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BENEFICIATION OF ORES BY FROTH FLOTATION USING SULFOSUCCINAMATES

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ABSTRACT OF THE DISCLOSURE

Various ores, particularly tin ores, oxide iron ores, and also some sulfide and other non-sulfide ores, are beneficiated by froth flotation using N-alkyl sulfosuccinamates as flotation collectors.

RELATED APPLICATIONS

This application is a continuation-in-part of my prior application Ser. No. 699,765, filed Jan. 23, 1968, which in turn was a continuation-in-part of a prior application Ser. No. 529,267, filed Feb. 23, 1966. Both applications are now abandoned.

Highly selective froth flotation for the benefication of ores has been used for many decades. Certain ores, such as those of cassiterite, have not been effectively treatable by froth flotation under economically satisfactory conditions.

The mineral cassiterite, which is stannic oxide in chemical composition, is the principal source of tin. It is found in either alluvial or lode deposits.

For recovery of a concentrate suitable for smelting, the tin bearing material, after crushing and grinding in the case of lode ores or directly with alluvials, is commonly subjected to processing based on the relatively high specific gravity of the mineral. This processing depends on the difference in settling rates between the cassiterite and the gangue minerals. Various types of equipment are employed, including jigs, shaking tables, slime tables and the like. These gravity methods of concentration can operate on coarser particle size ranges with high efficiency because of the high specific gravity of cassiterite, which varies from 6.8 to 7.1. However, as in all hydraulic processes involving differential settling rates, there is a lower limit to the particle size which can be effectively treated, because finer particles, even of high specific gravity, have relatively slow settling rates. For example, with sizes below 325 or 400 mesh, gravity separation methods become inefficient, and below 10 to 20 microns entirely ineffective.

This problem has become increasingly important in recent years as the grade of tin ores has declined and the grain size of cassiterite in its ores has become progressively finer. Currently, recoveries of fifty percent or less on the average are common in gravity processes; this represents a serious economic loss because of the relatively high value of tin, which is one of the higher priced metals. These losses occur predominantly in finer particle sizes which, as noted above, are not effectively amenable to gravity separation methods.

Another problem arises because many tin ores may contain minerals, which interfere with froth flotation operations either because they form slimes or because their floatability is close to that of cassiterite. In most attempts to beneficiate cassiterite by froth flotation, collectors of the fatty acid or fatty acid salt type have been used. It has also been proposed to use certain sulfuric acid esters of aliphatic alcohols, such as cetyl sulfate. Sulfuric acid esters of hydroxy fatty acid esters have also been proposed. In each of these cases the collector is a sulfuric acid ester,

that is to say, the sulfur is attached to the hydrocarbon chain through oxygen. However, these attempts have had very limited success; recoveries and concentrate grades were low, and operating conditions difficult, particularly in the presence of contaminating minerals.

Iron oxide ores because of their extremely low value per ton have also presented a serious economic problem because the cost of froth flotation, particularly reagent cost, has resulted in concentrates which, while in many cases sufficiently beneficiated to meet blast furnace standards, an iron content in the high 50 percents or low 60's, represented costs exceeding the value of the concentrate or were at best of questionable economic value. Among flotation reagents which have been used to produce iron ore concentrates are included water and oil soluble sulfonic acids from the refining of oil, the so-called mahogany and green acids; the fatty acids of talloel from sulfate paper pulp processes have also been proposed as collectors. However, the flotation economics were for many years such that these processes have not been used extensively in the United States until very recently in spite of their technical operativeness, at least in the case of the mahogany and green acids.

In the United States the beneficiation of iron ore of low grade has been primarily effected by magnetic means, which are of course usable only with magnetic taconites. This process is used on an enormous scale, many millions of tons, but there still is a demand for a more economic froth flotation process usable with non-magnetic iron ores. This is particularly the case with ore bodies which do not contain magnetic taconite and is of interest in other parts of the world where the ores sometimes present a different problem than in the United States.

Summary of the invention

The process of the present invention depends on the use of reagent types belonging to a class which are ordinarily not considered as flotation collectors. These are surface active agents with high wetting powers, which ordinarily are useless for froth flotation collectors because the operation of a collector depends on differential wetting.

The collectors of the present invention belong to the class of N-alkyl sulfosuccinamates. It should be noted that these collectors are true sulfo compounds in which the sulfur is linked directly to the hydrocarbon chains, and not through oxygen as in the case of sulfuric acid esters. The N-alkyl groups constituting the hydrophobic portion of the molecule should be fairly long, having the formula C_nH_{n2+1} in which n is an integer from 12 to 22 inclusive. The preferred reagents are mono N-octadecyl sulfosuccinamates. Flotation ordinarily is considered to require that the minerals to be floated adsorb the polar portion of the molecule of a collector with the non-polar or hydrophobic portion available for attachment to the air bubbles. The effect of collector adsorption in the flotation operation is to render the particles hydrophobic, flocculated and floatable. Wetting agents, on the other hand, tend to make solids wettable, or hydrophilic, dispersed, and non-floatable. As a matter of fact, surface active agents of the wetting agent type are often used in froth flotation operations to keep slimes in a dispersed form so that they are not floatable. That the conditions of the flotation operation have not destroyed this well known characteristic of the reagents of this invention is shown by the fact that in some cases and at certain pH's when cassiterite ores containing fine hydrated iron oxide minerals are treated, these iron oxides are effectively dispersed while the cassiterite is made floatable and is recovered with a minimum of contamination by the iron minerals. The reagents of the present invention thus show the anomalous property of being extraordinarily powerful collectors for cassiterite, even in extremely low con-

centrations, while at the same time and under certain conditions acting as dispersants for iron oxide slimes. The reasons for this surprising and abnormal behavior have not been determined, and it is not desired to limit the present invention by any theoretical explanation of this phenomenon.

The reagents of the present invention, the N-alkyl sulfosuccinamates, have a relatively large number of polar groups. Ordinarily this also is not thought to be a desirable characteristic in froth flotation collectors. It thus adds to the anomalous and unexpected nature of the present invention, particularly since the N-alkyl sulfosuccinamates are markedly better collectors than dialkyl sulfosuccinates even though the latter have smaller numbers of polar groups. Again, no reason for this unexpected aspect of the present invention can be advanced.

In the case of the modification involving the beneficiation of cassiterite, which is perhaps the single most important field for the invention in parts of the world where such ores are found, there is another surprising result in the fact that extraordinarily low concentrations of reagents are effective.

Excellent flotation is obtained with the reagents in the concentration range from 10^{-6} to 10^{-4} moles per liter of pulp per stage. The lower figure corresponds to about 0.02 pound per ton of ore at the usual solid/liquid proportions. These are concentrations as low or lower than those useful with the best sulfide collector reagents in the flotation of the most easily floatable sulfide ores and are quite unique in oxide flotations.

The effectiveness for flotation of the present invention is so great that it is possible to treat an extended size range, including material as coarse as 65 to 100 mesh, in spite of the high gravity of the cassiterite mineral. This wide range of sizes is a practical advantage because even though some of the coarser fractions could be beneficiated by gravity separation means, it is often advantageous, with an ore which has to be ground fairly fine in order to liberate values, if the whole size range can be treated by one beneficiation method. The present invention thus is quite flexible and can be used either in combination with gravity separation methods for coarser material, or where the material size range is suitable as the only method of beneficiation.

In the case of beneficiation of iron oxide ores and some other ores, the amount of reagent required is sometimes not quite as extraordinarily low as with cassiterite but represents nevertheless processes of sufficiently low cost to be of economic importance with many of these ores in many parts of the world.

It is an important advantage of the present invention that flotation is not adversely affected by very impure water. In many cases mine waters can be used which have quite high concentrations of Ca^{++} and Fe^{++} ions.

The collectors of the present invention are used in water solution and normally as their sodium salts. However, the cation is not of importance since it does not take part in the actual collector action. Therefore, other alkali metal or even alkaline earth metal salts may be employed. Similarly, it is an advantage of the invention that it is not critical either with respect to the machines used, the frothers employed, which are the conventional frothers, or the pH of flotation. In general, any mechanical flotation machines may be employed, or else air cells may be used. The pH may vary over the range 2.0 to 10, with acid pH values advantageous in some cases.

The froth flotation of the present invention is carried out in accordance with good flotation practice and usually, though not always, involves flotation in rougher cells followed by one or more cleanings of the rougher concentrate. The reagents are effective in such small amounts that it is possible to carry out rougher and cleaner flotation with a single addition of the reagents at the beginning of the operation. On the other hand, it is sometimes advantageous to use staged additions of the reagent, for example as little as 0.02 lb. of collector per ton of ore treated on a dry weight basis per stage, with the number of stages and the amount of collector per stage depending on the grade of ore and the associated minerals. Pulp densities are in general the same as in other applications of froth flotation, for example about 15 to 30 percent of solids by weight. A frother may be used although in some cases the collector alone may provide sufficient froth.

Considering the important field of cassiterite beneficiation, while it is practical, and for most operations preferable, to float with the reagents of the present invention as the only collectors, it is also possible to use as activators for the cassiterite ions of polyvalent metals; for example, soluble salts of ferric iron, lead, zinc, or copper, in amounts not exceeding 10^{-2} moles per liter. When such polyvalent metal ions are used, it is also possible to add small amounts of typical sulfide collectors, such as zanthates, and this is not excluded.

With some cassiterite ores there are present such minerals as tourmaline, topaz, fluorite, siderite, and iron oxides such as hematite, or magnetite. These minerals, especially iron oxides, are floated to some extent and can contaminate the rougher concentrates. Where the amounts of the contaminants are significant they may be depressed in the cleaner circuit by the addition of small amounts of soluble silicates, fluosilicates, ferrocyanides, of ferricyanides; for example, 0.1 to 1 lb. per ton of ore. In general these can be used either in the rougher or cleaner operation, although for reasons of economy it is often preferable to add the reagents only to the cleaners. Any quartz, feldspars, and micas which may be present in the ore are not affected by the collector; hence these minerals are removed if carried into the rougher concentrates by simple cleaning. Sulfide minerals, in general, will respond to the collectors and hence should be removed before cassiterite flotation with conventional sulfide flotation reagents and practices. In this respect the present invention can follow normal good flotation practice, and critical or unusual techniques are not necessary.

A further advantage to the present invention is that only a minimum or no conditioning is necessary before flotation. When the attempt is made to treat ores such as cassiterite by flotation with fatty acids, it is usually necessary to employ intensive conditioning in the forms of agitation of the pulp for relatively long periods of time and often with large quantities of hydrocarbon oil. This requires additional equipment and expenditure of electric energy. In contrast, with this modification of the present invention no conditioning is necessary, the collectors being added directly to the flotation cells.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Example 1

The flotation feed was a finely disseminated complex ore from Bolivia, containing pyrite, cassiterite, tourmaline, and other siliceous minerals. The material was ground wet in a laboratory ball mill to pass 100 mesh. The sulfide materials were floated off with a xanthate collector. The resulting product, assaying 1.16 percent tin, was treated in a Denver M–1 laboratory flotation cell as follows: A rougher concentrate was removed in four stages at pH 2.3 using a total of 0.33 lbs. per ton of N-octadecyl tetrasodium, 1.2 dicarboxyethyl sulfosuccinamate as collector. The rougher concentrate was dewatered, repulped, and cleaned once at pH 2 with 4 pounds per ton of sodium silicofluoride. The results were as follows:

Product	Weight percent	Tin assay, percent	Tin distribution, percent
Cleaner concentrate	6.56	29.42	88.9
Cleaner tailing	11.19	0.40	2.9
Rougher tailing	82.25	0.15	8.2
Rougher concentrate (calculated)	17.75	7.93	91.8

Example 2

The flotation feed was the same as in Example 1, and the rougher preparation and rougher flotation were the same. The rougher concentrate after dewatering and repulping was cleaned twice at pH 2 with the addition of 0.10 lb. per ton of fuel oil and 0.05 lb. per ton of collector to the first cleaning and no reagents to the second cleaning. The results were—

Product	Weight percent	Tin assay, percent	Tin distribution, percent
Cleaner Concentrate	5.22	24.38	84.1
Cleaner Tailing #2	4.05	2.35	6.2
Cleaner Tailing #1	9.35	0.26	1.6
Rougher Tailing	81.38	0.15	8.1
Rougher Concentrate	18.62	7.48	91.9

Attempts to float this ore with oleic acid collectors require 10 times the amount of collector, intensive conditioning, and give much lower recoveries for the same grade of concentrate.

Example 3

The flotation feed was a higher grade material made up of pyrite in smaller proportions than in the previous cases, feldspars and other silicates, and cassiterite, with a tin assay of 2.7 percent. In this case the pyrite was not floated off first but instead was dispersed with cyanide. The sample was ground to minus 65-mesh and treated in the Denver M–1 laboratory flotation machine as follows: There was added 0.43 lb. per ton of sodium cyanide giving a pH of 9.4. After four mintues of conditioning the collector was added in three stages for a total of 0.11 pound per ton. The first and second rougher stages were taken for cleaning, the third stage set aside as a scavenger. The rougher concentrate was conditioned with lime at pH 11 for 3 minutes, then floated with a total of 0.06 lb. per ton of collector. The first cleaner concentrate was recleaned without reagents. The results were as follows:

Product	Weight percent	Tin assay, percent	Tin distribution, percent
Recleaner concentrate	4.21	46.62	72.4
Recleaner tailing	1.38		9.7
Cleaner tailing	1.18	8.40	3.7
Scavenger	3.80	8.96	12.6
Rougher tailing	89.43	0.05	1.6
Rougher concentrate [1]	10.57	25.2	98.4
Cleaner concentrate [2]	5.59	39.8	82.1

[1] Including scavenger.
[2] Excluding scavenger.

Even the first or rougher concentrate in this case was of commercial grade.

Example 4

The feed was an iron ore containing specular hematite and a siliceous gangue. It was received from the treatment plant already ground. Sample weights were 700 grams (moist) with tests carried out in a Denvier M–1 flotation machine, using a 2-liter cell.

After desliming the pH was adjusted to 2.5 with sulfuric acid and maintained between this value and 3.0 during the test. The addition of sulfuric acid may be by sequential additions. Four stages of rougher flotation were carried out. To each 25 mg. of anhydrous collector, 60 mg. of fuel oil and 4 mg. of frother, Aerofroth 65, were added after predispersing the oil in the collector frother solution. The collector was N-octadecyl tetrasodium 1.2 dicarboxyethyl sulfosuccinamate. No conditioning was necessary, the flotation froth removal starting immediately after addition of the reagent mixture. The successive concentrates were collected and assayed separately.

The following results were obtained:

PERCENTS CUMULATIVE

Product	Weight gms.	Iron	Distribution of metal	
Concentrate:				
1+2	195.6	61.52	56.4	
1+2+3	312.5	57.96	84.9	
1+2+3+4	345.3	56.91	[1] 92.1	[2] 86.7
Tailing	248.1	4.19		
Slimes	69.1	19.48		
Feed (calculated)	662.5	34.25		

[1] Based on flotation feed.
[2] Based on original feed.

Reagent consumption (lbs./ton):

Collector (anhydrous reagent)	0.057
Oil	0.73
Frother	0.049

Example 5

The procedure was the same as in Example 1 except that the collector was disodium N-octadecyl sulfosuccinamate. Two flotation stages were used with the pH maintained at 2:5 with sulfuric acid. Two stages of collector additions were used, each at 25 mg. of anhydrous reagent, with 60 mg. oil per stage and a total of 20 mg. of a frother, Aerofroth 65. The results were as follows:

PERCENTS CUMULATIVE

Product	Weight	Iron assay	Distribution of metal	
Concentrate:				
1	259.4	65.09	76.10	
1+2	361.5	58.06	[1] 94.60	[2] 91.2
Tailing	260.4	4.61		
Slimes	67.9	19.3		
Feed		39.2		

[1] Based on flotation feed.
[2] Based on original feed.

Reagent consumption (lbs./ton):

Collector	0.145
Oil	0.32
Frother	0.058

It will be noted that the disodium compound is more selective than the tetrasodium compound. In comparison with the usual oleic acid collectors, the amounts required with the new collectors are 1/20 or less on a weight basis, and the results are more selective also.

Example 6

The procedure was the same as in Example 4 except that the second rougher stage used four stages of collector, use totaling 0.1 lb. of anhydrous reagent per ton. The total scavenger concentrate was cleaned once without reagent at pH 2.5.

The results were—

	Wt.	Grade, percent Fe	Cumulated grade, percent Fe	Cumulated recovery
Primary concentrate	238.2	65.51	65.51	68.4
Cleaned scavenger primary concentrate	86.5	56.38	63.08	89.8
Cleaner tails	50.1	20.79	57.43	94.3
Rougher tails	254.0	5.11		

The following five examples were all based on 500 gram charges instead of 700 gram charge of Example 4.

Example 7

Galena—silicates, quartz

Grind, minus 100-mesh; pulp density, 20 percent; pH, 3.8;

Collector 0.10 lb./ton; Aerofroth 65, 0.016 lb./ton; Flotation time, 8 minutes

Results	Weight, percent	Lead assay, percent	Lead recovery, percent
Concentrate	10.0	36.40	84.5
Tailing	90.0	0.75	15.5
Feed (calculated)	100.0	4.31	100.0

Example 8

Cerussite (lead carbonate)—silicates, quartz
Grind, minus 100-mesh; pulp density, 20 percent; pH, 6.1; Collector, 0.12 lb./ton; Aerofroth 65, 0.024 lb.; Flotation time, 4 minutes

Results	Weight, percent	Lead assay, percent	Lead recovery, percent
Concentrate	14.5	43.60	93.6
Tailing	85.5	0.50	6.4
Feed (calculated)	100.0	6.75	100.0

Example 9

Anglesite (lead sulfate)—silicates, quartz
Grind, minus 100-mesh; pulp density, 20 percent solids; pH, 6.2;
Collector, 0.10 lb./ton; Aerofroth 60, 0.024;
Flotation time, 4 minutes

Results	Weight, percent	Lead assay, percent	Lead recovery, percent
Concentrate	18.0	36.60	95.7
Tailing	82.0	0.35	4.3
Feed (calculated)	100.0	6.70	100.0

Example 10

Sphalerite (zinc sulfide)—silicates, quartz
Grind, minus 100-mesh; pH, 3.9;
Collector, 0.13 lb./ton; Aerofroth 65, 0.024 lb./ton; Flotation time, 5 minutes

Results	Weight percent	Zinc assay, percent	Zinc recovery, percent
Concentrate	18.0	28.80	86.3
Tailing	82.0	1.00	13.7
Feed (calculated)	100.0	6.00	100.0

Example 11

Chalcocite (copper sulfide)—quartz
Grind, minus 100-mesh; pulp density, 20 percent; pH, 3.0; Collector, 0.05 lb./ton; Aerofroth 60, 0.008 lb./ton; Flotation time, 3 minutes

Results	Weight, percent	Copper assay, percent	Copper assay, percent
Concentrate	10.0	34.80	91.6
Tailing	90.0	0.35	8.4
Feed (calculated)	100.0	3.79	100.0

It will be noted that the same unexpected results of the surface active collectors of the present invention are obtained not only with tin ores in which the principal mineral is cassiterite but also other ores, such as iron ore, sulfide ores, various lead ores of the non-sulfide type, and the like. This is not at all what one would expect, because it is well known that cassiterite flotation presents problems that are entirely different from those presented by iron ore, sulfide ores, and lead ores of the non-sulfide type. Normally these ores are considered to belong to entirely different classes from that of cassiterite and they are utterly different in the nature of the flotation collectors usually employed with them. It is not known why the N-alkyl sulfosuccinamates are equally useful for classes of ores which are normally considered to have little or no common characteristics of floatability. It is not intended to limit the present invention to any theory of why a single type of collector can be used in froth flotations which were formerly considered to require different and unrelated collectors. This is particularly surprising as the collectors of the present invention belong to a class which is normally considered as unsuitable for flotation collectors because of their surface activity, which produces a non-selective wetting of mineral particles.

I claim:

1. A method of beneficiating cassiterite-containing material which comprises comminuting a cassiterite ore to liberate the cassiterite values, subjecting an aqueous pulp of the comminuted ore to froth flotation in the presence of an N-alkyl sulfosuccinamate in which the alkyl group has the formula C_nH_{2n+1} in which n is an integer from 12 to 22 inclusive and floating off the cassiterite values from gangue.

2. A method according to claim **1** in which the collector is an N-monooctadecyl sulfosuccinamate.

3. A process according to claim **2** in which the pH of the flotation circuit is less than 2.5.

4. A process according to claim **2** in which the collector is N-octadecyl tetrasodium 1,2,dicarboxyethyl sulfosuccinamate.

5. A process according to claim **2** in which the collector is disodium N-octadecyl sulfosuccinamate.

6. A process according to claim **1** in which the ore contains additional minerals selected from the group consisting of topaz, fluorite, siderite, iron oxides, tourmaline, and other iron silicates, and the flotation is carried out with the addition of depressants for the additional minerals in a rougher stage, the depressants being selected from the group consisting of silicates, fluosilicates, ferrocyanides, and ferricyanides, the depressants being added to the rougher concentrate before cleaning.

7. A method of beneficiating material in which the values are selected from the group consisting of iron oxide metal sulfides, carbonates of lead and sulfates of lead, which comprises comminuting the materials sufficiently to liberate the values, subjecting an aqueous pulp of the comminuted materials to froth flotation in the presence of collector consisting of a water dispersible N-alkyl sulfosuccinamate in which the alkyl group has the formula C_nH_{2n+1} in which n is an integer from 12 to 22 inclusive and floating the values away from gangue.

8. A method according to claim **7** in which the collector is an N-monooctadecyl sulfosuccinamate.

9. A method according to claim **8** in which the collector is N-octadecyl sodium 1,2,dicarboxyethyl sulfosuccinamate.

10. A method according to claim **8** in which the collector is disodium N-octadecyl sulfosuccinamate.

11. A method according to claim **8** in which the values comprise an iron oxide and the flotation is effected at a pH below 5.0.

12. A method according to claim **8** in which the values floated comprise a metal sulfide.

13. A method according to claim **8** in which the value is a lead salt selected from the group consistting of lead carbonate and lead sulfate.

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