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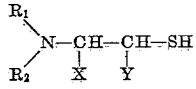
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FLOTATION OF ORES

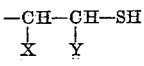
Lionel B. Luttinger, Stamford, Conn., assignor to American Cyanamid Company, New York, N.Y., a corporation of Maine

No Drawing. Filed Nov. 6, 1959, Ser. No. 851,254
8 Claims. (Cl. 209—166)

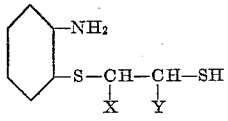
This invention relates to the flotation of zinc sulfide ores. More specifically, this invention relates to a method of separating zinc sulfide from ores, which comprises the steps of comminuting said ores, subjecting the comminuted ores to froth flotation in the presence of a promoter of the formula



in which each of R_1 and R_2 may be hydrogen, an organic radical or another



group, X and Y each may be either hydrogen or alkyl; or a promoter of the formula

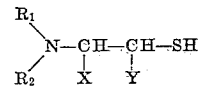


in which X and Y have the same meaning as above.

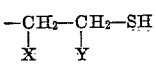
Sphalerite, zinc sulfide, cannot ordinarily be floated with the common reagents used in processing unless the ground ore is first conditioned ("activated") with a copper salt. The amounts of the latter vary with different ores but a quantity equivalent to from 0.5 to 2.0 pounds per ton of ore is typical. One result of this is that a large part of the cost of such flotation is represented by the copper salt. Further, the use of such copper salts frequently introduces a further contaminant into the floated material which must be later separated. There is consequently, a need for a method of flotation of zinc sulfide without prior activation.

I have found a method of floating zinc sulfide from its ores using a class of promoter entirely different from those usually employed in zinc flotation. This class of promoter which is represented by the formula given above is especially advantageous in that it is so active that prior activation of the zinc sulfide is not needed in many cases. It is also advantageous, however, in that with small amounts of activation even more complete separation of the zinc sulfide from the ore can be obtained than was possible with prior promoters.

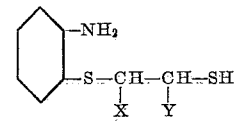
In the method of my invention a zinc sulfide ore is comminuted to free the zinc mineral from gangue generally by grinding the ore to about 65 mesh. The comminuted ore is then subjected to froth flotation in the presence of at least 0.001 pound per ton of said ore of a promoter of the formula



in which each of R_1 and R_2 may be hydrogen, an organic radical or another

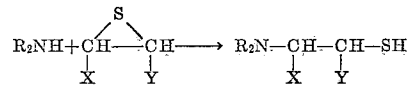


group, and X and Y each may be hydrogen or alkyl or a promoter of the formula



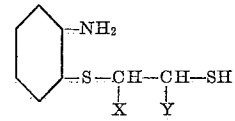
in which X and Y are as defined above. After the froth flotation step, the floated zinc sulfide is separated and recovered.

The promoters which are used in the method of my invention are defined by the above formulae. They are often used in the form of a salt such as the hydrochloride, sulfate, or the like. They are prepared by the reaction of an amino compound having a replaceable hydrogen on the nitrogen with an episulfide. This reaction can be represented by the following equation



Thus when X and Y are hydrogen the episulfide is ethylene-sulfide. Higher episulfides can readily be used in which case either or both X and Y become alkyls. Similarly, the equation above shows a secondary amine. The amine can also be a primary amine in which case it is possible to have two mercaptoethyl or other mercaptoalkyl groups on the nitrogen. The greater the number of mercapto groups, the better the promoter.

When o-aminothiophenol is used in the reaction the mercaptoethylation takes place on the sulfur of the mercaptan group, giving the second type of promoter used in my invention, namely those of the structure



in which X and Y are as defined above.

Episulfides which may be used in the preparation of my promoters include any episulfide. In general, however, the episulfides derived from the aliphatic series are preferable. In ordinary practice, the ones which will be principally used will be ethylene sulfide, propylene sulfide, butylene sulfide, and the like although the higher episulfides, while more difficult to obtain and more costly, can also be used.

The amines which are reacted with the episulfides to form the promoters of my invention include any amino compound having a replaceable hydrogen on the nitrogen. These include the alkyl amines such as methylamine, ethylamine, isopropylamine, hexylamine, laurylamine, octadecylamine; the secondary dialkyl amines such as dimethylamine, diethylamine, methylethylamine, methylpropylamine, diisopropylamine, butylmethylamine, diamylamine, laurylethylamine and the like; substituted alkyl amines such as cyanoethylamine, chlorethylamine and the like; aryl amines such as aniline, toluidine, anisidine, cresidine, xylidine, naphthylamine, aminobiphenyl, chloraniline, bromaniline, diphenylamine and nuclear substituted products thereof; aralkyl amines such as benzylamine; and cyclic amines such as morpholine, piperidine, pyrrolidine, cyclohexylamine and the like. In addition, ammonia itself can be used which permits at least two mercapto alkyl groups on the nitrogen and possibly three. In this latter case the R of the general formula becomes a second mercapto alkyl group, such

as a mercapto ethyl or the like. When one starts with a primary amine, there being two replaceable hydrogens, it is possible to put up to two mercapto alkyl groups on the same nitrogen, whereas secondary amines admit a substitution of one mercapto alkyl group.

Among the compounds which may be formed by the above reactions and used as promoters in my invention there may be named the following:

2-chloro-N-(2 mercaptoethyl)-aniline hydrochloride
N-(2 mercaptoethyl)-piperidine hydrochloride
N-(2-mercaptoethyl)-morpholine hydrochloride
N-butyl-2-mercaptoethylamine hydrochloride
N-(2 mercaptoethyl)-piperidine methiodide
N-(3 mercaptopropyl)-piperidine hydrochloride
Dibutyl-2-mercaptoethylamine hydrochloride
N-(2 mercaptopropyl)-piperidine hydrochloride
Cyclohexyl 2 mercaptoethylamine hydrochloride
Butyl ethyl 2-mercaptoethylamine hydrochloride
N-2 mercaptoethyl-aniline hydrochloride
N-(2 mercaptoethyl)-N-methylaniline
N-(2 mercaptoethyl)-pyrrolidone
Bis-(isobutyl)-2-mercaptoethylamine
Benzyl butyl 2-mercaptoethylamine
2-mercaptoethyl bis(n-propyl)amine
sec-Butyl-2-mercaptoethylamine
1-(2 mercaptoethyl)-4-(thiazolyl-2)-piperazine dihydrochloride
1-(2 mercaptoethyl)-4-(pyridyl-2)-piperazine dihydrochloride
N-(2 mercaptoethyl)-2,2,4,6-tetramethyl piperidine
n-Butyl bis-(2-mercaptoethyl) amine
sec-Butyl bis-(2 mercaptoethyl) amine
Mercaptoethylamine hydrochloride
N,N bis-(2 mercaptoethyl)-aniline
N,N bis (2 mercaptoethyl)-2-naphthylamine

Of the above compounds, especially to be preferred are the mercaptoethyl derivatives of aniline and substituted aniline such as 2-chloro N-(2-mercaptoethyl) aniline hydrochloride, N(2-mercaptoethyl) aniline hydrochloride and N,N-bis(2-mercaptoethyl) aniline hydrochloride as well as n-butyl bis(2 mercaptoethylamine)hydrochloride.

Although we do not wish to be limited to the theory of how this invention works, it should be noted that under the conditions of flotation these compounds may be partially transformed into disulfides and consequently, to a certain extent such reactions may occur in the flotation mixture. Disulfides corresponding to these mercaptans have been tested and found to be equally operable although somewhat slower than the mercaptan and should be regarded as their equivalent.

The promoters are used in my invention in a usage of at least 0.001 lb. per ton of ore. Usually considerably larger quantities are desirable such as 0.1 lb. per ton of ore. The usage will of course vary with each promoter since some of the promoters are much more active.

The promoters of my invention may be used either as the free amine or as their salts such as the hydrochloride. They are preferably used as the salts, since more rapid dispersion into the flotation mixture is obtained. However, since some of these flotations may be on the alkaline side, the salts are sometimes transformed into the free amines in situ. The free amines and salts should be regarded as equivalent.

It is an advantage of my invention that if the proper conditions are used activation is not necessary for the flotation of zinc sulfide. This is especially true of the preferred species such as the mercaptoethyl anilines and the bis(2 mercaptoethyl)butylamine. It is contemplated that the method of my invention will be used with or without activation as desired. I have a new class of promoter with advantages even when a copper ion activation is used. Some ores contain zinc sulfide in a form in which it is extremely difficult to float and these ores require the use of a copper activating agent such as copper sulfate. In such cases it is possible with my promoters to employ activators in much lower amounts than with the promoters such as xanthates or dithiophosphates commonly used in flotation practice. At present the cost of copper activators frequently amounts to 60–75% of the total chemical costs in the flotation of zinc ores, the use of the promoters of this invention with no activators or with very low quantities of activators represents a considerable practical advantage over the usual promoters. But even here one can obtain a better recovery with the procedures used in my invention than is obtainable with the standard reagents.

My invention can be illustrated by the following examples.

EXAMPLE 1

A southeastern ore containing 3.8–4.0% zinc as sphalerite is ground at 50% solids to minus 65 mesh. It is charged to a Fagergren machine. Where a metal activator is used, the copper sulfate pentahydrate is added and the ore is conditioned with this for about 5 minutes. If no conditioner is used, this step is omitted. The collector is then added and the ore is conditioned for 10 minutes with it. 0.09 lb. per ton portion of ore of pine oil frother is then added and the ore is floated at 22% solids for 2 to 3 minutes. The floated material is skimmed off, filtered, washed, dried and analyzed for zinc. The tailings are likewise filtered, washed, dried and analyzed for zinc.

The results obtainable by these tests are given in Table I.

Table I

Run No.	Quantity of $CuSO_4$ Activator (lb./ton of ore)	Collector		Flotation	
		Chemical Identity	Usage (lb./ton of ore)	Percent of Zn Floated	Tailing Analysis, Percent Zn
1	0.5	Di-n-butyl-2-mercaptoethyl amine·HCl.	0.1	98	0.097
2	None	----------	0.1	98	0.097
3	None	----------	0.1	90–95	0.061
4	None	n-Butyl bis (2-mercaptoethyl) amine.	0.2	95	0.091
5	None	sec-Butyl bis (2-mercaptoethyl) amine.	0.1	99	0.061
6	0.5	N-(2-mercaptoethyl) aniline·HCl.	0.016	95	0.06
7	None	do	0.1	98	0.09
8	0.5	Bis(2-N-phenylaminoethyl) disulfide.	0.1	95	0.1
9	None	N-(2-mercaptoethyl)-N-methylaniline·HCl.	0.1	95	0.071
10	None	2-chloro-N-(2-mercaptoethyl) aniline·HCl.	0.1	80	Not analyzed
11	0.5	N-(2-mercaptoethyl) piperidine·HCl.	0.1	95	0.101
12	0.5	N-(2-mercaptopropyl)piperidine·HCl.	0.1	95	0.08
13	None	N,N-bis(2-mercaptoethyl)aniline.	0.1	95	0.01
14	None	N-(2-mercaptoethylanisidine.	0.1	90	0.061
15	None	N-(2-mercaptoethyl)1-naphthylamine.	0.1	80	0.441
16	None	S-(2-mercaptoethyl)-o-aminothiophenol.	0.1	95	0.051
17	0.5	2-mercaptoethylamine·HCl.	0.1	90	0.22
18	0.5	n-Butyl(2-mercaptoethyl)amine·HCl.	0.1	98	0.091
19	0.5	n-Butyl ethyl (2-mercaptoethyl)-amine·HCl.	0.1	90	0.142
20	0.5	Cyclohexyl (2-mercaptoethyl) amine·HCl.	0.1	98	0.081
21	0.5	N-(2-mercaptoethyl)morpholine·HCl.	0.1	90	0.151

EXAMPLE 2

A western zinc ore having 12.3% zinc as sphalerite is floated by the procedure of Example 1, using the following variations:

Run 1.—The ore is conditioned with 0.43 lb. per ton of ore of soda ash and 1.5 lbs./per ton of ore of $CuSO_4 \cdot 5H_2O$. It is then subjected to froth flotation with 0.2 lb. per ton of ore of technical grade sodiumdiethyldithiophosphate, the standard reagent for the flotation of this ore.

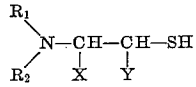
Run 2.—The ore is subjected to froth flotation (without conditioning with cupric ion) using 0.2 lb. per ton of ore of N,N-bis(2-mercaptoethyl)aniline.

The results of these runs are as follows:

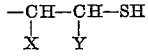
Run	Zn Recovered, Percent	Analysis of Tailing Percent of Zn
1	90	0.15
2	95	0.04

I claim:

1. A method of separating zinc sulfide from ores containing it which comprises comminuting said ore to free the zinc minerals subjecting said comminuted ore to froth flotation in the presence of at least 0.001 lb. per ton of said ore of a promoter of the formula



in which each of R_1 and R_2 is selected from the group consisting of hydrogen, an organic radical, and a further group



and X and Y are selected from the group consisting of hydrogen and alkyl, separating the floated zinc sulfide from the tailings and recovering said zinc sulfide.

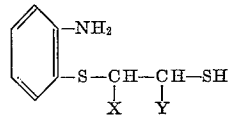
2. The method of claim 1 in which the said ore is unactivated.

3. The method of claim 2 in which the promoter is N,N-bis(2-mercaptoethyl)aniline.

4. The method of claim 2 in which the promoter is N-(2-mercaptoethyl)aniline.

5. The method of claim 2 in which the promoter is dibutyl (2-mercaptoethyl)amine.

6. A method of separating zinc sulfide from ores containing it which comprises comminuting said ore to free the zinc minerals, subjecting the said comminuted ore to froth flotation in the presence of at least 0.001 pound per ton of said ore of a promoter of the formula



in which each of X and Y are selected from the group consisting of hydrogen and alkyl.

7. The method of claim 6 in which the promoter is o(2-mercapto ethyl thio)aniline.

8. The method of claim 2 in which the promoter is bis-(2-mercaptoethyl)butylamine.

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