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FLOTATION REAGENTS AND METHOD OF USE

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This invention relates to the recovery of values from ores by subjecting the same to a flotation operation in the presence of certain reagents.

I have discovered that certain organic substances of the general formula RSH (in which R denotes a hydro-carbon radical, S—sulphur, and H—hydrogen), such as mercaptans and thiophenols, are particularly good collectors of copper minerals, oxidized as well as sulphides, as well as of the sulphides of zinc. Likewise the oxidation products of these organic hydro-sulphides such as the sulphides and di-sulphides are substantially as good collectors as the mercaptans themselves for the sulphide minerals only.

The use of these reagents in the recovery of minerals by flotation is of particular advantage in that they are not good collectors for iron sulphides such as pyrite or pyrrhotite, and hence their use on pyritic copper ores is particularly valuable in that they collect the copper minerals to the more complete exclusion of the iron minerals than is obtained through the use of other collectors, of which the xanthates are typical.

The ability of mercaptans to collect oxidized copper minerals makes the recovery of the oxidized content of sulphide ores more efficient since from 1/3 to 3/4 of the total copper loss in sulphide copper ores by flotation is due to their oxidized content.

The mercaptans require less alkaline circuits than the xanthates for the securing of conditions which result in the depression of iron minerals and therefore the use of the former in place of xanthates effects economies in the use of lime or corresponding alkali.

The higher alkyl mercaptans, that is, those in the series higher than ethyl mercaptan, to wit, propyl, butyl, amyl, hexyl, heptyl, octyl, are of particular advantage because of their greater collecting ability and their lesser volatility as compared to the mercaptans lower in series. The lesser volatility is of prime importance from a practical standpoint because it lessens the discomfort caused by the semi-poisonous vapors and loss of reagent.

I have discovered that the oxidation products of the mercaptans, that is, the sulphides and di-sulphides, are substantially as good collectors for the sulphide ores as the mercaptans themselves. On the other hand, unlike mercaptans they do not react with dissolved base metal salts so that they can be used with circuits containing various amounts of these salts without loss. In the case of certain ores the use of sulphides and di-sulphides makes possible a considerable saving in the alkaline reagents which otherwise are required to eliminate the soluble salts before using mercaptans or other flotation reagents, such as the xanthates.

As an illustration of the depressing effect of mercaptans upon iron minerals as compared with the xanthates, a flotation operation conducted in a circuit containing pure pyrite in the presence of 0.05 lb. per ton of potassium ethyl xanthate, recovered the entire amount of the iron. Using the same amount of thio-beta-naphthol a concentrate was obtained which contained 97% of the iron. When pure chalcocite was subjected to a flotation operation under the same circumstances with the above two reagents the recovery was 62% and 96% respectively. In the same manner the recoveries of these minerals with 0.03 lb. per ton of potassium ethyl xanthate and isoamyl mercaptan, is respectively 93% and 86% for the pyrite and 57% and 92% for the chalcocite.

Similarly, in synthetic mixtures of pyrite and chalcocite, xanthate favors the recovery of pyrite, while mercaptans favor the recovery of the copper mineral. Upon mixtures consisting of 25 grams of minus 200 and plus 400 mesh pure pyrite, and 25 grams of the same size pure chalcocite, the following recoveries were obtained with amyl xanthate and amyl mercaptan, each used in the amount of .03 lb. per ton.

Reagent	Pyrite recovery	Chalcocite recovery
	Percent	Percent
Amyl xanthate.....	98	93
Amyl mercaptan.....	82	96

The pyrite which occurs in ores is generally substantially less floatable than the pure pyrite used in the above tests. This is probably due to the presence of oxidized coatings on its surface. The absolute values obtained in tests with ores are therefore not in agreement with those obtained with pure minerals, but the relatively greater floatability of pyrite with xanthate and chalcocite with mercaptan again manifests itself. For instance, a copper ore containing 1.72% copper, largely as chalcocite and 4.3% iron, largely as pyrite, was subjected to flotation with the following reagents, with the recoveries indicated.

Reagent	Lb. per ton	Iron recovery	Copper recovery
		Percent	Percent
Ethyl xanthate.....	0.05	72	81
Amyl xanthate.....	0.05	91	92
Amyl mercaptan.....	0.05	74	93

In all of the above quoted tests a frother was used in conjunction with the various collectors, the amount of frother being the same in each case.

I have also found that the mercaptans are par-

particularly well suited to collect oxidized copper minerals such as malachite, azurite, cuprite and melaconite. Thus an 80% recovery of malachite required 1.3 lbs. per ton isoamyl mercaptan or 1.9 lbs. per ton n-butyl mercaptan, whereas 2.0 lbs. per ton isoamyl xanthate and 4.1 lbs. per ton n-butyl xanthate were required to give the same recovery. Similar results were obtained with azurite.

A particularly good flotation of oxidized copper minerals by mercaptans is of interest in the flotation of sulphide ores since the greater portion of the copper loss in such minerals is due to the presence of the values in oxidized form. A sulphide copper ore carrying chalcopryrite as the principal copper mineral, assaying 1.95% copper, of which 0.17% was oxidized copper, gave a tailing of 0.26% copper when floated with 0.10 lb. per ton sodium ethyl xanthate. The copper content of the tailing was reduced to 0.12% when isoamyl mercaptan was substituted pound for pound for xanthate.

The following data illustrates the advantage secured from the use of higher mercaptans, showing the amount of reagent in pounds per ton required to float 80% of the ore indicated.

Reagent	Minus 100 plus 800 mesh chalcocite	10:40 mixture of minus 100 plus 600 mesh malachite and calcite
Ethyl mercaptan.....	0.14	2.8
n-Propyl mercaptan.....	0.06	1.9
n-Butyl mercaptan.....	0.035	1.3
Isoamyl mercaptan.....	0.02	1.3

In the above experiments the mercaptans or thioalcohols were added to the flotation cell as alcoholic solutions. Obviously the reagent may be added to the ball mill prior to flotation or to the flotation cell or to some conditioning or emulsifying tank between the grinding and flotation stages. Reagent additions may be made in the solid or liquid form or in solutions in some inert solvent such as methyl alcohol, an amine, a phenolic compound or one of the usual flotation oils, such as pine oils. The greater solubility of mercaptans as compared with thiophenols is of distinct advantage in this particular.

The use of the higher hydrosulphides is advantageous as compared with the use of the lower hydrosulphides in that the former are considerably less volatile than the latter and this, together with the fact that smaller amounts of the higher hydrosulphides are required, minimizes the danger of the reagent occurring in the air to a dangerous concentration.

Further, I have discovered that the oxidation products of organic hydrosulphides, especially sulphides and disulphides, are substantially as good collectors for sulphide minerals as are the hydrosulphides themselves. Copper-bearing sulphide minerals in particular are readily floated by organic sulphides and disulphides.

Unlike organic hydrosulphides, organic sulphides do not react with dissolved base-metal salts. Flotation of sulphide ores containing soluble salts is therefore prohibited if organic hydrosulphides are used as reagents unless the pulp is first freed of the soluble salts by the addition of a precipitation agent or other metal ion abstracting agent. The use of sulphides or disulphides of the above type obviates the necessity and cost of adding such a precipitation agent.

The following table illustrates a flotation operation conducted upon the copper-bearing sulphide mineral, chalcocite.

Reagents	Recovery percent
0.05 amyl mercaptan.....	100
0.05 amyl mercaptan+0.25#/T hydrated CuSO ₄	27
0.05 amyl sulphide.....	100
0.05 amyl sulphide+0.25#/T hydrated CuSO ₄	99
0.05 amyl disulphide.....	100
0.05 amyl disulphide+0.25#/T hydrated CuSO ₄	98

Similarly with a copper ore in which the copper existed as chalcopryrite and chalcocite, together with some copper in solution, the following results were obtained.

Reagent	Amount of reagent	Recovery percent
Benzyl mercaptan.....	0.10	40
Benzyl mercaptan.....	0.10	84
+Lime.....	4.0	87
Benzyl disulphide.....	0.10	87

I have further discovered that mercaptans or thiophenols are much more efficient as flotation reagents for sulphide zinc-bearing ores than xanthates.

It has been known for some time that the use of soluble copper salts makes zinc sulphides more amenable to flotation reagents. I have found that the beneficial effects of copper salts in the flotation of zinc sulphide is due to the formation of a thin coating of copper sulphide upon the surface of the mineral and furthermore that the copper activated sphalerite is particularly amenable to flotation by reagents which are well suited to the flotation of cupriferous ores. Among these reagents are the organic hydrosulphides and their oxidation products as above set forth.

I have found that the use of mercaptans or thiophenols in floating copper activated sphalerite makes possible the floatability thereof over a substantially-extending alkaline range, which is not secured by the use of xanthates. Thus, with a certain amount of xanthate, material depression results at pH 12, whereas such an effect does not manifest itself when using the same amount of the corresponding mercaptan until about pH 13. This discovery is of practical value in the treating of iron-bearing zinc ores or pyritic copper ores. It is illustrated in the following table:

Reagents	pH tailing pulp	Recoveries, percent	
		Zn	Fe
0.75#/T CuSO ₄ , 5 H ₂ O.....	10.8	78	21
0.10 K. ethyl xanthate.....			
2.0 CaO.....			
0.75#/T CuSO ₄ , 5 H ₂ O.....	10.6	92	12
0.08 amyl mercaptan.....			
2.0 CaO.....			
0.75#/T CuSO ₄ , 5 H ₂ O.....	12.2	89	5
0.08 amyl mercaptan.....			
4.0 CaO.....			

A great many organic compounds of the general formula RSH are known and probably many others exist which have not been specifically identified. I have found that ethyl, propyl, butyl, amyl, hexyl and heptyl mercaptans as well as

their oxidation products, are particularly efficient for the purpose set forth. Broadly speaking, the reactions of these various compounds are similar and hence they are to be construed in this application as being typical and I do not wish to be limited specifically to any of the particular reagents named, but the claims appended hereto should be construed broadly.

What I claim is:

10 1. A method of recovering values from oxidized ores which consists in subjecting the same to a flotation operation in the presence of an alkyl mercaptan higher in the series than ethyl mercaptan.

15 2. A method of recovering values from oxidized copper and zinc ores which consists in subjecting the same to a flotation operation in the presence

of an alkyl mercaptan higher in the series than ethyl mercaptan.

3. A method of recovering oxidized copper ore values from the gangues in crude copper ore, which consists in subjecting the crude ore to a froth flotation operation in the presence of amyl mercaptan.

4. A method of recovering values from ores containing both sulfides and oxidized products of the same metal which comprises subjecting the same to a flotation operation in the presence of an alkyl mercaptan higher in the series than ethyl mercaptan.

5. A method according to claim 4 in which the ore contains copper sulfide and oxidized copper compounds.

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