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FLOTATION OF SPHALERITE

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This invention relates to flotation of minerals and, more particularly, to the flotation of sphalerite from zinc sulfide ore.

Sphalerite, a mineral form of zinc sulfide as it appears in zinciferous ores, can be floated by many collectors, but there are relatively few collectors known heretofore which will float untreated sphalerite without simultaneously floating non-sulfide minerals accompanying the sphalerite. Accordingly, it has been the general practice for many years to pretreat, or activate, the sphalerite by subjecting it to the action of the salt of another metal such as copper in order to render the resulting sphalerite particles amenable to selective flotation. The cost of this activation, however, is normally the largest item of reagent expense in zinc sulfide flotation mills, and therefore there has been a continuing search for a sphalerite collector which would be selective without previous activation of the sphalerite.

The collectors known heretofore to have selectivity for sphalerite have been characterized by mercapto or amino groups, or both. For example, alkyl mercaptans have been used as sphalerite collectors, but those alkyl mercaptans that are sufficiently water-soluble to be effective not only have an offensive odor but are so volatile that they are rapidly lost, whereas those that have a more acceptable volatility are so difficultly water-soluble as to be relatively ineffective collectors. The effectiveness of the mercapto group has been enhanced by the addition of an amine group, for example by the reaction between an amine and an episulfide, but the expense of making these mercapto-amines at least partially offsets the elimination of the activation cost.

We have now discovered a class of mercaptans which, although not also containing an amine group, are fully as effective as the mercapto-amines as selective collectors for sphalerite yet are relatively inexpensive, have adequate water-solubility for maximum effectiveness, and are not unduly volatile or toxic. These novel sphalerite collectors are esters of mercapto carboxylic acids.

The sphalerite collectors of our invention are used in substantially the same manner in which other collectors have been used for this purpose in the past. Thus, a zinc sulfide ore is comminuted to the same extent as in previous operations, the degree of comminution varying somewhat with the nature and source of the ore. In general, grinding of the ore to about 98% minus 48 mesh (Tyler standard) is sufficient to free the sphalerite from the gangue. The ground ore is then subjected to froth flotation without the necessity of any intermediate treatment for the activation of the sphalerite. It is also possible to charge the ground ore directly to the flotation operation without preliminary conditioning, although conditioning for as little as one-quarter minute or more appears to be somewhat beneficial. After flotation for one to several minutes, the floated sphalerite is separated and recovered by conventional means.

The esters of mercapto carboxylic acids that we use

as sphalerite collectors pursuant to our invention generally have the formula

$$R-O-\overset{O}{\overset{\|}{C}}-[C_nX]-Y$$

in which R is an alkyl or aryl-substituted alkyl radical, n is an integer such that the ester has sufficient water-solubility to function as the collector when used in an amount up to about 0.5 pound per ton of ore, X is a total of 2 times n radicals of which at least one is an SH (hydrosulfide) radical and at least one is a hydrogen, alkyl, aryl, aryl-substituted alkyl or halogen radical, and Y is a hydrogen, alkyl, aryl, aryl-substituted alkyl or halogen radical. Representative compounds of this type which we have found to be particularly effective in practicing our invention are the isopropyl, isobutyl, n-amyl, benzyl and iso-octyl thioglycolates (α-mercaptoacetates), isopropyl β-mercaptopropionate and isobutyl thiolactate.

The esters of mercapto carboxylic acid are used pursuant to our invention in an amount of at least about 0.001 pound per ton of ore and preferably in an amount of about 0.1 pound to 0.5 pound per ton of ore. All of these collectors are sufficiently soluble in water to be effective in the operation of any conventional flotation machine, particularly where the molecular weight of the compound is not substantially greater than about 200. The more limited water solubility of our esters of mercapto carboxylic acids having molecular weights above about 200 may necessitate the use of amounts in excess of 0.5 pound per ton of ore in order to effectively float the sphalerite. Regardless of their molecular weights, our novel collectors are also compatible with conventional frothing agents, although the use of such a frothing agent is not always essential.

The following examples are illustrative of the practice of our invention:

EXAMPLE I

Zinc sulfide ore from the Jefferson City mine of The New Jersey Zinc Company, containing 5.67 percent zinc as sphalerite, was wet ground at 65 percent solids to about 98 percent minus 48 mesh (Tyler) and was charged to a Fagergren laboratory flotation machine.

In test No. A, which is representative of prior art flotation and not of the practice of our invention, the ore was first conditioned for five minutes with 0.40 pound of $CuSO_4 \cdot 5H_2O$ per ton of ore. Technical grade sodium di-isopropyl dithiophosphate, the standard collector for flotation of this ore, and as a conventional frothing agent, a polypropylene glycol monomethyl ether having an average molecular weight of about 450 in the amount of 0.06 pound per ton of ore, were then added. The ore was conditioned with these reagents for an additional two minutes and then floated for two minutes. A second collector addition was thereafter made, the ore was conditioned for one-half minute, and then the ore was floated for an additional two minutes.

In tests Nos. B, C, D, E, F and G, which are illustrative of the practice of our invention, no copper activator was employed. The same conventional frother and the collector specified in Table 1 were added, the ore was conditioned for one-half minute and was then floated for two minutes. A second addition of the same specified collector was thereafter made, the ore was conditioned for one-half minute, and then the ore was floated for an additional two minutes.

In all of the tests, the material floated off during the

two flotation periods was combined, filtered, dried and analyzed for zinc. The results obtained from these tests are given in Table 1.

Table 1

Test No.	Collector		Percent of Sulfide Zinc Floated	Tailing, Percent Sulfide Zinc
	Type Used	Usage, Lb. Per Ton of Ore		
A	Sodium Di-isopropyldithiophosphate	0.040	98.8	0.086
B	Isopropyl Thioglycolate	0.100	98.8	0.088
C	Isobutyl Thioglycolate	0.128	99.2	0.064
D	Benzyl Thioglycolate	0.165	98.6	0.102
E	Iso-octyl Thioglycolate	0.108	95.8	0.287
F	Isopropyl β-Mercaptopropionate	0.116	99.0	0.073
G	Isobutyl Thiolactate	0.101	99.2	0.057

EXAMPLE II

Zinc sulfide ore from the Friedensville mine of The New Jersey Zinc Company, containing 4.89 percent zinc as sphalerite, was floated by the procedure of Example I with variations as follows:

In test No. H, which is representative of prior art flotation and not of the practice of our invention, the ore was conditioned for five minutes with 0.60 pound of $CuSO_4 \cdot 5H_2O$ per ton of ore and was then subjected to froth flotation with technical grade sodium di-isopropyldithiophosphate, the standard reagent for flotation of this ore.

In tests Nos. J, K, L and M, which are illustrative of the practice of our invention, the ore was subjected to froth flotation with the specified esters of thioglycolic acid without prior conditioning with a copper salt.

The results of these tests are given in Table 2.

Table 2

Test No.	Collector		Percent of Sulfide Zinc Floated	Tailing, Percent Sulfide Zinc
	Type Used	Usage, Lb. Per Ton of Ore		
H	Sodium Di-isopropyldithiophosphate	0.05	96.1	0.23
J	Isopropyl Thioglycolate	0.10	94.9	0.31
K	Isobutyl Thioglycolate	0.10	95.6	0.27
L	n-Amyl Thioglycolate	0.10	95.4	0.27
M	Iso-octyl Thioglycolate	0.22	94.7	0.13

It will be seen, accordingly, that the use of esters of mercaptocarboxylic acids as collectors for sphalerite pursuant to our invention makes possible high recoveries of zinc values from a wide variety of zinc sulfide ores without the expense of prior activation with a salt of another metal.

Although these zinc sulfides have colors varying from black and brown through the red, green, yellow and white, and are generally referred to as "sphalerite," they are often termed "marmatite" when they contain more than about 10% iron. The method of our invention applies equally well to all of these marmatites.

We claim:

1. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector 0.001 to 0.5 pound per ton of ore of an ester of a mercapto carboxylic acid which has sufficient water-solubility to function as the collector when used in said amount.

2. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector an ester of a mercapto carboxylic acid having a molecular weight not substantially greater than 200.

3. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector an effectively water-soluble ester of a mercapto carboxylic acid having the formula

$$R-O-\overset{O}{\overset{\|}{C}}-[C_nX]-Y$$

in which:

R is a radical of the group consisting of alkyl and aryl-substituted alkyl radicals,

n is an integer such that the ester has sufficient water-solubility to function as the collector when used in an amount up to about 0.5 pound per ton of ore,

X is a total of 2*n* radicals of which at least one is an SH radical and at least one is a radical of the group consisting of hydrogen, alkyl, aryl, aryl-substituted alkyl and halogen radicals,

and Y is a radical of the group consisting of hydrogen, alkyl, aryl, aryl-substituted alkyl and halogen radicals.

4. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector between about 0.001 and 0.5 pound per ton of ore of an effectively water-soluble ester of a mercapto carboxylic acid having the formula

$$R-O-\overset{O}{\overset{\|}{C}}-[C_nX]-Y$$

in which:

R is a radical of the group consisting of alkyl and aryl-substituted alkyl radicals,

n is an integer such that the ester has sufficient water-solubility to function as the collector when used in an amount up to about 0.5 pound per ton of ore,

X is a total of 2*n* radicals of which at least one is an SH radical and at least one is a radical of the group consisting of hydrogen, alkyl, aryl, aryl-substituted alkyl and halogen radicals,

and Y is a radical of the group consisting of hydrogen, alkyl, aryl, aryl-substituted alkyl and halogen radicals.

5. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector an effectively water-soluble ester of a mercapto carboxylic acid having the formula

$$R-O-\overset{O}{\overset{\|}{C}}-[C_nX]-Y$$

in which:

R is a radical of the group consisting of alkyl and aryl-substituted alkyl radicals,

n is an integer such that the ester has sufficient water-solubility to function as the collector when used in an amount up to about 0.5 pound per ton of ore,

X is a total of 2*n* radicals of which at least one is an SH radical and at least one is a radical of the group consisting of hydrogen, alkyl, aryl, aryl-substituted alkyl and halogen radicals,

and Y is a radical of the group consisting of hydrogen, alkyl, aryl, aryl-substituted alkyl and halogen

radicals, the molecular weight of said ester being not substantially greater than about 200.

6. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector isopropyl thioglycolate.

7. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector isobutyl thioglycolate.

8. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector benzyl thioglycolate.

9. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector isopropyl β-mercapto propionate.

10. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector isobutyl thiolactate.

11. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector iso-octyl thioglycolate.

12. In the method of recovering sphalerite from a ground zinc sulfide ore which comprises subjecting the ground ore to froth flotation in the presence of a flotation collector and separating the thus-floated sphalerite, the improvement which comprises using as the collector n-amyl thioglycolate.

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