It has been found that the organic radical should contain about 8 carbon atoms or more, as the organic phosphoric acids and phosphates containing fewer carbon atoms are frequently unsatisfactory as a collector due to appreciable water solubility. In support of this statement, it should be noted that the mono- and di-octyl phosphoric acids give froths which tend to be watery and too thin under certain conditions but, in general are rather satisfactory.

Also, it would appear that the degree of branching of the alkyl or aryl radical should affect the suitability of a particular phosphoric acid derivative. Accordingly, when the N-octyl phosphoric acids were compared with the 2-ethyl hexyl phosphoric acids, it was noticed that the 2-ethyl hexyl phosphoric acids gave foams which were sometimes slimy, voluminous and watery. Therefore, it is thought the normal alkyl derivatives may be slightly superior to the branched alkyl derivatives as collectors.

The upper limit on the size or number of carbons in the organic radical of said phosphoric or pyrophosphoric acid derivatives is determined primarily by the factors of whether the organic derivative is substantially water insoluble and non-reactive with minerals. In general, as the hydrocarbon radical approaches 16 to 22 carbon atoms in length, the organic phosphates are no longer relatively non-viscous liquids, but are solids, semisolids or viscous materials of limited water solubility. In addition to the aforesaid change in properties, the high molecular weight organic phosphates ionize to produce ions of little activity. Hence, the preferred organic phosphoric or pyrophosphoric acid derivatives contain from 10 to 14 carbon atoms but those of 8 to 14 are normally satisfactory as collectors.

The method of making the various organic phosphoric acid derivatives is well known and described in the literature. Therefore, their method of preparation does not constitute a part of this invention.

In the use of my collectors to float the mineral values, the ore is crushed and sized to at least about 60 mesh and preferably to a smaller size. The crushed and sized ore is pulped and then is ready for treatment in the flotation equipment with the collector and auxiliary agents, if any are to be used. In the flotation cell the ore pulp is contacted with air or a gas to form a froth to achieve the desired separation of metal values from the gangue. Normally, the metal values present in the froth overflow from each cell or stage. In most cases it is advantageous to use a multiple stage flotation process to treat the underflow or partially metal value barren pulp to increase the degree of separation or to enhance the degree of recovery. Also, the use of varying amounts of depressants, promoters, etc. in the different stages may be used to advantage to obtain the optimum yields and best separations.

In general, one embodiment of my invention comprises treating a crushed, sized and pulped oxidized ore with a suitable organic phosphoric acid and/or organic phosphate wherein the alkyl or aryl radical contains from 8 to 22 carbon atoms in the presence of air or gas agitation to form a froth and hence float the froth away as an overflow while the tailings go from the treater as an underflow. Where the oxidized ore is a manganese oxide ore, it usually contains appreciable rhyolite which tends to float. Therefore, a gangue depressant such as triisooctyl phosphorothionate is added to suppress the flotation of ryholite in the manganese concentrate. In most cases, it is advantageous to use several flotation cells and stages and to vary the ratio of collector and depressant added in each stage to control the selectivity. When using this technic, applicant obtained manganese flotation concentrates which were exceptionally free of gangue.

The tri-substituted organic phosphates are rather ineffective collectors for the oxidized ores of copper but are exceptionally good collectors for copper sulfide ores and the related pyrites. On the other hand, the mono- and di-organic phosphoric acids afford excellent flotation and collection action when used to treat the oxidized ores of copper.

Consequently, it is indeed fortunate that the usual method of preparing the phosphoric acids normally gives a mixture of the mono-, di- and tri-substituted derivatives of said phosphoric acid and, that this product may be used very successfully without incurring the expense of purification. Hence, the most economical and most readily available organic phosphoric acid is the mixtures sold commercially as decyl phosphoric acid, undecyl phosphoric acid, duodecylphosphoric acid, etc. These readily available commercial mixtures of the mono- and di-derivatives of phosphoric acid are particularly desirable as collectors in my invention because they frequently contain sufficient tri-organo phosphate or pyro phosphate to float any traces of sulfide ore which is frequently present with the oxide type ores. Also, it goes without saying that if these commercial mono- and di-substituted phosphates do not contain a sufficient amount of the tri-organo phosphate it may be added to the original mixture in any or all stages of the flotation process to achieve the desired level of copper reduction in the liquor going to tailings.

Although the organo phosphoric acids and phosphates are particularly well suited and even preferred collectors for the ores of copper and manganese, they are not limited to these ores. The oxide ores of lead and zinc are readily floated with the dialkyl phosphoric acids but the selectivity is only fair because these ores normally contain appreciable calcium carbonate and iron oxide. These particular impurities tend to float instead of remaining behind with the gangue. Consequently, the use of auxiliary treating agents in large amounts is necessary to achieve the desired level of selectivity.

Although a single cell or stage flotation operation is possible with my invention, a multiple cell or stage operation is frequently desirable because it permits greater freedom in the use of the collectors with auxiliary chemicals where such chemicals are needed.

The above discussion illustrates my invention in a broad

and general way but for a detailed illustration thereof the examples are set forth below.

A comparison of the action of a standard commercial oxide type ore collector with those of my invention on a manganese oxide or is shown in EXAMPLE I.

EXAMPLE I

A manganese oxide ore containing principally calcite gangue was ground and sized to 60 mesh. Then the crushed and sized ore was pulped with water. A flotation test was run on the pulp at a collector treatment of 2.0 pounds per ton of ore. The results of these tests on the above ore using different collectors are as follows:

Collector used	Concentrate, wt. percent	Tail, wt. percent
Emersol 300 [1]	8.0	92.0
Commercial Decyl Phosphoric Acid	14.00	86.0
Monooctylortho-Phosphoric Acid	22.1	77.9

[1] Emersol 300 is a commercial grade of fatty acid consisting principally of oleic acid.

These organo phosphoric acids were rated as at least as satisfactory if not better than the preferred collector for oxide type ore.

EXAMPLE II

An oxidized ore of the manganese oxide type containing 11% Mn from the Red Hill area south of Socorro, New Mexico, was crushed and sized to pass a 65-mesh screen. A preliminary flotation test with decyl phosphoric acid indicated rhyolite was being collected with the manganese. Rhyolite is a variety of silica-rich igneous rock composed of quartz, feldspar, sand and sometimes volcanic glass.

Therefore, the sized ore pulp was given a three-stage flotation treatment with varying dosages of collector and rhyolite depressant in each stage to achieve a more selective concentration of the manganese.

In the first stage of the flotation process, the ore pulp received a treatment at the rate of 2#/ton of ore with each of the following agents: Triisooctyl phosphorothionate (the ryholite depressant) and decyl phosphoric acid (the collector). This treatment gave a froth overflow from the first flotation cell consisting of a concentrated black heavy material containing a high percentage of manganese. The underflow from the first cell formed the charge to the second cell. The underflow from the first cell received an additional treatment on a pound/per ton of ore basis consisting of 1 pound of decyl phosphoric acid (DPA) and 2 pounds of triiooctyl phosphorothionate. This additional treatment of the underflow from the first cell caused the froth overflow from the second cell to the third cell to tend to become watery. Consequently, the overflow from the second stage consisting of a black heavy material containing manganese also contained some ryholite when the froth thinned. Therefore, the amount of decyl phosphoric acid was increased in this stage to prevent the froth from thinning and thus suppress the tendency of the ryholite to float. At the treatment rate of about 2 pounds of decyl phosphoric acid per ton and one pound of triisooctyl phosphorothionate per ton, a very satisfactory froth was obtained even though the manganese concentrate still contained some ryholite at this rate of treatment. The underflow pulp going to tailings from the third stage were essentially free of manganese except for a small amount of particles too coarse to be readily amendable to flotation. Hence, it is possible to float a manganese oxide type ore in conjunction with the use of a depressant to obtain manganese concentrates exceptionally free of gangue.

EXAMPLE III

Trouble is frequently experienced with iron oxides during the flotation of manganese ores. Consequently, it is necessary to resort to auxiliary agents to prevent these troubles. In illustration of this problem a manganese oxide ore containing rhyolite, which gave trouble with iron oxides and silicates during flotation, was subjected to the flotation test using auxiliary agents in addition to the collector to avoid said difficulties.

Manganese flotation test.—A 500-gram sample of the above manganese ore sized to 35 mesh was pulped and floated in a Fagergren laboratory flotation machine. Since this manganese ore gave trouble with flotation of iron oxides, it was treated with sodium cyanide (1.0#/ton of ore) and it was further treated with sodium silicate (0.5#/ton of ore) to depress quartz and silicate minerals and to disperse the silicate and iron oxide slimes. The collector treatment comprises decyl phosphoric acid (3.0#/ton of ore) and kerosene (0.5#/ton). The kerosene was added to help adjust the texture of the froth. The results of this flotation test is shown below on the dried, assayed and weighed fractions.

Fraction	Weight (grams)	Percent Mn	Distribution, Percent
Concentrate	130	37.9	77.5
Middling	24	9.0	3.5
Tails	346	3.5	19.0

EXAMPLE IV

Another 500 grams of the ore of Example III was floated on the Fagergren laboratory flotation machine. The treating agents for the pulp were as follows:

Sodium silicate (0.5#/ton), sodium carbonate (2.0#/ton), O,O,O-triisooctyl phosphorothionate (4.0#/ton) and decyl phosphoric acid (4.0#/ton).

The results of this test were as follows:

Fraction	Weight (gm.)	Assay, Mn Percent	Distribution, Percent
Concentrate	130	38.6	81.3
Tails	370	3.1	18.7

It should be noted that this flotation occurred at a pH of about 8–10.

EXAMPLE V

A copper ore, which analyzed 2.8% copper as chalcopyrite and close to 20% as pyrite, was used to run flotation tests to compare a collector of this invention, i.e., trioctyl phosphate (TOP) with that of the best commercial flotation agent for copper sulfide ores; this best commercial flotation agent for copper sulfide was potassium ethyl xanthate (Ket Xan).

The results of these tests are indicated below:

Collector	Treatment, #/ton	Concentrate grade	Recovery of Cu
Ket Xan	0.5	18.2	78
TOP	2	19.8	79

The above data obtained with these collectors indicate that the trialkyl phosphates are at least as good a collector as the preferred collectors for copper sulfide ore.

EXAMPLE VI

500 grams of an ore containing chalcocite, malachite and chrysocolla in a siliceous gangue, and analyzing 10.3% total copper was tested on a Fagergren 500-gram flotation cell. The collector used was commercial decyl phosphoric acid (1#/ton of ore) with a treatment time of ten minutes. The tailings from this cell contained 1% copper and the heads contained the rest of the copper essentially free of gangue. Again, it was demonstrated that decyl phosphoric acid is a suitable collector for copper ores of the oxidized type while the tri-substituted phos-

phoric acid, present as an impurity in this commercial product, floated the sulfide to leave most of the copper ore of the silicate type in the tailings.

EXAMPLE VII

A copper ore from the Chino mine which contained chalcocite (sulfide ore), malachite (oxide ore), and chrysocolla (silicate) was treated under flotation conditions with trioctyl phosphate. A visual inspection of the tailings indicated the chalcocite had been floated selectively and essentially completely.

The tailings were sent to a second stage flotation treatment and mono decyl phosphoric acid was added. The malachite was floated away to leave principally chrysocolla in the tails.

EXAMPLE VIII

To obtain a quantitative comparison of the effectiveness of the organic phosphates as collectors with that of two preferred commercial collector treatments, the following flotation tests were run under comparable conditions on an ore analyzing 7.3% by weight of total copper and present as chalcocite, malachite and chrysocolla in a siliceous gangue. The conditions of Runs Nos. 1, 2 and 3 are as follows:

Run No. 1

Triisooctyl phosphate was used to float the chalcocite and then the underflow was treated with decyl phosphoric acid to float the malachite.

Run No. 2

Amyl xanthate was used to float the chalcocite and then the underflow was treated with sodium sulfide and more amyl xanthate to float the malachite.

Run No. 3

Amyl xanthate was used to float the chalcocite and the underflow was treated with oleic acid to float the malachite.

The results of these comparative tests were as follows:

Run No.	Collector	Treatment Rate, #/ton	Concentrate Grade	Recovery
1	{TIOP {DPA	2 2	17.5	69
2	{Amyl xan. {Na sulfide	2	28.0	66
3	{Amyl xan. {Oleic acid	0.2 0.7	17.7	60

Again it was demonstrated that the combination of collectors useful in applicant's invention are superior to the best commercial practice for recovering copper from its ores.

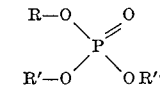
EXAMPLE IX

An oxidized ore containing 11 percent zinc, mainly as zinc carbonate, and a few percent of lead as the sulfate or carbonate was treated with decyl phosphoric acid and floated to obtain a concentrate. Although a concentrate of zinc was obtained, the selectivity of the separation was poor because the gangue consisted principally of calcium carbonate and iron oxides. Hence, it was again apparent that auxiliary collectors were needed to successfully handle some types of oxidized ores.

It is understood that the foregoing detailed discussion is for the purpose of illustration only, and it is not intended as being limiting to the spirit or scope of the appended claims.

What I claim is:

1. A method of beneficiating ores selected from the group consisting of the sulfide and oxide ores of the metals copper, manganese, lead and zinc by froth flotation to produce a froth concentrate of desired metal values which comprises effecting the froth flotation of the ore in the presence of a collector having the following formula:



in which R is an organic radical selected from the group consisting of alkyl, aryl alkyl, alkyl aryl, and aryl, and R′ and R″ are selected from the group consisting of hydrogen and the organic radicals of alkyl, aryl alkyl, alkyl aryl, and aryl, at least one of said organic radicals containing about 8–22 carbon atoms, and recovering a froth concentrate relatively rich in the desired metal values to leave the tailings relatively poorer in the desired metal values.

2. The method according to claim 1 in which the ore is selected from the sulfide and oxide ores of copper and manganese.

3. The method of claim 2 in which the collector is an alkyl derivative of phosphoric acid wherein the alkyl radical contains from about 10 to 14 carbon atoms.

4. A method of beneficiating ores selected from the group consisting of the oxide ores of the metals copper and manganese by froth flotation to produce a froth concentrate of desired metal values which comprises effecting froth flotation of the ore in the presence of a collector comprising at least one alkyl phosphoric acid having at least one hydrogen atom, at least one alkyl radical of the alkyl phosphoric acid containing 8 to 22 carbon atoms, and recovering a froth concentrate relatively rich in the desired metal values to leave tailings relatively poor in the desired metal values.

5. The method of claim 4 wherein the alkyl phosphoric acid contains from 8 to 16 carbon atoms per alkyl radical.

6. A method of beneficiating the sulfide ores of copper and manganese by froth flotation to produce a froth concentrate of desired metal values which comprises effecting the froth flotation of the ore in the presence of a trialkyl phosphate, at least one of the alkyl radicals of the trialkyl phosphate containing from 8 to 22 carbon atoms, and recovering a froth concentrate relatively rich in the desired metal values to leave tailings relatively poor in the desired metal values.

7. The method of claim 6 wherein the trialkyl phosphate contains 8 to 16 carbon atoms per alkyl radical and the ore contains copper.

8. The method of claim 6 wherein at least one of the alkyl radicals of the trialkyl phosphate is selected from the radicals consisting of octyl, nonyl, decyl, undecyl and dodecyl and the ore contains copper.

9. A method of obtaining a concentrate of metal values by flotation of at least one ore selected from the class consisting of the sulfide and oxide ores of copper and manganese with a collector comprising at least one trialkyl phosphate for the sulfide ores and at least one of the alkylphosphoric acids having at least one unsubstituted hydrogen for the oxide ores, at least one alkyl radical of the trialkyl and alkyl phosphoric acids containing 8 to 22 carbon atoms, comprising contacting a pulp of said ore with a gas in the presence of said collector to obtain a froth containing said metal values and separating the froth from the tailings.

10. The method of claim 9 wherein at least one alkyl radical of the trialkyl and alkyl phosphoric acids contains from 10 to 14 carbon atoms.

11. A method for flotation of the oxide ores of metals selected from the group consisting of copper, manganese, lead and zinc containing deleterious amounts of iron oxide and silicates comprising treating a pulp of the oxide ores with an alkyl phosphoric acid having at least one acidic hydrogen and air to form a froth in the presence of an auxiliary treating agent having iron oxide and silicate depressing effects, at least one alkyl radical of the alkyl phosphoric acid containing from 8 to 22 carbon

atoms and separating the froth concentrate from the tailings.

12. The method of claim 11 wherein the oxide ore is selected from the class consisting of copper and manganese oxide ores.

13. The method of claim 11 wherein at least one alkyl radical of the alkyl phosphoric acid contains from 10 to 14 carbon atoms.

14. The method of claim 11 wherein at least one alkyl radical of the alkyl phosphoric acid is selected from the class consisting of octyl, nonyl, decyl, undecyl and dodecyl.

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