United States Patent

[11] 3,590,997

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[54] FLOTATION OF SULFIDE ORES

8 Claims, No Drawings

[52] **U.S. Cl.** **209/166,** 260/327, 260/340.9, 260/455

[51] **Int. Cl.** **B03d 1/00,** C07c 153/00

[50] **Field of Search** 209/166, 167; 260/455, 327, 340.9

[56] **References Cited**

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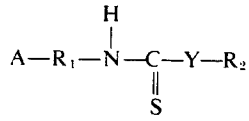
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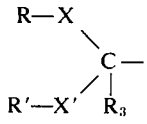
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Primary Examiner—Frank W. Lutter
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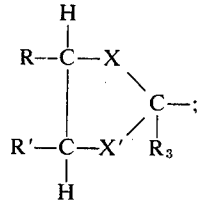
ABSTRACT: An improvement in the concentration of ores by flotation which comprises subjecting a sulfide ore in the form of a pulp to a flotation process in the presence of an effective quantity of a flotation collector corresponding to the formula



wherein A is a radical corresponding to the formula



or



X and Y consist of —S— or —O—; R, R′ and R_2 are hydrocarbyl groups, R_1 is an alkylene group and R_3 is H or a lower alkyl group. Certain of the indicated compounds provide for enhanced selectivity and/or recovery of sulfide minerals of Cu, Zn, Mo, Co, Ni and Pb over iron sulfide.

FLOTATION OF SULFIDE ORES

BACKGROUND

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 the like materials present in the ore, by introducing a gas into the liquid (or providing a gas in situ) to produce a froth 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 certain 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.

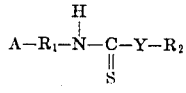
It is of importance to bear in mind that additaments of the above type are selected for use according to the nature of the ore, the mineral sought to be recovered, and the other additaments which are to be used in combination therewith.

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 and 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 sulfide copper minerals, sulfide zinc minerals, sulfide molybdenum minerals and others from sulfide iron minerals. The present invention concerns a novel class of compounds. These unique compounds can be used as collection agents in a flotation process. With some of the compounds better recoveries are realized and with others improved selectivity is achieved. Certain of the novel compounds produce an improvement in both aspects.

DESCRIPTION OF THE INVENTION

The novel compounds of the present invention correspond to the general formula



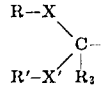
wherein

a. R_1 is an alkylene group containing up to about 10 carbon atoms, preferably up to about 5 carbon atoms;

b. R_2 is a hydrocarbyl group, other than an aryl group wherein an atom in the ring structure is bonded directly to Y;

c. Y is -S- or -O-; and

d. A is a radical corresponding to the formula

(I) 

wherein

i. R_3 is H or a lower alkyl group containing up to about 7 carbon atoms and preferably up to about 3 carbon atoms; and

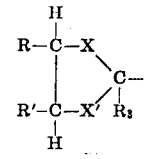
ii. when R_3 is an alkyl group, X and X′ are both -S- or -O-;

iii. when X and X′ are both -O- and R_3 is a lower alkyl group, R and R′ are independently an alkyl, alkenyl, cycloalkyl or cycloalkenyl group containing up to about 7 carbon atoms and preferably up to 3 carbon atoms;

iv. when X and X′ are both -S- and R_3 is a lower alkyl group, R and R′ are the same alkyl, alkenyl, cycloalkyl or cycloalkenyl group containing up to about 7 carbon atoms and preferably up to about 3 carbon atoms;

v. when R_3 is H, X and X′ are independently -S- or -O- and R and R′ are independently an alkyl, alkenyl, cycloalkyl or cycloalkenyl group containing up to about 7 carbon atoms and preferably up to 3 carbon atoms;

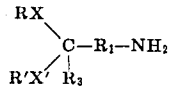
or (2) A is a radical corresponding to the formula



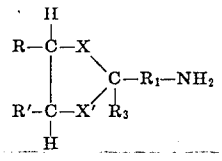
wherein X and X′ are independently -O- or -S-; R and R′ are independently H, or an alkyl group containing up to about 5 carbon atoms and preferably up to about 3 carbon atoms, and R_3 is H or an alkyl group containing up to 7 carbon atoms, preferably up to 3 carbon atoms.

Preferably R_2 is a member selected from the group consisting of an alkyl or alkenyl group containing up to 18 carbon atoms, preferably up to about 10 carbons; a cycloalkyl, or cycloalkenyl group containing up to about 8 carbon atoms, or an aralkenyl or aralkyl group wherein the alkyl or alkenyl portion contains up to about 5 carbon atoms and is bonded to Y.

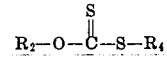
The novel compounds can be prepared, for example, by reacting an aminoacetal, aminoketal, aminothioacetal or aminothioketal compound corresponding to the formula,



or



wherein R, R′, X, X′, R_1 and R_3 are the same as defined hereinbefore, with a xanthate ester corresponding to the formula



wherein R_2 is the same as defined hereinbefore and R_4 is usually a lower alkyl group such as methyl or ethyl. A mercaptan R_4SH is evolved during the reaction.

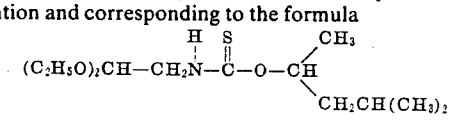
The compounds as defined herein are particularly suitable for use in standard flotation processes as flotation collectors to concentrate copper sulfide and other like minerals from sulfide ores. In such processes a pulp is first prepared by wet

grinding the 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 compound as defined herein is then added, preferably ranging from about 0.01 lb. to about 0.25 lb. per ton of pulp and the pulp is then agitated and aerated. The copper minerals and other like sulfide minerals collect as a froth which is readily overflowed or skimmed off from the residual gangue and nondesired 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.

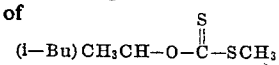
Example 1

One species of a compound within the scope of the present invention and corresponding to the formula



was prepared in the following manner.

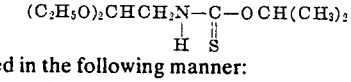
To 19.2 grams of



was added 13.3 grams of $H_2N\text{-}CH_2\text{-}CH(OC_2H_5)_2$. The reaction was warmed on the steam bath to 60° C. CH_3SH was evolved. Heating was continued under a reduced pressure of 30 mm. until CH_3SH ceased to be evolved. The yield was 94 percent. The product was subjected to infrared and NMR analysis, said analysis confirming the structure set forth directly above.

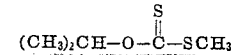
Example 2

Another compound within the scope of the present invention corresponding to the formula



was prepared in the following manner:

In a manner similar to that described in Example 1, 13.2 grams of distilled

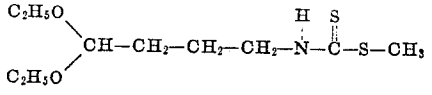


was reacted with 11.7 grams of $H_2NCH_2CH(OC_2H_5)_2$.

A 90 percent yield of product was obtained. The structure of the compound set forth above was confirmed for the product by infrared and NMR analysis. Partial calculated analysis for the compound is C-52.98 percent, H-9.00 percent and N-5.95 percent. Actual partial analysis of the product obtained was C-50.6 percent, H-8.5 percent and N-6.3 percent.

Example 3

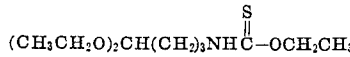
Another compound within the scope of the present invention, corresponding to the formula



was prepared in the following manner. To 13.8 grams of dimethyl trithiocarbonate was added 16.1 grams of the diethyl acetal of 4-aminobutanal. The temperature of the reaction mixture rose to about 50° C. with the evolution of CH_3SH. The reaction was completed by heating the mixture at a temperature of from about 55° to 60° C. under a reduced pressure of about 30 mm. until CH_3SH was no longer evolved. The product was an oil, obtained in about 92 percent yield. The above assigned structure for the compound was confirmed by infrared and NMR analysis.

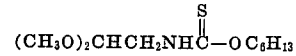
Other species of compounds within the scope of the present invention were prepared in a manner similar to that defined in the previous examples. The compounds corresponded to the following formula:

1.



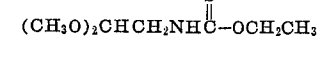
Calculated partial analysis is C-52.98 percent, H-9.30 percent and N-5.62 percent. Actual partial analysis of the prepared product was C-52.8 percent, H-9.3 percent and N-5.5 percent;

2.



and

3.

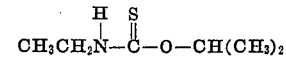


Calculated partial analysis for this compound is C-43.50 percent, H-7.82 percent and N-7.25 percent. Actual partial analysis of the prepared product was C-42.9 percent, H-7.52 percent and N-7.2 percent.

All the formulas of these products were confirmed by infrared and NMR techniques of analysis.

Example 4

Various novel compounds within the scope of the present invention were employed in a flotation separation of copper sulfide from an ore obtained from the Southwestern United States. A standard flotation collector compound corresponding to the formula



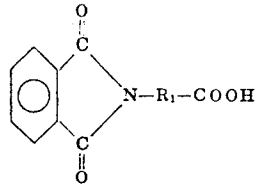
was employed as a control.

An ore sample was ground for 5 minutes at a pulp density of 59 percent solids together with 0.6 lb./ton of lime. The pulp was then diluted and conditioned for 2 minutes with the indicated amount of a collector compound, listed in Table I, and 0.088 lb./ton of frother. The pH of the pulp was 9.4. Flotation was then carried out for 8 minutes. The concentrate and tailings obtained were dried and assayed. The results obtained, the collector compounds and amount employed are set forth in the following Table I.

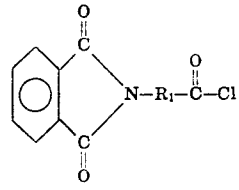
TABLE I

Run Number	Collector compound	Lbs./ton added	Percent Cu recovered
Control	Control	0.016	81.1
Do	do	0.032	82.1
Do	do	0.160	82.8
Do	do	0.240	83.5
1		0.160	81.0
2		0.016	83.2
3	Same as above	0.032	80.4
4	do	0.160	81.4
5		0.160	81.4
6	Same as above	0.240	83.2
7		0.016	81.0
8	Same as above	0.032	82.5
9	do	0.160	82.6

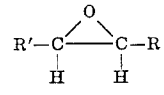
Cyclic aminoacetals useful in preparing compounds within the scope of the present invention can be prepared by a number of procedures known in the organic synthesis art. For example potassium phthalimide can be reacted with an α-chloro (or α-bromo) carboxylic acid to form a compound corresponding to the formula



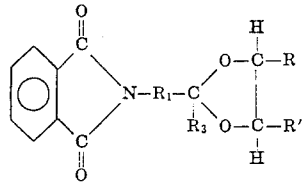
This compound can then be contacted with thionyl chloride and a base to provide a compound corresponding to the formula



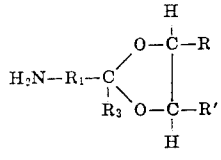
After this compound is purified it is reduced by the Rosenmund method with hydrogen over a regulated Pd° catalyst at the lowest temperatures at which HCl evolves to form the corresponding aldehyde. The aldehyde is condensed in the presence of $SnCl_4$ with an alkylene oxide,



in an anhydrous solvent to give a compound corresponding to the formula

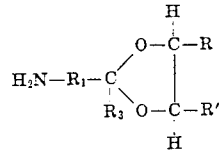


wherein R_3 is H. Treatment with hydrazine gives the cyclic aminoacetal corresponding to the formula

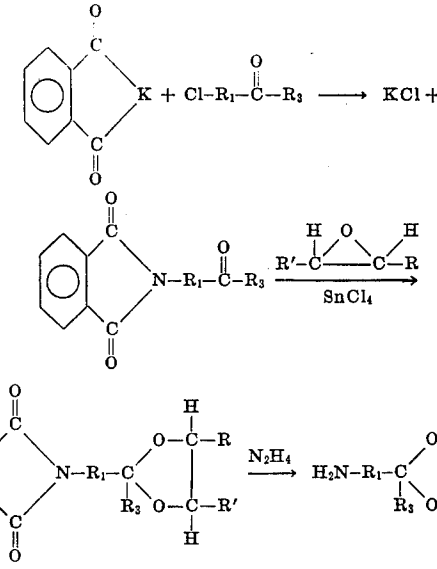


wherein R, R′ and R_1 are the same as defined hereinbefore and R_3 is H.

Cyclic aminoketals i.e. compounds corresponding to the general formula



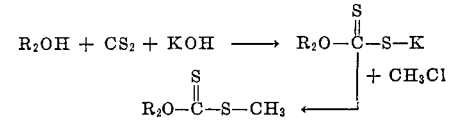
wherein R, R′, and R_1 are the same as defined hereinbefore and R_3 is a lower alkyl group, can be prepared in the following manner. A chloro or bromo ketone is reacted with a phthalimide salt. The product is condensed in the presence of $SnCl_4$ with an alkylene oxide in an anhydrous solvent, and the resulting product treated with hydrazine to produce the cyclic aminoketal. The sequence of the reaction steps can be summarized as follows



Other cyclic species can be prepared by the condensation of cyano or nitro substituted ketones or aldehydes with epoxides, followed by the reduction of the cyano or nitro group to the NH_2 group.

Noncyclic aminoacetals can be made by known methods for converting carbonyl compounds to the corresponding acetal or ketal, employing carbonyl compounds substituted with cyano or nitro groups and then effecting reduction of the groups to the $-NH_2$ group, and also be employing certain aminocarbonyl compounds directly. Also, aminoacetal and aminoketal compounds, both cyclic and noncyclic, can be made by amination of halo acetals, etc., the latter compounds being prepared by halogenation of carbonyl compounds prior to their conversion to the acetals or ketals by known methods. Wagner and Zook; *Synthetic Organic Chemistry*, PP 261—275, 1953, can be referred to for detailed description of various procedures for preparing various acetals and ketal starting materials employed in the present invention.

The xanthate starting materials can be prepared, for example, by reacting an alkali metal alkoxide* with CS_2 and then with methyl chloride. The reaction is represented by

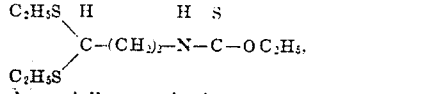


*To prepare the alkoxide of a tertiary alcohol a separate preliminary reaction with potassium metal is employed.

wherein R_2 is the same as defined hereinbefore and K represents an alkali metal. Suitable alcohols include cyclohexanol, cyclohexenol, allyl alcohol, cinnamyl alcohol, crotyl alcohol, 2,3,5-trimethyl-3-hexanol; 2,3,4-trimethyl-2-hexanol and other like alcohols.

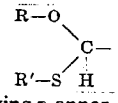
Both cyclic and noncyclic aminothioacetals and aminothioketals can be prepared in a manner similar to those previously described for the preparation of the cyclic and noncyclic aminoacetal and aminoketal compounds. A process for preparing dithiolane acids and esters is taught in U.S. Pat. No. 2,839,445. The so prepared compounds can be converted by methods known in the art to the corresponding nitriles or amides and the latter reduced to the amine intermediates which can then be reacted with suitable xanthate compounds to provide compounds within the scope of the present invention. One specific compound within the scope of the present invention is prepared in the following manner: To 13.6 grams of methyl ethyl xanthate is added 12.9 grams of 3,3-bis(ethylthio)propyl amine. After the spontaneous evolution

of methyl mercaptan ceases the reaction mixture is heated at 60° C. under reduced pressure to complete the removal of the mercaptan. The product, an oil, corresponding to the formula

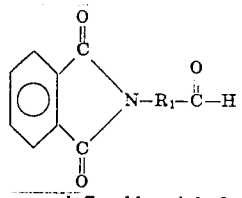


is produced in substantially quantitative amounts.

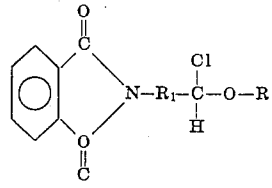
Other aminoacetals which can be employed to prepared compounds within the scope of the present invention wherein A- corresponds to the radical



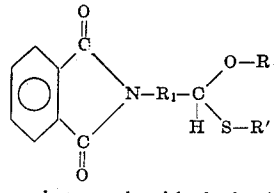
are prepared in the following manner. An aldehyde compound corresponding to the formula



wherein R_1 is the same as defined hereinbefore, is reacted with a primary or secondary alcohol, ROH wherein R is the same as defined hereinbefore, and a dry hydrogen halide e.g. HCl, at ice temperature to form a compound corresponding to the formula (when HCl is employed).

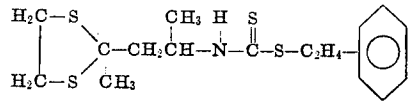


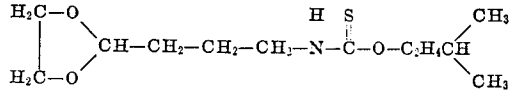
This compound is reacted with R'SNa to form the compound

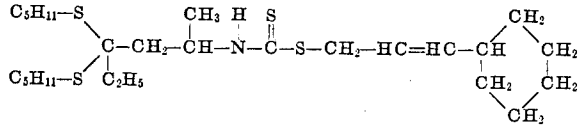


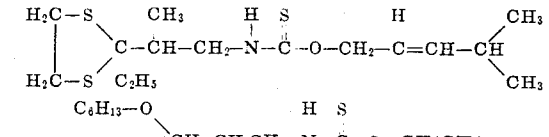
and this compound treated with hydrazine to give the aminoacetal starting material.

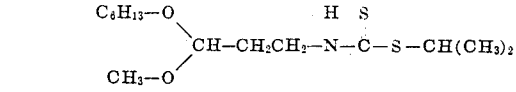
Other novel compounds which can be prepared by a method as defined hereinbefore and which are useful as flotation collectors in the concentration of sulfide compound containing ores include for example:

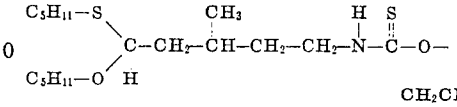


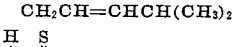


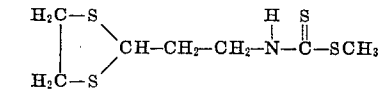


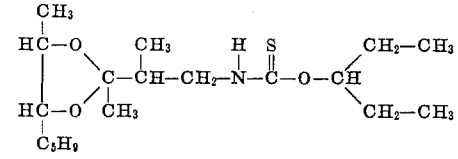


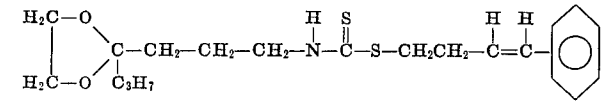


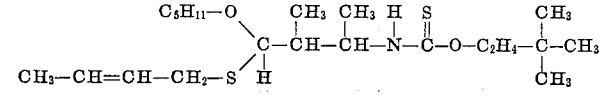


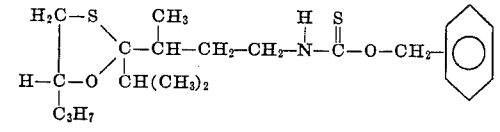


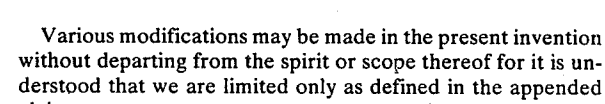








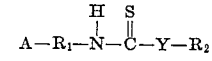




Various modifications may be made in the present invention without departing from the spirit or scope thereof for it is understood that we are limited only as defined in the appended claims.

What we claim is:

1. In the process of concentrating sulfide ores by froth flotation in the presence of a flotation collector compound the improvement which comprises: subjecting the sulfide ore in pulp form to a flotation collector comprising a compound corresponding to the formula

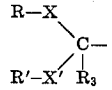


wherein

a. R_1 is an alkylene group containing up to about 10 carbon atoms;

b. wherein R_2 is a member selected from the group consisting of an alkyl or alkenyl group containing up to 18 carbon atoms, a cycloalkyl or cycloalkenyl group containing up to about 8 carbon atoms, or an aralkyl or aralkenyl group wherein the alkyl or alkenyl portion contains up to about 5 carbon atoms and is bonded to Y.

c. Y is a member selected from the group consisting of -S- or -O-; and d. A is a radical selected from the group consisting of a radical corresponding to the formula

(1) 

wherein

i. R_3 is a member selected from the group consisting of H or an alkyl group containing up to about 7 carbon atoms; and

ii. when R_3 is an alkyl group, X and X' are both the same members selected from the group consisting of -S- or -O-;

iii. when X and X' are both -O- and R_3 is an alkyl group containing up to about 7 carbon atoms, R and R' are in-

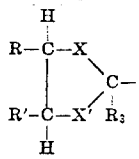
dependently a member selected from the group consisting of an alkyl, alkenyl, cycloalkyl or cycloalkenyl group containing up to about 7 carbon atoms:

iv. when X and X′ are both -S- and R_3 is an alkyl group containing up to 7 carbon atoms, R and R′ are both the same member selected from the group consisting of alkyl, alkenyl, cycloalkyl, cycloalkenyl group containing up to about 7 carbon atoms;

v. when R_3 is H, X and X′ are independently a member selected from the group consisting of -S- and -O- and R and R′ are independently an alkyl, alkenyl, cycloalkyl or cycloalkenyl group containing up to about 7 carbon atoms;

or,

2. A is a radical corresponding to the formula

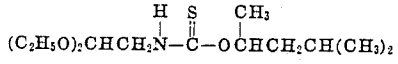


wherein

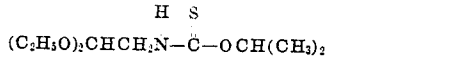
X and X′ are independently a member selected from the group consisting of -O- or -S-; R and R′ are independently a member selected from the group consisting of H or an alkyl group containing up to about 5 carbon atoms, and R_3 is a member selected from the group consisting of H or an alkyl group containing up to 7 carbon atoms.

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

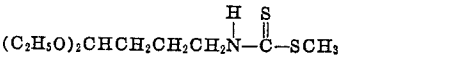
3. The process as defined in claim 1 wherein said flotation collector corresponds to the formula



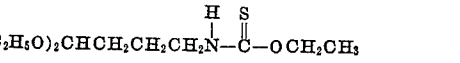
4. The process as defined in claim 1 wherein said flotation collector corresponds to the formula



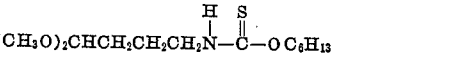
5. The process as defined in claim 1 wherein said flotation collector corresponds to the formula



6. The process as defined in claim 1 wherein said flotation collector corresponds to the formula



7. The process as defined in claim 1 wherein said flotation collector corresponds to the formula



8. The process as defined in claim 1 wherein said flotation collector corresponds to the formula

