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MINERAL FLOTATION

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This invention relates to mineral flotation. More particularly the invention relates to the concentration of minerals in sulfide ores with a 2-mercaptobenzimidazole flotation collector.

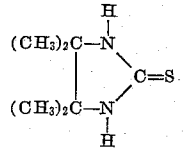
A primary object of the invention is to provide new flotation reagents.

A further object of the invention is to provide new and effective collectors for the flotation of sulfide ores.

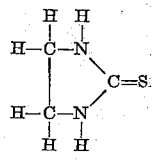
A still further object is to provide new collectors for the flotation of sulfide ores which are especially effective in floating zinc, lead and copper sulfides.

A still further object of the invention is to provide new collectors for the selective flotation of zinc sulfide in the recovery of zinc sulfide from lead tails.

It has been proposed heretofore to utilize 2-thio - 4,4,5,5, tetramethyltetrahydroimidazole, which has the structure



as a collector in the flotation of copper sulfide. See for example U. S. Patent 1,801,319 granted April 21, 1931 to Moses, Hess and Perkins. In spite of this disclosure, flotation agents of this type have not found favor in industry. It has been found, however, that compounds containing the thiotetrahydroimidazole ring structure are not useful in selective flotation of zinc sulfide in lead-zinc sulfide ores. The simplest of this series, namely ethylene thiourea, which has the



structure is wholly unsatisfactory for this purpose and a closely allied compound, 1-hydroxyethyl-2-mercapto-4,5-dihydroimidazole has been shown to act not as a collector on lead-zinc sulfide ores but, on the contrary, as a depressor.

We have now found that the above objects are accomplished and the aforementioned limitation of the prior art are avoided by effecting the flotation in the presence of certain mercaptoimidazoles as distinguished from the mercaptohydroimidazoles of the prior art. We have found for example that certain 2-mercapto-4,5-aryleneimidazoles are effective for the flotation of copper sulfide, markedly more so than the thiotetrahydroimidazole of the prior art, and, what is even more surprising, that these same compounds are unusually effective for the flotation of zinc sulfides. We have found also that these same compounds are effective for the flotation of lead sulfides.

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The 2-mercapto-imidazoles which are useful in floating sulfide ores according to the invention are compounds containing not more than twelve carbon atoms which have an aromatic ring fused with an imidazole ring and which are free of hydrophilic, or water solubilizing substituents other than the mercapto group. The compounds may be referred to generically as 2-mercapto-4,5-aryleneimidazoles which are free of hydrophilic substituents and contain not more than twelve carbon atoms.

The 2-mercapto-4,5-aryleneimidazoles useful in the processes of the invention are well known in the art and may be prepared in any suitable manner as, for example, from carbon disulfide and ortho - arylenediamines. Suitable compounds, for example, may be prepared by the interaction of carbon disulfide or thiophosgene with ortho-phenylenediamine and 1,2-naphthylenediamine as well as the homologues thereof, such as 3,4-diaminotoluene, and other alkyl derivatives thereof. By suitable choice of reagents, it is possible to produce 2-mercaptobenzimidazoles having one or more of the nuclear hydrogen atoms replaced by an alkyl radical, or radicals, having less than a total of six carbon atoms; 2-mercaptobenzimidazoles having one or more of the nuclear C-hydrogen atoms replaced by an alkoxy radical, or radicals, having less than a total of six carbon atoms; 2-mercaptobenzimidazoles containing a methyl group attached to either the carbocyclic ring or heterocyclic ring and 2-mercaptonaphthimidazoles containing a methoxy group attached to the carbocyclic ring. Suitable substituent groups include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, t-butyl, mixed amyl, t-amyl and the corresponding alkoxy radicals. (Lellmann, Liebig's Annelen der Chemie, 221, pages 9 and 10; Billester, Steiner, Ber. der Deutschen Chemischen Gesellschaft,20, pages 229 to 231; Kyn. Journal für Praktische Chemie, (2), 75, page 324).

The collectors of the invention are difficultly soluble in water and soluble in alkaline solutions. They may be introduced into the flotation circuit as such or in solution in alkaline solutions or as their water soluble salts, such as the sodium, potassium, or other alkali metal salt. When the

material is introduced as such, i. e., without solubilizing alkali, it is desirable that it be conditioned by fine grinding to micron size with or without admixture of inert solids, such as clays, as well as wetting agents and/or dispersing agents. Suitable wetting agents for this purpose include such anionic wetting agents as the aralkyl sulfonates, particularly the alkyl benzene sulfonates, and such non-ionic wetting agents as the polyether and polyester condensation products. The collectors may also be compounded with solid alkalies, such as sodium carbonate and lime, to provide a material which can be applied more readily by the mill operator.

In carrying out froth flotation in accordance with the invention, a 2-mercapto-4,5-aryleneimidazole which is free of hydrophilic substituents and contains less than twelve carbon atoms is incorporated into the mineral pulp in any suitable manner according to the practices of this particular art and the thus prepared mineral pulp subjected to froth flotation in any suitable apparatus according to the various practices well understood by those skilled in the art. The reagents, for example, may be added to the grinding mills in the preparation of the mineral pulp, or they may be added to the ground pulp in suitable conditioners, or they may be added directly to the flotation cells. However, introduced or incorporated in the mineral pulp, the reagents of the invention are effective in very small quantities. To effect the processes of the invention therefore, it is only necessary to incorporate in the mineral pulp a small amount of the collector. Actually less than one pound of these novel collectors per ton of ore to be treated suffices and, in most cases, as little as one-tenth of a pound or less is satisfactory.

It is to be understood that various conditioning agents may be incorporated in the various flotation circuits according to the practices well understood and common in the art. Thus, agents adapted to adjust the pH of the circuit may be introduced. Lime and sodium carbonate, for example, are commonly employed to adjust the alkalinity as required to give the best selective flotation. Similarly, frothers and other conditioners may be added as required to produce a desirable froth. Depressors and activators also may be added as required. Sodium cyanide and zinc sulfate, for example, may be incorporated in a lead circuit to act as depressors for zinc, while copper sulfate may be added to the lead tail in a zinc circuit to activate the zinc.

The collectors of the present invention are particularly effective in floating zinc sulfide. This is suitably illustrated in the following example. The parts designated herein, unless otherwise specified, are parts by weight.

EXAMPLE 1

A lead tail containing 6.70% zinc was subjected to froth flotation using 2-mercaptobenzimidazole as the collector. The zinc rougher concentrate contained 41.41% zinc and accounted for about 97.5% of the zinc contained in the lead tail. The zinc tail contained 0.17% zinc or about 2.5% of the zinc contained in the lead tail. The 2-mercaptobenzimidazole, therefore, gave a 97.5% recovery of the zinc of the lead tail.

The lead tail was obtained by subjecting a 14% lead, 6% zinc lead-zinc sulfide ore, to froth flotation in a lead circuit as follows: The ore was ground at 50% solids so that 3.8% remained on a 100 mesh screen and 51.3% passed through a 200 mesh screen, and conditioned with 0.2 pound of sodium cyanide, 1.0 pound zinc sulfate, 0.04 pound Minerec B (Minerec B is a trade-name for a collector obtained by reacting xanthate, sodium or potassium butyl xanthate, with ethyl chlorocarbonate) and 0.01 pound of Z3 (potassium ethyl xanthate) per ton of ore. The mineral pulp, adjusted to a density of 25% solids, and an alkalinity of pH 7.7, was then subjected to a 4-minute float, to float off the lead concentrate.

The zinc float was effected after neutralizing the zinc depressors (sodium cyanide and zinc sulfate) with 0.75 pound per ton of copper sulfate, adjusting the alkalinity to pH 9.8 with 2.25 pounds per ton of lime and adding 0.01 pound per ton 2-mercaptobenzimidazole added in the form of an aqueous solution prepared by dissolving 0.5 part of 2-mercaptobenzimidazole in a sodium hydroxide solution containing 1 part sodium hydroxide in 10 volume parts of water and thereafter diluting to 100 volume parts.

It will be seen from these data that 2-mercaptobenzimidazole is an effective zinc collector giving excellent recovery of the zinc, 97.5%, and an unusually high rougher concentrate, 41.41% zinc.

If desired, the 2-mercaptobenzimidazole can be used as the collector in the lead circuit, though generally speaking this is less desirable because its high efficiency as a zinc collector tends to cause it to pull too much zinc in the lead circuit thereby tending to reduce the overall recovery of the zinc from the ores. Thus, when 0.05 pound per ton of 2-mercaptobenzimidazole was used in place of the Minerec B and the Z3, along with 0.04 pound of pine oil per ton of ore as a frother, a lead rougher concentrate, containing 60.2% lead and accounting for 93% of the total lead in the ore, was obtained. The lead tail contained 1.29% lead or 7% of the total lead of the ore. It is believed, however, that the lead content of the tail can be lowered and the lead recovery improved by suitable adjustment of conditions, particularly with regard to the amount of zinc depressors and the amount of 2-mercaptobenzimidazole.

A further indication of the effectiveness of 2-mercaptobenzimidazole in floating zinc sulfide is given in the following example.

EXAMPLE 2

A lead tail containing about 3% zinc was subjected to froth flotation, as described in Example 1, using 2-mercaptobenzimidazole as the collector. Comparison runs were made with B–140 (a thiopyrimidine obtained by the condensation of mesityl oxide and ammonium thiocyanate) and ethylene thiourea.

The comparative results are shown in the following table.

Table I

Zn Collector	lb./ton	Zn Concentrate, Percent Zn	Zn Tail, Percent Zinc	Recovery in Percent of Total Zn in Lead Tails
2-mercaptobenzimidazole	0.1	14.12	0.22	94
Do	0.05	20.38	0.35	90
B–140	0.05	13.32	0.50	84.5
Ethylene thiourea	0.1	13.92	1.74	45
Do	0.05	14.73	1.79	47.5

From these data it will be seen that for this particular ore 2-mercaptobenzimidazole is somewhat more effective as a zinc collector than the standard B–140, which is one of the most effective zinc collectors known. It will be noted particularly that with ethylene thiourea as a collector, more of the total zinc was left in the tail than was collected in the concentrate, while with 2-mercaptobenzimidazole, up to 15 times as much zinc was recovered in the concentrate as was lost in the tail.

The lead tail used in the above test was obtained using the procedure described in Example 1 with a lead-zinc ore analyzing about 9.5% lead and about 3.1% zinc. This ore was ground to a fineness such that 3.5% remained on a 65 mesh screen, 7.8% on a 100 mesh screen, 23.2% on a 200 mesh screen, and 65.5% passed through a 200 mesh screen. The lead float was made with 1.0 pound zinc sulfate, 0.20 pound sodium cyanide, 0.04 pound Minerec B, 0.01 pound Z3, and 0.04 pound pine oil, whereas the lead tail used in the zinc float was conditioned with 0.04 pound pine oil, 2.25 pounds lime, 0.75 pound copper sulfate, and the indicated proportion of collector.

The utility of the collectors of the invention in floating copper sulfide is illustrated in the following example.

EXAMPLE 3

A 3.4% copper ore was ball milled with 4.5 pounds per ton of lime, and part of the collector was added, and the pulp at 25% solid was conditioned for one minute. 0.04 pound of a mixture of Pentasol (mixed amyl alcohols) and pine oil was added, and the copper floated for 3 minutes. Thereafter, another part of the collector and a further quantity of 0.04 pound Pentasol and pine oil mixture was added and the pulp conditioned for 1 minute. A second float was then carried out for 4 minutes. Comparison runs were made between 2-mercaptobenzimidazole and B–140, one of the more effective copper collectors.

The results obtained are given in the following table.

Table II

Collector	Lbs./Ton	Concentrate		Middlings		Tail		Percent Recovery of Total Copper
		Percent Cu	Percent Recovery	Percent Cu	Percent Recovery	Percent Cu	Percent Loss	
2-mercaptobenzimidazole	0.01 + 0.01	25.55	69.3	7.74	26.6	0.8	4.1	95.9
Do	0.01 + 0.03	23.43	88.9	2.27	9.0	0.10	2.1	97.9
B–140	0.01 + 0.01	21.5	89.9	5.13	7.8	0.10	2.3	97.7

It is significant to note from the data given in this table that 2-mercaptobenzimidazole is substantially as effective as the standard thiopyrimidine, the total recovery in all three cases ranging from 96% to 98%.

It is interesting to compare the data of Table II with the data given in the patent to Moses 1,801,319 where twenty-five times as much thiotetrahydroimidazole collecting agent is used as the 2-mercaptobenzimidazole collecting agent as shown in Table II. The Moses et al. recovery is 76.7% of copper as compared to 98% copper recovery with the present invention, it being understood that different ores were used in making these tests, but they are both described as copper sulfide ores.

The preferred form of the invention having been thus described, what is claimed as new is:

We claim:

1. In a process for the froth flotation of a sulfidic ore the step of effecting the flotation in the presence of 2-mercaptobenzimidazole.

2. A method of concentrating minerals of sulfide ores comprising preparing a mineral pulp of said ore, incorporating therein a small amount of 2-mercaptobenzimidazole and subjecting the mixture to froth flotation.

3. The method defined in claim 2 in which the 2-mercapto-4,5-aryleneimidazole is conditioned by fine grinding to micron size with a wetting agent to assist its incorporation in the mineral pulp in the flotation cell.

4. A method of concentrating zinc sulfide in sulfide ores comprising preparing a mineral pulp of said ore, incorporating therein a small amount of 2-mercaptobenzimidazole and subjecting the mixture to froth flotation.

5. A method of concentrating lead sulfide in sulfide ores comprising preparing a mineral pulp of said ore, incorporating therein a small amount of 2-mercaptobenzimidazole and subjecting the mixture to froth flotation.

6. A method for preparing a concentrate of a copper sulfide ore which comprises preparing a mineral pulp of said ore incorporating therein a small amount of 2-mercaptobenzimidazole and subjecting the mixture to froth flotation.

7. A method of concentrating zinc sulfide in a tail obtained in the froth flotation of lead sulfide from a lead-zinc sulfide ore comprising preparing a mineral pulp of said tail neutralizing zinc depressor therein and incorporating therein a small amount of 2-mercaptobenzimidazole and subjecting the mixture to froth flotation.

8. In a method of separating lead and zinc sulfides in sulfidic ores by means of froth flotation in which a mineral pulp is first subjected to froth flotation to float the lead sulfide and leave a lead tail containing the bulk of the zinc sulfide and then the lead tail subjected to a second froth flotation to carry off a zinc concentrate and leave the zinc tail containing the bulk of the gangue, the improvement which comprises effecting said froth flotation of said lead tail in the presence of 2-mercaptobenzimidazole.

9. A method of concentrating minerals of sulfide ores containing lead and zinc sulfides comprising preparing a mineral pulp, incorporating therein a lead collector together with a zinc depressor and subjecting the mixture to froth flotation to carry off a lead concentrate and to leave a lead tail containing zinc, then incorporating a zinc activator together with a small amount of 2-mercaptobenzimidazole and subjecting the

mixture to froth flotation to recover a zinc concentrate.

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WILLIAM H. HILL.

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