

United States Patent [19]

Harris et al.

[11] 3,853,751

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[54] **FLOTATION OF SULFIDE ORES USING DITHiocarbamates**

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[52] U.S. Cl. **209/166**

[51] Int. Cl. **B03d 1/02**

[58] Field of Search **209/166, 167**

[56] **References Cited**

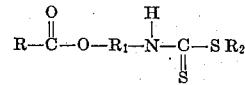
UNITED STATES PATENTS

2,375,083	5/1945	Cooper	260/455 A
3,424,730	1/1969	Lee	260/455 A X
3,464,551	9/1969	Falvey	209/166
3,590,996	7/1971	Harris	209/166
3,590,997	7/1971	Harris et al.	209/166

Primary Examiner—Robert Halper
Attorney, Agent, or Firm—J. Roger Lochhead

[57] **ABSTRACT**

A process of concentrating ores by flotation which comprises subjecting a sulfide ore in the form of a pulp to a flotation process in the presence of an effective quantity of a flotation collector comprising a compound corresponding to the formula



wherein R and R₂ are hydrocarbyl groups and R₁ represents an alkylenyl or heteroalkylenyl group. These indicated compounds provide enhanced recovery of and/or selectivity for sulfide minerals of Cu, Zn, Mo, Co, Ni, Pb and As. The compounds are also useful as fungicides and herbicides.

10 Claims, No Drawings

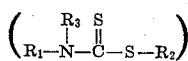
FLOTATION OF SULFIDE ORES USING DITHIOCARBAMATES

BACKGROUND

The present invention relates to novel dithiocarbamate esters and their use as flotation agents in the separation of sulfide ores.

Flotation is a process of treating a mixture of finely divided mineral solids, e.g., a pulverulent ore, suspended in a liquid whereby a portion of such solids are separated from other finely divided mineral solids, e.g., clays and other like materials present in the ore, by introducing a gas (or providing a gas in situ) in the liquid to produce a frothy mass containing certain of the solids on the top of the liquid, and leaving suspended (unfrothed) other solid components of the ore. Flotation is based on the principle that introducing a gas into a liquid containing solid particles of different materials suspended therein causes adherence of some gas to certain suspended solids and not to others and makes the particles having the gas thus adhered thereto lighter than the liquid. Accordingly, they rise to the top of the liquid to form a froth.

Various flotation agents have been admixed with the suspension to improve the frothing process. Such added agents are classed according to the function to be performed: collectors, e.g., high carbon chain compounds such as collectors for sulfide minerals including xanthates, thionocarbamates, and the like; frothers which impart the property of forming a stable froth, e.g., natural oils such as pine oil and eucalyptus oil, modifiers such as activators to induce flotation in the presence of a collector, e.g., copper sulfate; depressants, e.g., sodium cyanide, which tend to prevent a collector from functioning as such on a mineral which it is desired to retain in the liquid, and thereby discourage a substance from being carried up and forming a part of the froth; pH regulators to produce optimum metallurgical results, e.g., lime, soda ash and the like. U.S. Pat. No. 3,464,551 discloses using dialkyl dithiocarbamates



as flotation collectors; U.S. Pat. No. 3,590,996 describes flotation of sulfide ores using certain thionocarbamates.

It is of importance to bear in mind that additives of the above type are selected for use according to the nature of the ore, the mineral sought to be recovered, and the other additaments which are to be used in combination therewith.

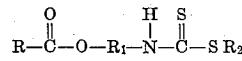
An understanding of the phenomena which makes flotation a particularly valuable industrial operation is not essential to the practice of the present invention. They appear, however, to be largely associated with selective affinity of the surface of particulated solids, suspended in a liquid containing entrapped gas, for the liquid on one hand, the gas on the other.

The flotation principle is applied in a number of mineral separation processes among which is the selective separation of such minerals as sulphide copper minerals, sulphide zinc minerals, sulphide molybdenum minerals and others from sulphide iron minerals. The present invention concerns a novel class of compounds.

These compounds can be employed as collection agents in a flotation process. With some of these compounds better recoveries are realized and with others, improved selectivity is achieved. Certain of these compounds produce improvement in both aspects with some of the preceding sulphides.

SUMMARY

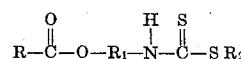
The present invention concerns novel compounds 10 corresponding to the formula



15 wherein R represents H, a hydrocarbyl group, or a heterohydrocarbyl group, wherein said groups can be substituted with up to two functional groups and contain from 1 to 10 carbon atoms; R₁ represents an alkylene or heteroalkylene group having a heteroatom substituted in the carbon chain, and R₂ represents a hydrocarbyl or heterohydrocarbyl group, except for aryl, wherein either of said groups can be substituted except in the alpha position with up to two functional groups. The novel compounds can be prepared by the reaction 25 of an amino alcohol with a trithiocarbonate ester and reacting the resulting hydroxyalkyl dithiocarbamate product with an acyl halide. The novel compounds can be employed to improve the flotation process of separating sulfide minerals from ores by employing an effective quantity of at least one of the novel compounds set forth herein in the flotation process. The novel compounds are also useful as fungicides and herbicides.

PREFERRED EMBODIMENTS

35 The preferred compounds of the present invention correspond to the formula



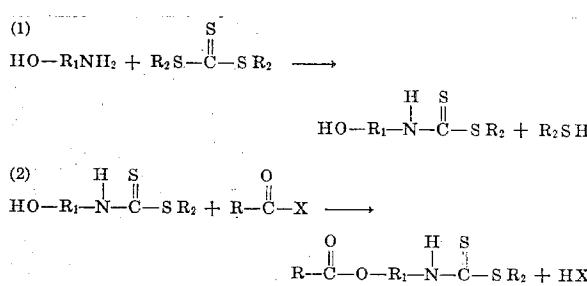
40 wherein R represents H, a hydrocarbyl group selected from the group consisting of alkyl (e.g., methyl, ethyl, propyl, butyl, decyl) or alkenyl (e.g., vinyl, allyl, propenyl) containing up to 10 carbon atoms, alkaryl (e.g., tolyl), aryl (e.g., phenyl), aralkyl (e.g., benzyl, phenethyl), cycloalkyl (e.g., cyclopropyl, cyclohexyl), cycloalkenyl (e.g., cyclohexenyl), aralkenyl (e.g., phenylvinyl, cinnamyl), or acylalkyl (e.g., acetyl methyl) groups, wherein the acyclic carbon chain portions preferably contain up to three carbon atoms and the cyclic group contains from five to 10 carbon atoms and a heterohydrocarbyl radical selected from the group consisting of alkoxy (e.g., methoxy), alkenyloxy (e.g., allyloxy), alkoxy carbonyl (e.g., methoxycarbonyl), alkoxycarbonylalkyl, aryloxy (e.g., phenoxy), arylalkoxy, alkylthio (e.g., ethylthio), alkylthioalkyl and arylthio groups, wherein said heterohydrocarbyl groups can 45 contain up to two identical or different functional groups preferably selected from the group consisting of halo, alkoxy, cyano, acetonyl, and lower dialkylamino groups; R₁ represents an alkylene (e.g., ethylene, butylene (1,4 or 1,2) or heteroalkylene group containing up to eight carbon atoms and wherein the heteroatom is substituted in the carbon chain and is preferably selected from the group consisting of —O—, —S— and 50 55 60 65 70 75 80 85 90



wherein X is a hydrocarbyl group and not H; preferably X is a lower alkyl group containing up to five carbon atoms; and R₂ represents a hydrocarbyl group selected from the group consisting of an alkyl (e.g., methyl, ethyl, propyl, octyl) or alkenyl (e.g., allyl, hexenyl) group, preferably containing up to eight carbon atoms, an aralkyl group (e.g., benzyl, phenethyl, phenylpropyl), preferably containing from one to three carbon atoms, in the alkyl portion, and an cycloalkyl or cycloalkenyl group, preferably containing from three to eight carbon atoms, wherein said hydrocarbyl groups can be substituted, except in the alpha position, with up to two identical or different functional groups preferably selected from the group consisting of alkoxy, halo, cyano, acetyl and lower dialkylamino groups. R, R₁ and R₂ are further characterized in that the total number of carbon atoms in said groups preferably ranges from about four to about 25.

METHODS OF PREPARATION

The novel compounds as defined herein can be prepared, for example, by reacting an amino alcohol with a trithiocarbonate ester to prepare a hydroxy dithioether and then acylating the HO—R₁ moiety with an acyl halide, anhydride or ketene. The reactions can be represented as follows:

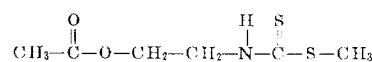


The novel compounds as defined herein have a special utility as flotation collectors and can be employed in standard flotation processes to concentrate nickel and molybdenum sulfides and other like minerals from sulfide ores in preference to iron sulphides. In a flotation process a pulp is first prepared by wet grinding a sulphide containing ore to a suitable size with or without a pH modifier. A suitable frothing agent is then added, e.g., pine oil, cresylic acid, polyalkoxyparaffin and the like. An effective quantity of a flotation collector compound as defined herein is then added, usually ranging from about 0.01 lbs. to about 0.25 lbs. per ton of pulp, and the pulp is usually agitated and aerated. Sulfide minerals, e.g., copper, nickel, zinc, molybdenum sulphides, and other like sulfide minerals collect as a froth which is readily over-flowed or skimmed off from the residual gangue and other undesired materials and the metal values therein recovered.

The following examples will facilitate a more complete understanding of the present invention but they are not meant to limit the scope of the invention to the specific embodiments incorporated therein.

EXAMPLE 1

A compound within the scope of the present invention and having the formula



was prepared in the following manner:

To 15.1 gms. of methyl 2-hydroxyethylidithiocarbonate (0.10 mole) and 8.7 gms. of pyridine (0.11 mole) was added 11.2 gms. of acetic anhydride (0.11 mole) while cooling the mixture by means of an ice bath. The reaction temperature was allowed to rise to about 60°C and after the reaction had subsided 10 ml. of methanol was added to consume any unreacted anhydride. The product was taken up in ether, washed with water, dilute HCl, saturated sodium bicarbonate solution and dried over MgSO₄. Removal of the solid and solvent left 15 grams of product, the structure of which was confirmed by infrared and NMR analyses.

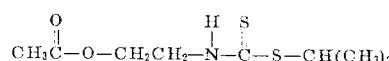
Calc. for C₆H₁₁NO₂S₂

20	% C	% H	% N
Calc.	37.28	5.74	7.25
Obs.	37.5	5.6	7.3



EXAMPLE 2

A novel compound corresponding to the formula



35 was prepared in the following manner:

To 8 gms. of isopropyl 2-hydroxyethylidithiocarbonate (0.045 mole) in 150 ml. of ether was added 3.5 gms. of acetyl chloride and then 4.4 gms. of triethylamine. After several hours, water was added; the ether layer was washed with water, saturated salt solution, and then dried over MgSO₄ powder. Removal of the solid and solvent gave 9.2 gms. of amber yellow syrup (92 percent yield).

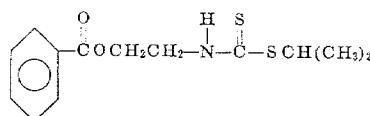
Calc. for C₈H₁₅NO₂S₂

45	% C	% H	% N
Calc.	43.11	6.84	6.32
Obs.	43.8	6.7	6.4



EXAMPLE 3

A new compound within the scope of the invention defined herein and corresponding to the formula



65 was prepared in the following manner:

To 9 gms. of isopropyl 2-hydroxyethylidithiocarbonate and 5.5 gms. of triethylamine in ether was added

7 gms. of benzoyl chloride. The next day the solid was removed and the filtrate was washed with water, saturated aqueous sodium bicarbonate and then dried over $MgSO_4$ powder. Removal of the solid and solvent left a syrup that became crystalline on standing. The melting point was 102° - 4° C.

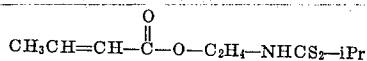
Calc. for $C_{13}H_{17}NO_2S_2$

	% C	% H	% N
Calc.	55.29	6.04	4.94
Obs.	55.9	6.2	5.0

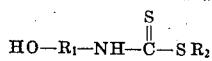


EXAMPLE 4

In a like manner to Example 3, the corresponding crotonyl compound was prepared from 9.2 grams of isopropyl 2-hydroxyethylthiocarbamate, 5.5 gms. of triethylamine and 5.2 grams of crotonyl chloride.



Other species of compounds within the scope of the present invention can be prepared according to the procedures set forth in Examples 1-4. The starting materials consist of a compound corresponding to the formula



and an acylating agent which provides the



moiety of the novel compounds. Various combinations of R_1 , R_2 and the acylating agent are set forth in the following Table I, together with the empirical formulas of the products which are formed.

TABLE I

Compound empirical	R_1	R_2	Acylating agent
$C_9H_{13}NO_2S_2$	$-\text{CH}_2\text{CH}_2-$	$-\text{iPr}^*$	$(\text{CH}_3\text{C}(=\text{O}))_2\text{O}$
$C_{14}H_{19}NO_2S_2$	CH_3	$-\text{iPr}$	$(\text{C}_6\text{H}_5\text{C}(=\text{O}))_2\text{O}^{**}$
$C_9H_{17}NO_2S_2$	C_2H_5	$-\text{C}_2\text{H}_5$	$(\text{CH}_3\text{C}(=\text{O}))_2\text{O}$
	$-\text{CH}_2-\text{CH}-$		

TABLE I-Continued

Compound empirical	R_1	R_2	Acylating agent
$C_9H_{17}NO_2S_2$	CH_3	$-\text{iPr}$	$(\text{CH}_3\text{C}(=\text{O}))_2\text{O}$
	$-\text{CH}-\text{CH}_2-$		
$C_{12}H_{23}NO_2S_2$	$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4-$	$-\text{iPr}$	$(\text{C}_6\text{H}_5\text{CH}_2\text{C}(=\text{O}))_2\text{O}$
$C_9H_{17}NO_2S_2$	$-\text{C}_2\text{H}_4-$	$-\text{iPr}$	$\text{C}_2\text{H}_5\text{O}-\text{C}(=\text{O})-\text{Cl}$
$C_9H_{17}NO_2S_2$	CH_3	$-\text{iPr}$	$(\text{CH}_3\text{C}(=\text{O}))_2\text{O}$
	$-\text{CHCH}_2-$		
$C_{10}H_{19}NO_2S_2$	CH_3	$-\text{iPr}$	$\text{C}_2\text{H}_5\text{O}-\text{C}(=\text{O})-\text{Cl}$
	$-\text{CHCH}_2-$		
$C_{13}H_{17}NO_2S_2$	$-\text{C}_2\text{H}_4-$	$-\text{iPr}$	$\text{C}_2\text{H}_5\text{O}-\text{C}(=\text{O})-\text{Cl}$
$C_{11}H_{21}NO_2S_2$	$-\text{C}_6\text{H}_5-$	$-\text{C}_2\text{H}_5$	$(\text{CH}_3\text{C}(=\text{O}))_2\text{O}$
$C_{13}H_{17}NO_2S_2$	$-\text{C}_2\text{H}_4-$	$-\text{iPr}$	$\phi-\text{O}-\text{C}(=\text{O})-\text{Cl}$
	$-\text{CH}(\text{CH}_3)_2$		
	$** \phi$ is		
25			
			CH_3
			Also, $\text{HO}-\text{C}_2\text{H}_4\text{N}-\text{C}_2\text{H}_4\text{NHCO}_2\text{S}_2-\text{C}_6\text{H}_5 + \text{CH}_2=\text{C}=\text{O}$ (gas) \longrightarrow
			$\text{CH}_3\text{CO}-\text{O}-\text{C}_2\text{H}_4\text{N}-\text{C}_2\text{H}_4\text{NHCO}_2\text{S}_2-\text{C}_6\text{H}_5$
			$\text{HO}-\text{C}(\text{C})-\text{S}-\text{C}-\text{C}-\text{C}-\text{NH}_2$ from trans 2-butylene oxide
			35
			$+ \text{HS}-\text{C}-\text{C}-\text{C}-\text{C}-\text{NH}_2$ is an example where $-\text{S}-$ is the hetero portion of R_1 .
			Suitable acylating agents wherein the source of R equals a substituted hydrocarbyl group include:
40			(1) $\text{C}-\text{C}-\text{C}-\text{C}-\text{C}(=\text{O})-\text{Cl}$
			Br
			(2) 3-cyanophenyl acetyl chloride: $\text{NC}-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{Cl}$
			(3) cyanoacetyl chloride: $\text{NC}-\text{C}(=\text{O})-\text{Cl}$

50 The collectors of Examples 2-3 were tested on a copper sulfide ore from the Southwestern United States. The ore sample was ground for 4 minutes at 62.5 percent solids with 1.0 lbs./ton of lime and 0.016 lbs./ton of collector. The pulp was conditioned for 1 minute with 0.136 lbs./ton of a standard commercial frother. The pulp was then floated for 5 minutes and the concentrate tailings assayed for copper, iron and molybdenum. The results obtained are set forth in the following Table II.

TABLE II

Collector used	Percent					
	Copper		Iron		Molybdenum	
	Content in concentrate	Recovery from ore	Content in concentrate	Recovery from ore	Content in concentrate	Recovery from ore
Example 2	15.8	56.1	17.4	19.3	0.46	76.3
Example 3	18.7	55.3	18.2	16.9	0.52	75.3

The collector of Example 2 was also tested on a nickel sulfide ore from Canada, a copper ore from North Central U.S.A. and a molybdenum ore from South Western U.S.A.

For the nickel ore, the sample was ground for 5 minutes at 60.5 percent solids with 0.4 lbs./ton of lime and 0.09 lbs./ton of collector. The pulp was conditioned for one minute with 0.064 lbs./ton of a standard commercial frother. The pulp was then floated for 5 minutes and the concentrate tailings assayed for copper, iron and nickel.

The copper ore from North Central U.S.A. was treated in the following manner: — Samples of ore were ground for 5 min. at a pulp density of 62.5 percent solids with 0.8 lbs./ton of lime and 0.128 lbs./ton of collector. The pulp was then transferred to a commercial laboratory flotation cell and conditioned for 1 min. with 0.094 lbs./ton of a standard frother. A concentrate was then removed in 5 mins. of flotation at a pH of 9.7. The concentrate and tailings were filtered, dried and assayed; results are presented below.

The molybdenum ore from South Western U.S.A. was tested in the following manner: — Samples of ore were ground for 4 mins. at a pulp density of 62.5 percent solids with 0.4 lbs./ton of lime and 0.048 lbs./ton of collector. The pulp was then transferred to a commercial laboratory flotation cell and conditioned for 1 min. with 0.078 lbs./ton of a standard frother. A concentrate was then removed in 5 mins. of flotation at a pH of 9.7. The concentrate and tailings were filtered, dried and assayed; results are presented below:

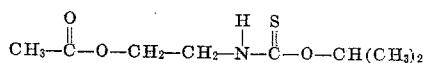
Table III summarizes the data.

TABLE III

Ore	Copper		Iron		Molybdenum		Nickel	
	Content in concentrate	Recovery from ore						
Ni ore	3.4	88.2	22.2	26.0	—	—	3.4	56.2
Cu ore	15.9	30.7	4.6	1.7	—	—	—	—
Mo ore	—	—	13.2	11.2	12.2	79.9	—	—

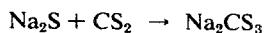
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For comparison, the O-ester or thiono analog of the Ex. 2 compound, i.e.,



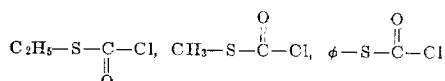
was employed in the same manner. Comparable results were noted for the copper ores. However, the recoveries of nickel sulfide from the nickel ore and molybdenum sulfide from the molybdenum ore were substantially greater for the present dithio compounds over the thiono analog, i.e., 37.7% recovered (thiono) vs. 56.2% recovered (dithio) for NiS; 75.2% recovered (thiono) vs. 79.9% recovered (dithio) for MoS.

The trithiocarbonate starting materials employed herein in the preparation of the novel compounds can be prepared in a manner well known in the art. For example,

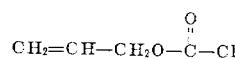


Acylating agents which can be used in preparing the novel compounds of the present invention can be prepared by converting carboxylic acids to the corresponding acyl chloride by contacting said acids with thionyl chloride by processes well known in the art. Carboxylic acids which may be employed include, for example, cinnamic acid, α -bromocaproic acid, pelargonic acid, methacrylic acid, 3-cyanophenylacetic acid, cyclohexylacetic acid, cyanoacetic acid, 2-phenoxybutanoic acid, methoxyacetic acid and the like.

Other acylating agents which can be employed to prepare the novel compounds include thiochloroformates such as

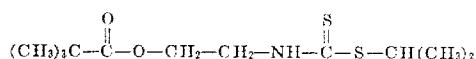


and alkenylchloroformates such as



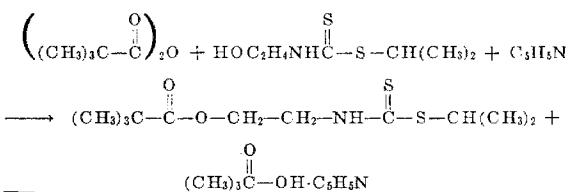
and the like.

Other novel compounds of the invention may be prepared in a manner similar to that described in the foregoing examples. For example, a compound corresponding to the formula

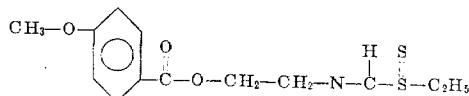


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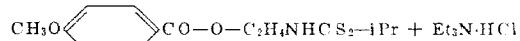
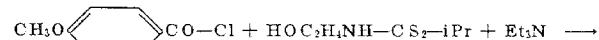
can be prepared by



Another compound corresponding to the formula



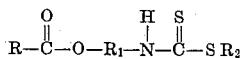
is prepared by the reactions:



Other compounds within the scope of the present invention may be prepared by a method as defined herein by choosing various starting materials.

What is claimed is:

1. A process of concentrating sulfide ores by flotation, which comprises subjecting a sulfide ore of copper, nickel or molybdenum, in the form of a pulp, to a flotation process in the presence of a flotation collector for said sulfides comprising a compound corresponding to the formula



wherein R represents a member selected from the group consisting of H, a hydrocarbyl or a heterohydrocarbyl group; R₁ represents a member selected from the group consisting of an alkylene or heteroalkylene group having the hetero atom substituted in the carbon chain and R₂ represents a hydrocarbyl radical other than an aryl group.

2. The process as defined in claim 1 wherein R represents a member selected from the group consisting of a hydrocarbyl or heterohydrocarbyl radical containing up to two functional groups substituted thereon, and R₂ represents a hydrocarbyl radical, other than an aryl group having up to two functional groups substituted thereon, other than in the alpha position of said hydrocarbyl.

3. The process as defined in claim 1 wherein R represents H, a hydrocarbyl radical selected from the group consisting of alkyl or alkenyl containing up to 10 carbon atoms, aryl, alkaryl, aralkyl, cycloalkyl, cycloalkenyl, aralkenyl or acylalkyl groups wherein the acyclic carbon chain portion contains up to three carbon atoms and the cyclic group contains from five to 10 carbon atoms, a heterohydrocarbyl selected from the group consisting of alkoxy, alkenyloxy, alkoxy carbonyl, alkoxy carbonylalkyl, aryloxy, alkylthio or arylthio groups; R₁ represents a member selected from the group consisting of an alkylene or heteroalkylene group containing up to eight carbon atoms wherein the hetero atom in the heteroalkylene group is selected from the group consisting of —O—, —S—, and



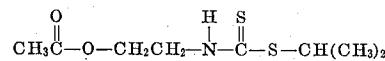
wherein X is a hydrocarbyl radical and R₂ represents a hydrocarbyl radical selected from the group consisting of an alkyl or alkenyl group, containing up to eight carbon atoms, an aralkyl, containing from one to three carbon atoms in the alkyl portion, and cycloalkyl or cycloalkenyl group, containing from three to eight carbon atoms, wherein R, R₁ and R₂ are further characterized in that the total number of carbon atoms in said groups range from about four to about 25.

4. The process as defined in claim 3 wherein R and R₂ contain up to two functional groups other than in the alpha position of R₂, selected from the group consisting of halo, alkoxy, cyano, acetyl or lower dialkylamino group.

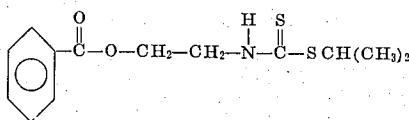
5. The process as defined in claim 3 wherein X is a lower alkyl group containing up to five carbon atoms.

6. The process as defined in claim 1 wherein from about 0.01 to about 0.25 pound of compound per ton of sulfide ore pulp is employed.

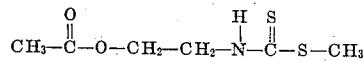
7. The process defined in claim 1 wherein said compound consists of



8. The process as defined in claim 1 wherein said compound consists of



9. The process as defined in claim 1 wherein said compound consists of



10. The process as defined in claim 1 wherein the sulfide ore is nickel sulfide ore or molybdenum sulfide ore.

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