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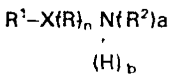
(54) **Novel collectors for the froth flotation of mineral values.**

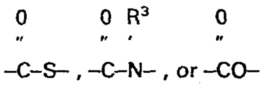
(57) A collector and process for ~~recovering metal values from~~ a metal ore by subjecting the metal ore, in the form of an aqueous pulp, to a froth flotation process in the presence of a collector wherein the collector comprises a compound corresponding to the formula



$$R^1-X(R)_n\underset{\displaystyle (H)_b}{N}(R^2)a$$

where R is $-CH_2-$, $-\underset{OH}{\overset{H}{C}}-$, $-\overset{O}{\overset{\|}{C}}-$, or mixture thereof and n is an integer from 1 to 6 or $(R)_n$ is $(CH_2)_mC\equiv$ where m is an integer from 0 to 6; R^1 and each R^2 are independently C_{1-22} hydrocarbyl or a C_{1-22} hydrocarbyl substituted with one or more hydroxy, amino, phosphonyl, alkoxy, imino, carbamyl, carbonyl, thiocarbonyl, cyano, carboxyl, hydrocarbylimino groups, with the proviso that R^2 can be a divalent radical with both valencies bonded directly to the atom

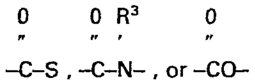
X is ~~$-S-$, $-O-$, $-N-R^3$~~,



$$-\overset{O}{\overset{\|}{C}}-S-,\ -\overset{O}{\overset{\|}{C}}-\overset{R^3}{N}-,\ \text{or}\ -\overset{O}{\overset{\|}{C}}O-$$

R^3 is H or a C_{1-22} hydrocarbyl;
a is an interger of 0, 1 or 2;
b is an interger of 0, 1 or 2;

with the proviso that the sum of a and b equals 2 except when R^2 is a divalent radical with both valencies bonded directly to the N atom, in which case, b=1 and a=0 or when (R) is $(CH_2)_mC\equiv$ in which case, a+b=0, and with the further proviso that when X is



$$-\overset{O}{\overset{\|}{C}}-S,\ -\overset{O}{\overset{\|}{C}}-\overset{R^3}{N}-,\ \text{or}\ -\overset{O}{\overset{\|}{C}}O-$$

the carbonyl moiety is bonded to R^1.

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NOVEL COLLECTORS FOR
THE FROTH FLOTATION OF
MINERAL VALUES

This invention relates to novel collectors for the recovery of mineral values from mineral ores by froth flotation.

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 is 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 <u>in situ</u>) 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 the selective 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, these particles rise to the top of the liquid to form a froth.

Various agents have been admixed with the suspension to improve the frothing and collection process. Such added agents are classed according to the function to be performed and include, for example; 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, and the like; modifiers such as activators to induce flotation in the presence of a collector, such as copper sulfate; depressants, such as 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, such as lime, soda ash, and the like.

It is of importance to bear in mind that additives of the hereinbefore described types 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.

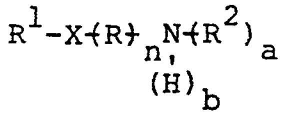
An understanding of the phenomenon which makes flotation a particularly valuable industrial operation is not essential to the practice of the present invention. It appears, however, to be largely associated with a selective affinity of the surface of particulated solids, suspended in a liquid containing entrapped gas, for the liquid on the 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 sulfide copper minerals, sulfide zinc minerals, sulfide molybdenum minerals and others from iron sulfide minerals, e.g., pyrite.

Among collectors commonly used for the recovery of sulfide-containing metal values are xanthates, dithiophosphates, and thionocarbamates. Collectors for the recovery of sulfide-containing metal values are common and used widely. The difficulty is in the recovery of oxide-containing mineral values, as collectors suitable for the recovery of such mineral values are generally not of a commercially acceptable quality.

What is needed are collectors which are useful for the recovery of a broad range of metal values from metal ores, including the recovery of sulfide-containing mineral values and oxide-containing mineral values. Furthermore, what is needed are collectors which give high rates of recovery of the mineral values along with good selectivities towards the mineral values over the gangue, that is, the undesired portions of the mineral ore.

The invention particularly resides in a collector for recovering metal values from a metal ore in which the metal ore, in the form of an aqueous pulp, is subjected to froth flotation, wherein the collector is a compound corresponding to the formula



$$R^1-X-(R)_n-\underset{(H)_b}{\underset{|}{N}}-(R^2)_a$$

where R is $-CH_2-$, $-\overset{H}{\underset{OH}{C}}-$, $-\overset{O}{\overset{\|}{C}}-$, or a combination thereof

and n is an integer from 1 to 6 or $-(R)_n$ is $-(CH_2)_m C\equiv$

where m is an integer from 0 to 6; R^1 and each R^2 are independently C_{1-22} hydrocarbyl or a C_{1-22} hydrocarbyl substituted with one or more hydroxy, amino, phosphonyl, alkoxy, imino, carbamyl, carbonyl, thiocarbonyl, cyano, carboxyl, hydrocarbylthio, hydrocarbyloxy, hydrocarbylamino or hydrocarbylimino groups, with the proviso that R^2 can be a divalent radical with both valencies bonded directly to the N atom

X is $-S-$, $-O-$, $-\overset{|}{N}-R^3$

$-\overset{O}{\overset{\|}{C}}-S-$, $-\overset{O}{\overset{\|}{C}}-\overset{R^3}{\overset{|}{N}}-$, or $-\overset{O}{\overset{\|}{C}}O-$;

R^3 is H or a C_{1-22} hydrocarbyl;

a is an integer of 0, 1 or 2;

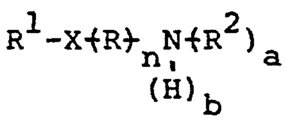
b is an integer of 0, 1 or 2;

with the proviso that the sum of a and b equals 2 except when R^2 is a divalent radical with both valencies bonded directly to the N atom, in which case, b=1 and a=0 or when $(R)_n$ is $(CH_2)_mC\equiv$ in which case, a+b=0, and with the further proviso that when X is

$-\overset{O}{\overset{\|}{C}}-S-$, $-\overset{O}{\overset{\|}{C}}-\overset{R^3}{\overset{|}{N}}-$, or $-\overset{O}{\overset{\|}{C}}O-$

the carbonyl moiety is bonded to R^1.

The invention also resides in a method for recovering metal values from a metal ore which comprises subjecting the metal ore, in the form of an aqueous pulp, to a froth flotation process in the presence of a flotation collector under conditions such that the metal values are recovered in the froth, wherein the collector comprises a compound corresponding to the formula



$$R^1-X(R)_n\underset{(H)_b}{\underset{|}{N}}(R^2)_a$$

wherein: R is $-CH_2-$, $-\overset{H}{\underset{OH}{C}}-$, $-\overset{O}{\overset{\|}{C}}-$, or mixtures thereof and n is an integer from 1 to 6 or $(R)_n$ is $(CH_2)_mC\equiv$ wherein m is an integer from 0 to 6; R^1 and each R^2 are independently C_{1-22} hydrocarbyl or a C_{1-22} hydrocarbyl substituted with one or more hydroxy, amino, phosphonyl, alkoxy, imino, carbamyl, carbonyl, thiocarbonyl, cyano, carboxyl, hydrocarbylthio, hydrocarbyloxy, hydrocarbylamino, or hydrocarbylimino groups;

X is $-S-$, $-O-$, $-\overset{|}{N}-R^3$,

$-\overset{O}{\overset{\|}{C}}-S-$, $-\overset{O}{\overset{\|}{C}}-\overset{R^3}{\overset{|}{N}}-$, or $-\overset{O}{\overset{\|}{C}}O-$;

R^3 is hydrogen or a C_{1-22} hydrocarbyl;

a is an integer of 0, 1 or 2;

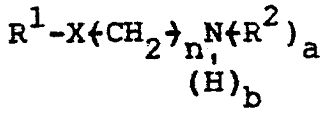
b is an integer of 0, 1 or 2;

with the proviso that the sum of a and b equals 2 except when R^2 is a divalent radical with both valencies bonded directly to the N atom, in which case, b=1 and a=0 or when $(R)_n$ is $(CH_2)_mC\equiv$ in which case, a+b=0, and with the further proviso that when X is

$-\overset{O}{\overset{\|}{C}}-S-$, $-\overset{O}{\overset{\|}{C}}-\overset{R^3}{\overset{|}{N}}-$, or $-\overset{O}{\overset{\|}{C}}O-$;

the carbonyl group is bonded to R^1.

In a preferred embodiment of the invention, the collector comprises a compound corresponding to the formula



$$R^1\text{-}X(CH_2)_n\underset{(H)_b}{N}(R^2)_a$$

wherein:

R^1 is C_{1-22} hydrocarbyl optionally substituted with one or more hydroxy, amino, phosphonyl, or alkoxy moieties;

R^2 is a C_{1-6} alkyl, a C_{1-6} alkylcarbonyl, or a C_{1-6} alkyl group optionally substituted with an amino, hydroxy or phosphonyl moiety, or a C_{1-6} alkylcarbonyl group optionally substituted with an amino, hydroxy or phosphonyl moiety;

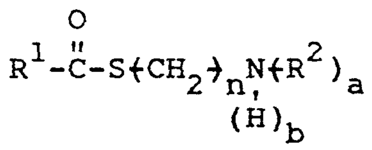
and X, a, b and n are as defined above.

Collectors of this invention surprisingly float a broad range of metal values including sulfide ores, oxide ores and precious metals. Furthermore, such collectors give improved recoveries of the mineral values including mineral oxides, mineral sulfides and precious metals. Not only are surprisingly high recoveries achieved, but the selectivity towards the desired mineral values is surprisingly high.

The preferred novel collectors of this invention include omega-(hydrocarbylthio)alkylamines; S-(omega-aminoalkyl)hydrocarbon thioates; N-(hydrocarbyl)-alpha,-omega-alkanediamines; (omega-aminoalkyl) hydrocarbon amides; omega-(hydrocarbyloxy-)alkylamines; omega-aminoalkyl hydrocarbonoates; or mixtures thereof. More preferred collectors include omega-(hydrocarbylthio)-alkylamines; N-(hydrocarbyl)-alpha,omega-alkanediamines; and omega-(hydrocarbyloxy-)alkylamines; or mixtures thereof. Most preferred collectors include omega--(hydrocarbylthio)alkylamines; N-(hydrocarbyl)-alpha,omega--alkanediamines; or mixtures thereof. The most preferred class of collectors are the omega-(hydrocarbylthio)-alkylamines.

In the hereinbefore presented formula of the preferred embodiment, R^1 is preferably C_{2-14} hydrocarbyl, and more preferably C_{4-11} hydrocarbyl. R^2 is preferably C_{1-6} alkyl or C_{1-6} alkylcarbonyl, more preferably C_{1-4} alkyl or C_{1-4} alkylcarbonyl, and most preferably C_{1-2} alkyl or C_{1-2} alkylcarbonyl. R^3 is preferably hydrogen or C_{2-14} hydrocarbyl, more preferably hydrogen or C_{4-11} hydrocarbyl, and most preferably hydrogen. Preferably, a is the integer 0 or 1. Preferably, b is the integer 1 or 2. Preferably, n is an integer from 1 to 4, and most preferably the integer 2 or 3. X is preferably -S-, $-\overset{|}{N}-R^3$, or -O-. X is more preferably -S- or $-\overset{|}{N}-R^3$. X is most preferably -S-.

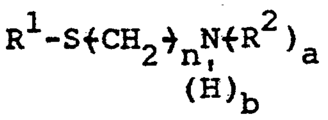
Preferred S-(omega-aminoalkyl) hydrocarbon thioates correspond to the formula



$$R^1-\overset{\overset{O}{\|}}{C}-S(CH_2)_n\underset{\underset{(H)_b}{|}}{N}(R^2)_a$$

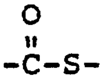
wherein R^1, R^2, a, b and n are as hereinbefore defined.

Preferred omega-(hydrocarbylthio)alkylamines correspond to the formula



$$R^1-S(CH_2)_n\underset{(H)_b}{N}(R^2)_a$$

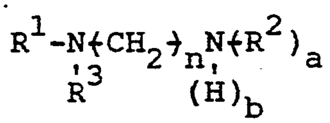
wherein R^1, R^2, a, b and n are as hereinbefore defined. In those embodiments wherein X is -S- or



$$-\overset{O}{\overset{\|}{C}}-S- ,$$

R^1 is preferably C_{4-10} hydrocarbyl.

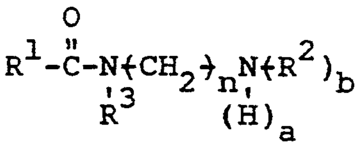
Preferred N-(hydrocarbyl)-alpha,omega-alkanediamines correspond to the formula



$$R^1-\underset{R^3}{N}(CH_2)_n\underset{(H)_b}{N}(R^2)_a$$

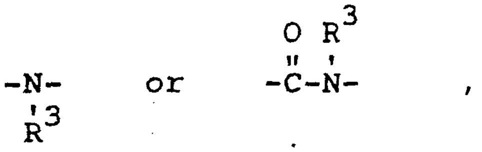
wherein R^1, R^2, R^3, a, b and n are as hereinbefore defined.

Preferred N-(omega-aminoalkyl) hydrocarbon amides correspond to the formula



$$R^1-\overset{O}{\overset{\|}{C}}-\underset{R^3}{N}(CH_2)_n\underset{(H)_a}{N}(R^2)_b$$

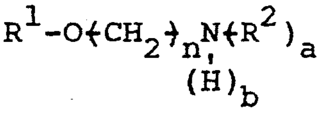
wherein R^1, R^2, R^3, a, b and n are as hereinbefore defined. In those embodiments wherein X is



$$-\underset{R^3}{N}- \quad \text{or} \quad -\overset{O}{C}-\overset{R^3}{N}- \quad ,$$

the total carbon content of the groups R^1 and R^3 is preferably from 1 to 23, more preferably from 2 to 16, and most preferably from 4 to 15.

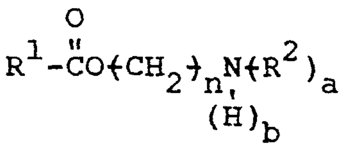
Preferred omega-(hydrocarbyloxy-)alkylamines correspond to the formula



$$R^1-O(CH_2)_n\underset{(H)_b}{N}(R^2)_a$$

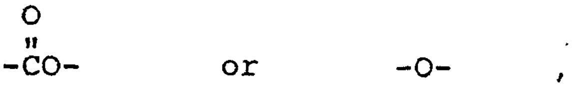
wherein R^1, R^2, a, b and n are as hereinbefore defined.

Preferred omega-aminoalkyl hydrocarbonoates correspond to the formula



$$R^1-\overset{O}{C}O(CH_2)_n\underset{(H)_b}{N}(R^2)_a$$

wherein R^1, R^2, a, b and n are as hereinbefore defined. In those embodiments wherein X is



$$-\overset{O}{C}O- \quad \text{or} \quad -O- \quad ,$$

R^1 is most preferably C_{6-11} hydrocarbyl.

Hydrocarbon means herein an organic compound containing carbon and hydrogen atoms. The term hydrocarbon includes the following organic compounds: alkanes, alkenes, alkynes, cycloalkanes, cycloalkenes, cycloalkynes, aromatics, aliphatic and cycloaliphatic aralkanes and alkyl-substituted aromatics. Aliphatic refers herein to straight- and branched-chain, and saturated and unsaturated, hydrocarbon compounds, that is, alkanes, alkenes or alkynes. Cycloaliphatic refers herein to saturated and unsaturated cyclic hydrocarbons, that is, cycloalkenes and cycloalkanes. The term aromatic includes biaryl, benzene, naphthene, phenanthracene, anthracene and two aryl groups bridged by an alkylene group.

Cycloalkane refers to an alkane containing one, two, three or more cyclic rings. Cycloalkene refers to mono-, di- and polycyclic groups containing one or more double bonds.

Hydrocarbyl means herein an organic radical containing carbon and hydrogen atoms. The term hydrocarbyl includes the following organic radicals: alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aryl, aliphatic and cycloaliphatic aralkyl and alkaryl. Aliphatic refers herein to straight- and branched-, and saturated and unsaturated, hydrocarbon radicals, that is, alkyl, alkenyl or alkynyl. Cycloaliphatic refers herein to saturated and unsaturated cyclic hydrocarbon radicals, that is, cycloalkenyl and cycloalkyl. The term aryl includes radicals of biaryl, biphenylyl, phenyl, naphthyl, phenanthrenyl, anthracenyl and two aryl groups bridged by an alkylene group. Alkaryl refers herein to an alkyl-, alkenyl- or alkynyl-substituted aryl substituent wherein aryl is as defined hereinbefore. Aralkyl means herein an alkyl, alkenyl or alkynyl group substituted with an aryl group, wherein aryl is as defined hereinbefore. Alkenearyl refers herein to a radical which contains at least one alkene portion and one aromatic portion, and includes those radicals in which more than one alkene radical alternates with more than one aryl radical. C_{1-20} alkyl includes straight- and branched-chain methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl groups. C_{1-5} alkyl includes methyl, ethyl, propyl, butyl and pentyl.

Cycloalkyl refers to alkyl groups containing one, two, three or more cyclic rings. Cycloalkenyl refers to mono-, di- and polycyclic groups containing one or more double bonds. Cycloalkenyl also refers to cycloalkenyl groups wherein two or more double bonds are present.

The process of this invention is useful for the recovery by froth flotation of metal values from metal ores. A metal ore includes the metal as it is taken out of the ground and comprises the metal values in admixture with the gangue. Gangue refers herein to those materials which are of no value and need to be separated from the metal values. This process can be used to recover metal oxides, metal sulfides and other metal values.

Sulfide ores for which these compounds may be used include copper sulfide-, zinc sulfide-, molybdenum sulfide-, cobalt sulfide-, nickel sulfide-, lead sulfide-, arsenic sulfide-, silver sulfide-, chromium sulfide-, gold sulfide-, platinum sulfide- and uranium sulfide--containing ores. Examples of sulfide ores from which metal sulfides may be concentrated by froth flotation using the process of this invention include copper-bearing ores such as, for example, covellite (CuS), chalcocite

(Cu_2S), chalcopyrite ($CuFeS_2$), valleriite ($Cu_2Fe_4S_7$ or $Cu_3Fe_4S_7$), bornite (Cu_5FeS_4), cubanite ($Cu_2SFe_4S_5$), enargite ($Cu_3(As_1Sb)S_4$), tetrahedrite (Cu_3SbS_2), tennantite ($Cu_{12}As_4S_{13}$), brochantite ($Cu_4(OH)_6SO_4$), antlerite ($Cu_3SO_4(OH)_4$), famatinite ($Cu_3(SbAs)S_4$), and bournonite ($PbCuSbS_3$); lead-bearing ores such as, for example, galena (PbS); antimony-bearing ores such as, for example, stibnite (Sb_2S_3); zinc-bearing ores such as, for example, sphalerite (ZnS); silver-bearing ores such as, for example, stephanite (Ag_5SbS_4), and argentite (Ag_2S); chromium-bearing ores such as, for example, daubreelite ($FeSCrS_3$); and platinum- and palladium-bearing ores such as, for example, cooperite ($Pt(AsS)_2$).

Oxide ores for which this process may be used include copper oxide-, aluminum oxide-, iron oxide-, iron titanium oxide-, magnesium aluminum oxide-, iron chromium oxide-, titanium oxide-, manganese oxide-, tin oxide-, and uranium oxide-containing ores. Examples of oxide ore from which metal oxides may be concentrated by froth flotation using the process of this invention include copper-bearing ores, for example cuprite (Cu_2O), tenorite (CuO), malachite ($Cu_2OH)_2CO_3$), azurite ($Cu_3(OH)_2(CO_3)_2$), atacamite ($Cu_2Cl(OH)_3$), chrysocolla ($CuSiO_3$); aluminum-bearing ores, for example corundum; zinc-containing ores, such as zincite (ZnO), and smithsonite ($ZnCO_3$); iron-containing ores, for example hematite and magnetite; chromium-containing ores, for example chromite ($FeOCr_2O_3$); iron- and titanium-containing ores, for example ilmenite; magnesium- and aluminum-containing ores, for example spinel; iron-chromium-containing ores, for example chromite; titanium-containing ores, for example rutile; manganese-containing ores, for example pyrolusite; tin-containing ores, for example cassiterite; and uranium-containing ores, for example uraninite; and uranium-bearing ores such as, for example, pitchblende ($U_2O_5(U_3O_8)$) and gummite (UO_3nH_2O).

Other metal values for which this process may be used include gold-bearing ores, for example sylvanite ($AuAgTe_2$) and calaverite ($AuTe$); platinum- and palladium-bearing ores, for example sperrylite ($PtAs_2$); and silver-bearing ores, such as hessite ($AgTe_2$), for example.

In a preferred embodiment of this invention, oxide- or sulfide-containing values are recovered. In a more preferred embodiment of this invention copper sulfide, nickel sulfide, lead sulfide, zinc sulfide or molybdenum sulfide values are recovered. In an even more preferred embodiment, copper sulfide values are recovered.

The collectors of this invention can be used in any concentration which gives the desired recovery of the desired metal values. In particular, the concentration used is dependent upon the particular metal value to be recovered, the grade of the ore to be subjected to the froth flotation process, the desired quality of the metal value to be recovered, and the particular mineral value which is being recovered. Preferably, the collectors of this invention are used in concentrations of from 5 g to 250 g per metric ton of ore, more preferably from 10 g to 100 g of collector per metric ton of ore to be subjected to froth flotation.

Froth flotation of this invention usually requires the use of frothers. Any frother well-known in the art, which results in the recovery of the desired metal value is suitable. Further, in the process of this invention it is contemplated that collectors of this invention can be used in mixtures with other collectors,eg. well-known in the art.

Collectors, known in the art, which may be used in admixture with the collectors of this invention are those which will give the desired recovery of the desired mineral value. Examples of collectors useful in this invention include alkyl monothiocarbonates, alkyl dithiocarbonates, alkyl trithiocarbonates, dialkyl dithiocarbamates, alkyl thionocarbamates, dialkyl thioureas, monoalkyl dithiophosphates, dialkyl and diaryl dithiophosphates, dialkyl monothiophosphates, thiophosphonyl chlorides, dialkyl and diaryl dithiophosphonates, alkyl mercaptans, xanthogen formates, xanthate esters, mercapto benzothiazoles, fatty acids and salts of fatty acids, alkyl sulfuric acids and salts thereof, alkyl and alkaryl sulfonic acids and salts thereof, alkyl phosphoric acids and salts thereof, alkyl and aryl phosphoric acids and salts thereof, sulfosuccinates, sulfosuccinamates, primary amines, secondary amines, tertiary amines, quaternary ammonium salts, alkyl pyridinium salts, guanidine, and alkyl propylene diamines.

Frothers useful in this invention include any frothers known in the art which give the recovery of the desired mineral value. Examples of such frothers include C_{5-8} alcohols, pine oils, cresols, C_{1-4} alkyl ethers of polypropylene glycols, dihydroxylates of polypropylene glycols, glycols, fatty acids, soaps, alkylaryl sulfonates, and the like. Furthermore, blends of such frothers may also be used. All frothers which are suitable for beneficiation of mineral ores by froth flotation can be used in this invention.

The omega-(hydrocarbylthio)alkylamines can be prepared by the processes disclosed in Berazosky et al., U.S. Patent 4,086,273; French Patent 1,519,829; or Beilstein, 4, 4 Ed., 4th Supp., 1655 (1979). The (omega-aminoalkyl) hydrocarbon amides can be prepared by the processes described in Fazio, U.S. Patent 4,326,067; Acta Polon Pharm, 19, 277 (1962); or Beilstein, 4, 4th Ed., 3rd Supp., 587 (1962). The omega-(hydrocarbyloxy-)alkylamines can be prepared by the processes described in British Patent 869,409; or Hobbs, U.S. Patent 3,397,238. The S-(omega-aminoalkyl) hydrocarbon thioates can be prepared by the processes described in Faye et al., U.S. Patent 3,328,442; or Beilstein, 4, 4th Ed., 4th Supp., 1657 (1979). The omega-aminoalkyl hydrocarbonoates can be prepared by the process described in J. Am. Chem. Soc., 83, 4835 (1961); Beilstein, 4, 4th Ed., 4th Supp., 1413 (1979); or Beilstein, 4, 4th Ed., 4th Supp., 1785 (1979). The N-(hydrocarbyl)-alpha,omega-alkanediamines can be prepared by the process well-known in the art, one example is the process described in East German Patent 98,510.

The following examples are included for illustration and are not intended to limit the scope of the invention or claims. Unless otherwise indicated, all parts and percentages are by weight.

In the following examples, the performance of the frothing processes described is shown by giving the rate constant of flotation and the amount of recovery at infinite time. These numbers are calculated by using the formula

$$r = R_{\infty} [1 - \frac{1-e^{-Kt}}{Kt}]$$

wherein: r is the amount of mineral recovered at time t, K is the rate constant for the rate of recovery and R_∞ is the calculated amount of the mineral which would be recovered at infinite time. The amount recovered at various times is determined experimentally and the series of values are substituted into the equation to obtain the R_∞ and K values. The above formula is explained in "Selection of Chemical Reagents for Flotation", Chapter 45, pp. 907-934, Mineral Processing Plant Design, 2nd Ed., 1980, by R. Klimpel AIME (Denver).

Example 1 - Froth Flotation of Copper Sulfide

In this example several of the collectors of this invention are tested for flotation of copper sulfide values. A 500-g quantity of Chilean copper ore, chalcopyrite copper sulfide ore, previously packaged is placed in a rod mill with 257 g of deionized water. The copper ore comprises 80.2 percent with a particle size of about 75 micrometers of less. A quantity of lime is also added to the rod mill, based on the desired pH for the subsequent flotation. The rod mill is then rotated at 60 rpm for a total of 360 revolutions. The ground slurry is transferred to a 1500 ml cell of an Agitair® Flotation machine. The float cell is agitated at 1150 rpm and the pH is adjusted to 10.5 by the addition of further lime, if necessary.

The collector is added to the float cell (at a rate of 50 g/metric ton), followed by a conditioning time of one minute, at which time the frother, DOWFROTH® 250 (Trademark of The Dow Chemical Company) is added (at a rate of 40 g/metric ton). After the additional one-minute conditioning time, the air to the float cell is turned on at a rate of 4.5 liters per minute and the automatic froth removal paddle is started. The froth samples were taken off at 0.5, 1.5, 3, 5 and 8 minutes. The froth samples are dried overnight in an oven, along with the flotation tailings. The dried samples are weighed, divided into suitable samples for analysis, pulverized to insure suitable fineness, and dissolved in acid for analysis. The samples are analyzed using a DC Plasma Spectrograph.

The collectors that were tested for flotation of copper sulfide values of a Chilean copper ore are compiled in Table I and demonstrate that a wide variety of compounds within the scope of the invention are effective in the recovery of copper sulfide values. A base case example which employed no collector is included in Table I for comparison. It should be noted that the collectors of the invention in Table I were not selected for optimum performance, but represent arbitrary selection of compounds that show a significant response in the recovery and selectivity of mineral values.

TABLE I (Part A)

Collectors of the Class $R^1\text{-(S)-}(CH_2)_2\text{-N}\genfrac{}{}{0pt}{}{\diagup R^2}{\diagdown H}$

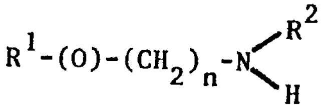
R^1	R^2	Cu		Gangue		Cu	Gangue	Selec-
		K	R	K	R	R-8[1]	R-8[1]	tivity[2]
heptyl	hydrogen	5.15	0.716	3.16	0.099	0.714	0.100	7.1
butyl	hydrogen	4.62	0.699	2.31	0.091	0.693	0.091	7.6
octyl	hydrogen	3.29	0.722	1.75	0.091	0.703	0.087	8.1
hexyl	hydrogen	4.14	0.730	2.19	0.095	0.724	0.094	7.7
methyl	hydrogen	3.92	0.490	3.51	0.064	0.479	0.064	7.5
dodecyl	hydrogen	2.31	0.605	1.94	0.048	0.586	0.047	12.5
octyl	ethylcarbonyl	1.79	0.716	1.13	0.073	0.638	0.062	10.3
hexyl	ethylcarbonyl	5.55	0.670	3.78	0.081	0.662	0.080	8.3
1,1-dimethyldecyl	ethylcarbonyl	1.46	0.640	0.82	0.097	0.571	0.080	7.1

1 - R-8 is experimental recovery after 8 minutes

2 - Selectivity is calculated as the copper recovery at 8 minutes divided by the gangue recovery at 8 minutes

TABLE I (Part B)

Collectors of the Class



$$R^1\text{-(O)-}(CH_2)_n\text{-N}\begin{matrix}\diagup R^2\\ \diagdown H\end{matrix}$$

R^1	R^2	n	Cu K	Cu R	Gangue K	Gangue R	Cu R-8[1]	Gangue R-8[1]	Selectivity[2]
nonylphenyl	hydrogen	2	2.61	0.583	3.48	0.080	0.572	0.081	7.1
nonylphenyl	TOFA[3]	2	2.22	0.430	3.41	0.116	0.410	0.112	3.7
nonyl	3-aminopropyl	3	4.03	0.603	2.89	0.077	0.586	0.073	8.0
nonyl	hydrogen	3	3.41	0.685	2.82	0.079	0.658	0.077	8.5
heptyl	hydrogen	3	1.59	0.675	1.31	0.082	0.622	0.076	8.2
nonylphenyl	ethylcarbonyl	2	2.44	0.358	2.94	0.054	0.341	0.053	6.4
phenyl	hydrogen	2	4.46	0.581	3.16	0.069	0.575	0.069	8.3
phenyl	ethylcarbonyl	2	2.56	0.295	4.04	0.071	0.287	0.070	4.1

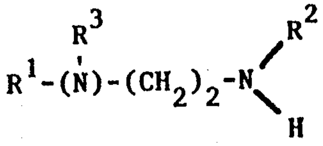
[1] - R-8 is experimental recovery after 8 minutes

[2] - Selectivity is calculated as the copper recovery at 8 minutes divided by the gangue recovery at 8 minutes

[3] - Tall oil fatty acid moiety

TABLE I (Part C)

Collectors of the Class

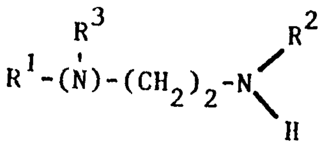


$R^1\text{-}(\overset{R^3}{N})\text{-}(CH_2)_2\text{-}N\begin{smallmatrix}R^2\\ H\end{smallmatrix}$

R^1	R^2	R^3	Cu		Gangue		Cu	Gangue	Selec-tivity[2]
			K	R	K	R	R-8[1]	R-8[1]	
butyl	hydrogen	butyl	4.61	0.628	3.12	0.056	0.622	0.057	10.9
butyl	ethylcarbonyl	butyl	4.16	0.443	3.31	0.084	0.428	0.081	5.3
ethyl	hydrogen	ethyl	3.55	0.488	3.37	0.056	0.475	0.056	8.5
ethylcarbonyl	hydrogen	hydrogen	2.15	0.298	3.57	0.053	0.284	0.052	5.5
heptylcarbonyl	hydrogen	hydrogen	5.66	0.636	3.68	0.095	0.630	0.094	6.7
hexyl	hydrogen	hexyl	3.52	0.608	2.36	0.069	0.587	0.067	8.8
hexyl	ethylcarbonyl	hexyl	1.54	0.438	1.06	0.080	0.394	0.068	5.8
heptylcarbonyl	hydrogen	hydrogen	4.32	0.532	2.33	0.099	0.523	0.097	5.4
nonylcarbonyl	hydrogen	hydrogen	5.22	0.669	3.06	0.091	0.654	0.089	7.3

TABLE I (Part C) Cont'd

Collectors of the Class



$$R^1-\overset{R^3}{\overset{|}{(N)}}-(CH_2)_2-N\begin{matrix}R^2\\H\end{matrix}$$

R^1	R^2	R^3	Cu		Gangue		Cu R-8[1]	Gangue R-8[1]	Selectivity[2]
			K	R	K	R			
4-((2-hydroxy)-butoxy)-3-methylphenyl	hydrogen	hydrogen	4.81	0.381	3.94	0.058	0.381	0.057	6.7
6-(2-hydroxy-propoxy)-2-ethylhexyl	hydrogen	hydrogen	3.06	0.438	2.82	0.062	0.422	0.061	7.0
(N-propyl)-8-(amino)-7-(hydroxy)-5-(ethyl)octyl	hydrogen	hydrogen	3.41	0.463	2.79	0.059	0.450	0.058	7.8
tetrahydro--2H-pyronyl	ethyl-carbonyl	hydrogen	3.27	0.295	6.37	0.073	0.289	0.073	4.0

[1] - R-8 is experimental recovery after 8 minutes

[2] - Selectivity is calculated as the copper recovery at 8 minutes divided by the gangue recovery at 8 minutes

TABLE I (Part D)

Compound	Cu		Gangue		Cu R-8[1]	Gangue R-8[1]	Selectivity[2]
	K	R	K	R			
3-(N,N-dimethyl)aminopropylamidononane	4.02	0.455	2.71	0.086	0.439	0.083	5.3
(1,2-ethanediyl(nitrilobis(methylene)))tetrakis phosphonic acid	2.68	0.318	2.74	0.076	0.306	0.072	4.2
No Collector[3]	2.63	0.298	3.20	0.060	0.289	0.098	4.9

[1] - R-8 is experimental recovery after 8 minutes

[2] - Selectivity is calculated as the copper recovery at 8 minutes divided by the gangue recovery at 8 minutes

[3] - Not an example of the invention

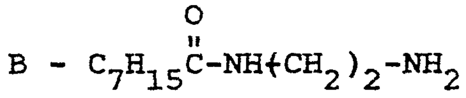
Example 2

A Central African copper oxide ore (Cu_2O) is subjected to the froth flotation process described in Example 1 using 40 grams per metric ton of the frother, DOWFROTH® 250 (Trademark of The Dow Chemical Company). The results are compiled in Table II with Collectors A and B being chosen from Table I.

TABLE II

Collector	Conc. g/ton	pH	Cu K	Cu R	Cu R-8
A	160	5.1	2.48	0.335	0.308
A	80	9.5	2.55	0.249	0.234
B	80	9.5	2.91	0.313	0.289
C	160	5.1	4.08	0.135	0.130

A - $C_6H_{13}\text{-S}(CH_2)_2\text{-}NH_2$



B - $C_7H_{15}\overset{O}{\overset{\|}{C}}\text{-NH}(CH_2)_2\text{-}NH_2$

C - Sodium isopropyl xanthate, not an embodiment of this invention

It is well known in the mining industry that existing commercial collectors such as sodium isopropyl xanthate do not float oxide minerals very effectively. It is therefore surprising that Collector A at a concentration of 80 g/ton will increase the recovery of copper values by 84.4 percent as compared to the Standard Collector C which was employed at a concentration of 160 g/ton, i.e. twice as much. When the performance of

Collector A, employing 160 g/ton is compared against the Standard C it can be seen that the recovery of copper values was increased by 148 percent. The fact that the collectors of this invention will float a substantially greater amount of copper values from copper oxide ore is indicative of the fact that the collectors of the invention are less sensitive to the form of the metal containing mineral, i.e. sulfide or oxide ore as compared to existing collectors.

Example 3

A Central Canadian sulfide ore containing copper sulfide, nickel sulfide, platinum, palladium and gold metal values is subjected to a series of froth flotations as described in Example 1 using the collectors of this invention and several collectors known in the art. The frother used is DOWFROTH® 1263 (Trademark of The Dow Chemical Company) at a concentration of 0.00625 lb/-ton (3.12 g/metric ton) The collectors are used at a concentration of 0.0625 lb/ton (31.2 g/metric ton). The froths produced are recovered at 0.5, 1.0, 2.0, 4.0, 7.0, 11.0 and 16.0 minutes. The results are compiled in Table III with collectors chosen from Table I.

TABLE III

Collector	Copper				Nickel				Pyrrhotite			Tailings[3]		
	K	R-4[1]	R-16[2]	R	K	R-4[1]	R-16[2]	R	K	R-16[2]	R	Pt	Pd	Au
Sodium amyl Xanthate*	5.4	.883	.934	.932	1.39	.696	.855	.876	0.49	0.275	.302	.0110	.0112	.0054
Z-2114*	4.7	.931	.958	1.00	0.87	.760	.889	.990	0.25	0.496	.612	.0071	.0100	.0049
OHTEA5	4.8	.885	.934	.936	1.94	.776	.890	.907	0.25	0.419	.540	.0054	.0094	.0048
Aerofloat 34776*	6.4	.909	.942	.949	1.31	.245	.325	.323	1.02	0.185	.177	.0139	.0116	.0054
NOPA7	4.4	.816	.887	.879	1.81	.637	.799	.789	0.66	0.199	.198	.0117	.0124	.0064

*Not an embodiment of this invention

[1] Recovery after 4 minutes

[2] Recovery after 16 minutes

[3] Ounces per metric ton - tailings represent amount of unrecovered metal contained in unfloated gangue material

[4] Trademark of The Dow Chemical Company - thionocarbonate

[5] OHTEA is omega-(hexylthio)ethylamine

[6] Trademark of American Cyanamide - dithiophosphate

[7] NOPA is 3-(nonyloxy)propylamine)

Table III illustrates the use of two novel compounds of this invention, i.e. OHTEA and NOPA as compared to three optimized industrial collector standards. The ore was complex containing various metal values. The collectors are comparable in performance in the recovery of copper values. The OHTEA collector was clearly superior in the recovery of nickel, platinum, palladium and gold. In the recovery of nickel, the R-16 value of OHTEA when compared to Z-211® showed a slight increase but a very surprising and significant decline in the recovery of pyrrhotite, i.e. 15.5 percent. A substantial improvement was also realized in the reduction of the tailings for platinum and palladium - the values were about equal for gold.

The collector NOPA showed a good recovery for copper and nickel when compared against the best known collectors employed in the field. It showed a superior performance in the reduction of R-16 pyrrhotite values when compared against the standards. The ratio of nickel recovery to pyrrhotite recovery is clearly superior when compared to known collectors, i.e., a 30 percent increase in the ratio. The selectivity of NOPA is significant if it is desired to lower the demand on smelters since much of the flotation product is undesired sulfur containing material.

<u>Example 4</u> - Froth flotation of Copper Sulfide

In this example several of the collectors of this invention are tested for flotation of copper sulfide values. A 500 gram quantity of Western Canada copper ore, a relatively high grade chalcopyrite copper sulfide ore with little pyrite, is placed in a rod mill having 1 inch rods, with 257 gram of deionized water and ground for

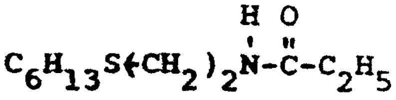
420 revolutions at a speed of 60 rpm to produce a size distribution of 25 percent less than 100 mesh. A quantity of lime is also added to the rod mill, based on the desired pH for the subsequent flotation. The ground slurry is transferred to a 1500 ml cell of an Agitair® Flotation machine. The float cell is agitated at 1150 rpm and the pH is adjusted to 8.5 by the addition of further lime.

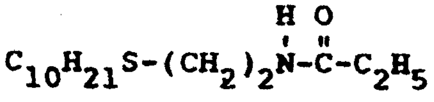
The collector is added to the float cell at the rate of 8 g/metric ton, followed by a conditioning time of 1 minute, at which time the frother, DOWFROTH® (Trademark of The Dow Chemical Company) is added at the rate of 18 g/metric ton. After the additional 1 minute conditioning time, the air to the float cell is turned on at a rate of 4.5 liters per minute and the automatic froth removal paddle is started. The froth samples were taken off at 0.5, 1.5, 3, 5 and 8 minutes. The froth samples are dried overnight in an oven, along with the flotation tailings. The dried samples are weighed, divided into suitable samples for analysis, pulverized to insure suitable fineness, and dissolved in acid for analysis. The samples are analyzed using a DC Plasma Spectrograph. The results are compiled in Table IV. The compounds that were used in Examples 1 through 31 in Table IV are separately tabulated herein below:

1*. No collector

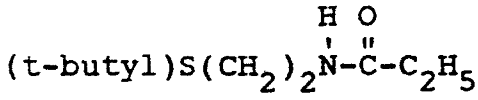
2. $C_6H_{13}S(CH_2)_2NH_2$

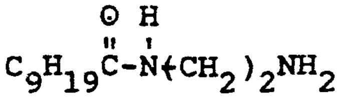
3. (t-butyl)$S(CH_2)_2NH_2$

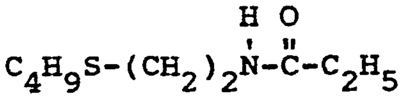
4.

$C_6H_{13}S(CH_2)_2\overset{H}{N}-\overset{O}{C}-C_2H_5$

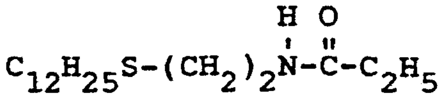
5.

$C_{10}H_{21}S-(CH_2)_2\overset{H}{N}-\overset{O}{C}-C_2H_5$

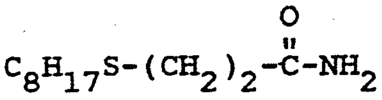
6. $(C_4H_9)_2-N-(CH_2)_2NH_2$

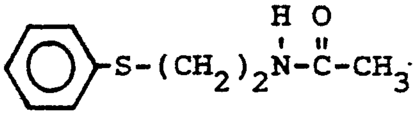
7. 
$(t\text{-butyl})S(CH_2)_2\overset{H}{N}-\overset{O}{C}-C_2H_5$

8. 
$C_9H_{19}\overset{O}{C}-\overset{H}{N}(CH_2)_2NH_2$

9. 
$C_4H_9S-(CH_2)_2\overset{H}{N}-\overset{O}{C}-C_2H_5$

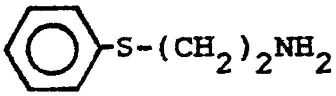
10. 
$C_{12}H_{25}S-(CH_2)_2\overset{H}{N}-\overset{O}{C}-C_2H_5$

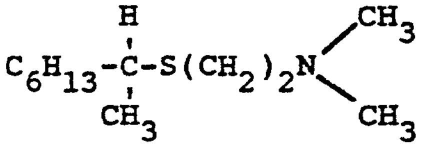
11. 
$C_8H_{17}S-(CH_2)_2-\overset{O}{C}-NH_2$

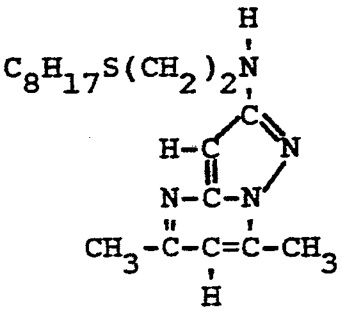
12. 
$\overset{H}{N}-\overset{O}{C}-CH_3$

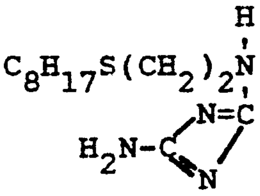
13. $C_8H_{17}S-(CH_2)_3NH_2$

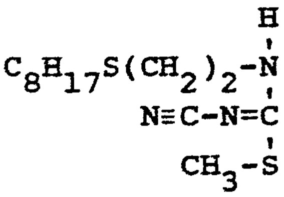
14. $C_6H_{13}S(CH_2)_2NCS$

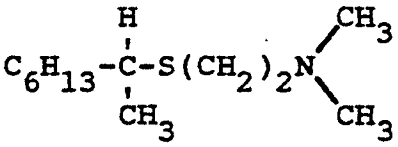
15. 

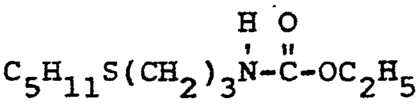
16. 

17. 

18. 

19. 

20. 

21. 
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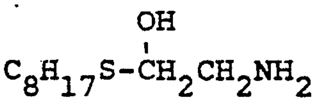
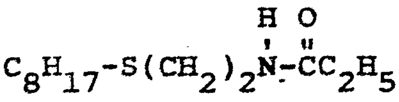
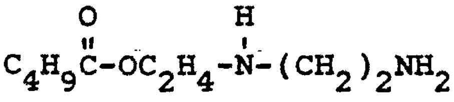
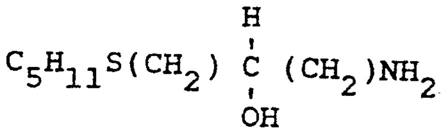
22. 
$C_8H_{17}S-\overset{OH}{C}H_2CH_2NH_2$

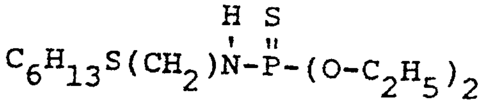
23. $C_8H_{17}S(CH_2)_2NH_2$

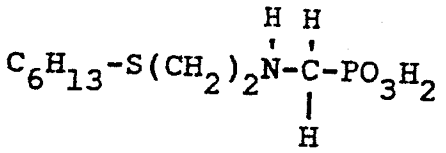
24. $C_4H_9S(CH_2)_2NH_2 \cdot HCl$

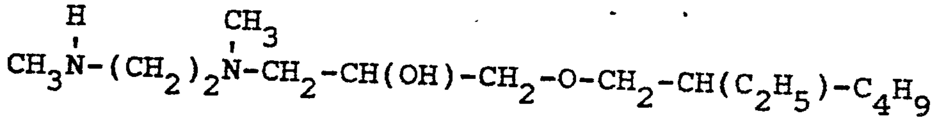
25. 
$C_8H_{17}-S(CH_2)_2\overset{H}{N}-\overset{O}{C}C_2H_5$

26. 
$C_4H_9\overset{O}{C}-OC_2H_4-\overset{H}{N}-(CH_2)_2NH_2$

27. 
$C_5H_{11}S(CH_2)\overset{H}{\underset{OH}{C}}(CH_2)NH_2$

28. 
$C_6H_{13}S(CH_2)\overset{H}{N}-\overset{S}{\overset{\|}{P}}-(O-C_2H_5)_2$

29. 
$C_6H_{13}-S(CH_2)_2\overset{H}{N}-\overset{H}{\underset{H}{C}}-PO_3H_2$

30. 
$CH_3\overset{H}{N}-(CH_2)_2\overset{CH_3}{N}-CH_2-CH(OH)-CH_2-O-CH_2-CH(C_2H_5)-C_4H_9$

31. $NH_2-CH_2-CH(OH)-CH_2-O-CH_2-CH(C_2H_5)-C_4H_9$

32. $C_6H_{13}-S(CH_2)C{\equiv}N$

1* - Not an example of the invention.

TABLE IV

Example Number	Copper K	Copper R	Gangue K	Gangue R	Copper R-8	Gangue R-8	Selectivity
1*	2.11	.306	1.61	.068	.291	.066	4.4
2	4.19	.629	3.63	.140	.606	.136	4.5
3	3.65	.621	4.28	.121	.600	.121	5.0
4	3.79	.943	2.95	.196	.906	.189	4.8
5	2.69	.789	2.37	.160	.730	.148	4.9
6	2.04	.382	1.88	.0735	.358	.0692	5.2
7	3.86	.585	3.44	.118	.562	.114	4.9
8	2.36	.435	2.15	.0858	.409	.0815	5.0
9	5.16	.742	4.43	.157	.719	.153	4.7
10	2.38	.499	2.10	.100	.469	.0951	4.9

TABLE IV (Cont.)

Example Number	Copper K	Copper R	Gangue K	Gangue R	Copper R-8	Gangue R-8	Selectivity
11	4.53	.869	3.59	.184	.838	.179	4.7
12	2.06	.448	1.80	.0895	.418	.0840	5.0
13	3.90	.572	3.22	.126	.551	.123	4.5
14	2.12	.863	1.59	.192	.809	.179	4.5
15	3.43	.534	2.90	.108	.513	.106	4.8
16	2.94	.424	2.45	.0841	.408	.0816	5.0
17	5.00	.641	4.33	.148	.622	.145	4.3
18	3.51	.682	3.01	.175	.649	.168	3.9
19	2.68	.451	2.29	.097	.429	.094	4.6
20	3.46	.449	2.96	.092	.431	.090	4.8
21	4.58	.909	3.44	.187	.878	.181	4.8
22	4.22	.540	3.60	.124	.523	.123	4.3
23	3.61	.514	2.96	.111	.493	.107	4.6
24	3.54	.542	3.21	.121	.520	.117	4.4
25	3.54	.832	2.73	.162	.802	.156	5.1
26	2.14	.367	1.61	.080	.345	.075	4.6
27	3.62	.520	2.98	.119	.501	.116	4.3
28	1.97	.848	1.56	.180	.788	.166	4.7
29	2.41	.308	2.11	.0676	.296	.066	4.5
30	2.35	.340	2.14	.0702	.324	.0676	4.8
31	2.25	.355	2.18	.0737	.338	.0710	4.8
32	7.17	.723	5.32	.156	.707	.155	4.6

1* - Not an example of the invention.

Example 4 is similar to Example 1 except that various different compounds within the scope of the invention were tested on a different copper sulfide ore. No optimization of the collectors was attempted but all of the compounds were found to be clearly superior when compared against "no collector" in the recovery of copper values. The collectors of this invention will show superior recovery and selectivity when compared to the standard known collectors and when optimized with regard to a particular ore under consideration.

Example 5 - Froth Flotation of Copper Sulfide and Molybdenum Sulfide

Bags of homogeneous ore are prepared with each bag containing 1200 grams. The rougher flotation procedure is to grind a 1200 gram charge with 800 cc of tap water for 14 minutes in a ball mill having a mixed ball charge (to produce appoximately a 13 percent plus 100 mesh grind). This pulp is transferred to an Agitair® 500 flotation cell outfitted with an automated paddle removal system. The slurry pH is adjusted to 10.2 using lime. No further pH adjustments are made during the test. The standard frother is methyl isobutyl carbinol (MIBC). A four-stage rougher flotation scheme is then followed.

STAGE 1: Collector - 0.0042 kg/ton
MIBC - 0.015 kg/ton
- condition - 1 minute
- float - collect concentrate for 1 minute

STAGE 2: Collector - 0.0021 kg/ton
MIBC - 0.005 kg/ton
- condition - 0.5 minute
- float - collect concentrate for 1.5 minutes

STAGE 3: Collector - 0.0016 kg/ton
MIBC - 0.005 kg/ton
- condition - 0.5 minute
- float - collect concentrate for 2 minutes

STAGE 4: Collector - 0.0033 kg/ton
MIBC - 0.005 kg/ton
- condition - 0.5 minute
- float - collect concentrate for 2.5 minutes

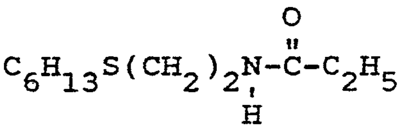
TABLE V

Copper/Molybdenum Ore from Western Canada

Collector	Dosage kg/-metric ton	Cu Rec R-7 min	Mo Rec R-7 min	Cu Grade	Mo Grade	Fe Grade
A	0.0112	0.776	0.725	0.056	0.00181	0.254
B	0.0112	0.688	0.682	0.063	0.00233	0.108
B	0.0067	0.659	0.759	0.099	0.00402	0.137
B	0.0112[1]	0.648	0.747	0.080	0.00314	0.127

A - potassium amyl xanthate
(Not an example of the invention)

B -



$\mathrm{C_6H_{13}S(CH_2)_2\underset{H}{N}-\overset{O}{\overset{\|}{C}}-C_2H_5}$

[1] The slurry was not treated with lime and the pH was adjusted to 8.2

Table V illustrates that a substantially higher grade was achieved for copper and molybdenum as compared to the Standard Collector A. For copper, the minimum increase was over 10 percent and the maximum increase was 77 percent. For molybdenum, the minimum increase in grade was about 30 percent and the maximum optimized increase was about 122 percent. Such improvements place a substantially smaller load on the smelter of a mining operation.

The grade for iron with any of the Collectors B of the invention again show a substantial reduction of about 50 percent as compared to the Standard Collector A, indicating that substantially less of the undesirable pyrite is collected. This surprising selectivity in the collection of metal sulfide values over iron sulfide values is highly advantageous in the downstream operation of a mining operation as it reduces sulfur emissions.

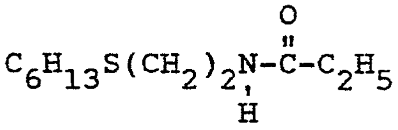
Example 6 - Froth Flotation of a Nickel/Cobalt Ore from Western Australia

A series of 750 gram charges of a nickel/cobalt ore are prepared in slurry form (30 percent solids). The flotation cell is an Agitair® LA-500 outfitted with an automatic peddle for froth removal operating at 60 rpm's. A standard run is to first add 0.2 kg/metric ton of $CuSO_4$, condition for 7 minutes, add 0.1 kg/ton collector, condition for 3 minutes, add 0.14 kg/ton guar depressant for talc, and 0.16 kg/metric ton collector, add a frother (e.g., triethoxybutane) to form a reasonable froth bed. Concentrate collection is initiated for 5 minutes (denoted as rougher concentrate). Then 0.16 kg/metric ton collector plus 0.07 kg/metric ton guar is added to remaining cell contents along with whatever frother is necessary and concentrate collection is initiated for 9 minutes (denoted as middlings) with the remaining cell contents denoted as flotation tails. After this, the rougher concentrate is transferred to a smaller cell, 0.08 kg/metric ton collector plus 0.14 kg/-metric ton guar is added to the cell with no frother, concentrate collection is initiated for 3 minutes (denoted as cleaner concentrate) with the cell contents denoted as cleaner tails. Samples are filtered, dried, and assayed using X-ray analysis methodology. Recoveries are calculated using standard metallurgical procedures. The results of this test are compiled in Table VI. The compounds that were used for Examples 1 to 5 in Table VI are tabulated hereinbelow:

<u>Collector</u>

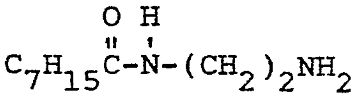
1* - Sodium ethyl xanthate

2 - $C_6H_{13}S(CH_2)_2NH_2$

3 - 

$C_6H_{13}S(CH_2)_2\underset{\mathrm{H}}{\underset{|}{N}}-\overset{\mathrm{O}}{\overset{\|}{C}}-C_2H_5$

4 - $(C_4H_9)_2-N-(CH_2)_2\ NH_2$

5 - 

$C_7H_{15}\overset{\mathrm{O}}{\overset{\|}{C}}-\overset{\mathrm{H}}{\overset{|}{N}}-(CH_2)_2NH_2$

*Not an example of the invention

TABLE VI

Nickel/Cobalt Ore from Western Australia

	Percent Nickel Recovery				Percent Cobalt Recovery			
Col-lector	Cleaner Conc.	Flotation Tail	Cleaner Tail	Middlings	Cleaner Conc.	Flotation Tail	Cleaner Tail	Middlings
1*	62.4	7.3	24.9	5.4	66.9	12.0	16.7	4.4
2	75.8	3.1	10.0	11.1	72.2	9.5	8.4	9.9
3	74.4	6.7	7.8	11.1	63.8	15.4	8.0	12.8
4	57.1	4.0	9.3	29.6	65.1	7.3	7.3	20.3
5	56.0	1.4	12.3	30.3	62.4	3.0	8.5	26.2

*Not an example of the invention

The data in Table VI represents a full scale simulation of a continuous industrial flotation process. The data in the column entitled "Flotation Tail" is the most significant data since it shows actual metal loss, i.e. the lower the value in the Flotation Tail column, the lower the metal loss. The superiority of the experimental collectors of the invention over the industrial standard in this category is apparent. At a minimum, the Flotation Tail for nickel recovery showed an 8 percent drop, at a maximum, the flotation tail drop showed a surprising 81 percent drop. For cobalt, similar improvements were realized except for Collector 3.

Example 7 - Froth Flotation of a Complex Pb/Zn/Cu/Ag Ore from Central Canada

Uniform 1000 gram samples of ore are prepared. For each flotation run, a sample is added to a rod mill along with 500 cc of tap water and 7.5 ml of SO_2 solution. 6-1/2 minutes of mill time are used to prepare a feed in which 90 percent of the particles have a size of less than 200 mesh (75 microns). After grinding, the contents are transferred to a cell fitted with an automated paddle for froth removal. The cell is attached to a standard Denver flotation mechanism.

A two-stage flotation procedure is then performed. In Stage I, a copper/lead/silver rougher, and in Stage II, a zinc rougher. To start the Stage I flotation, 1.5 g/kg Na_2CO_3 is added and the pH adjusted to 8.5, followed by the addition of the collector(s). The pulp is then conditioned for 5 minutes with air and agitation. This is followed by a 2-minute condition period with agitation only. MIBC frother is then added (standard dose of 0.015 ml/kg). Concentrate is collected for 5 minutes of flotation and labeled as copper/lead rougher concentrate.

The Stage II flotation consists of adding 0.3 kg/-metric ton of $CuSO_4$ to the cell remains of Stage I. The pH is then adjusted to 9.5 with lime addition. This is followed by a condition period of 5 minutes with agitation only. The pH is then rechecked and adjusted back to 9.5 with lime. At this point, the collector(s) is added, followed by a 5-minute condition period with agitation only. MIBC frother is then added (standard dose of 0.020 ml/kg). The concentrate is collected for 5 minutes and labeled as zinc rougher concentrate.

Concentrate samples are dried, weighed, and appropriate samples prepared for assay using X-ray techniques. Using the assay data, recoveries and grades are calculated using standard mass balance formulae.

TABLE VII

Pb/Zn/Cu/Ag Ore from Central Canada

	Stage (Rougher)	Col- lector	Dosage (Kg/t)	Ag		Cu		Pb		Zn	
				R-5	Grade	R-5	Grade	R-5	Grade	R-5	Grade
1*	Cu/Pb	A B	0.005 0.0075	0.843	0.286	0.926	0.120	0.738	0.053	0.179	---
	Zn	A C	0.020 0.015	0.109	---	0.057	---	0.155	---	0.808	0.314
2	Cu/Pb	D B	0.005 0.0045	0.826	0.320	0.914	0.129	0.710	0.057	0.153	---
	Zn	D	0.021	0.118	---	0.063	---	0.174	---	0.833	0.334

A - Sodium ethyl xanthate
B - dithiophosphate
C - thionocarbamate
D - $C_6H_{13}S(CH_2)_2NH_2$

R-5 is the actual recovery after 5 minutes

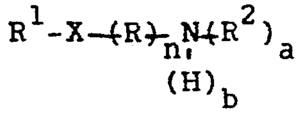
*Not an example of the invention

Table VII illustrates the performance of optimized industrial standard collectors when compared to the collector of the invention in the recovery of metal values. Stage I of test 1 employed a combination of standard collectors A and B, while Stage II employed a combination of standard collectors A and C. Stage I of test 2 employed a mixture of a standard collector B and collector D of the invention in approximate equal amounts. Stage II of test 2 employed collector D of the invention.

The goal in this test was to maintain the recovery level for silver and copper in Stage I and to increase the zinc recovery in Stage II. The results show that collector D approximately maintained the level of recovery for silver and copper with an accompanying improvement in grade. Most importantly, both the recovery (R-5) and grade of zinc in Stage II of test 2 were increased by 3 percent and 6 percent, respectively, over the standard collectors of test 1.

CLAIMS

1. A collector for recovering metal values from a metal ore by froth flotation, the collector being of the formula



$$R^1\text{-}X\text{-}(R)_n\text{-}\underset{(H)_b}{N}\text{-}(R^2)_a$$

wherein R is $-CH_2-$, $-\overset{H}{\underset{OH}{C}}-$, $-\overset{O}{\overset{\|}{C}}-$, or a combination thereof

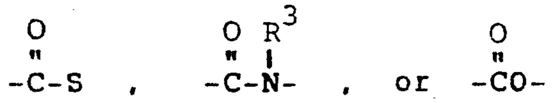
and n is an integer from 1 to 6 or $(R)_n$ is $(CH_2)_m C\equiv$ where m is an integer from 0 to 6; R^1 and each R^2 are independently C_{1-22} hydrocarbyl or C_{1-22} hydrocarbyl substituted with one or more hydroxy, amino, phosphonyl, alkoxy, imino, carbamyl, carbonyl, thiocarbonyl, cyano, carboxyl, hydrocarbylthio, hydrocarbyloxy, hydrocarbylamino and/or hydrocarbylimino groups, with the proviso that R^2 can be a divalent radical with both valencies bonded directly to the N atom

X is $-S-$, $-O-$, $-\overset{|}{N}-R^3$,

$-\overset{O}{\overset{\|}{C}}-S-$, $-\overset{O}{\overset{\|}{C}}-\overset{R^3}{\overset{|}{N}}-$, or $-\overset{O}{\overset{\|}{C}}O-$

R^3 is H or C_{1-22} hydrocarbyl;
a is an integer of 0, 1 or 2;
b is an integer of 0, 1 or 2;

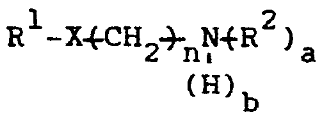
with the proviso that the sum of a and b equals 2 except when R^2 is a divalent radical with both valencies bonded directly to the N atom, in which case, b=1 and a=0 or when $\text{-}(R)_n\text{-}$ is $\text{-}(CH_2)_m C\equiv$ in which case, a+b=0, and with the further proviso that when X is



$$\overset{O}{\overset{\|}{\text{-}C\text{-}S}}\ ,\quad \overset{O\ \ R^3}{\overset{\|\ \ \ |}{\text{-}C\text{-}N\text{-}}}\ ,\quad \text{or}\quad \overset{O}{\overset{\|}{\text{-}CO\text{-}}}$$

the carbonyl moiety is bonded to R^1.

2. A collector as claimed in claim 1 and of the formula:



$$R^1\text{-}X\text{-}(CH_2)_n\text{-}\underset{(H)_b}{N}\text{-}(R^2)_a$$

wherein:

R^1 is C_{1-22} hydrocarbyl optionally substituted with one or more hydroxy, amino, phosphonyl and/or alkoxy moieties;

R^2 is a C_{1-6} alkyl, a C_{1-6} alkylcarbonyl or a C_{1-6} alkyl group optionally substituted with an amino, hydroxy or phosphonyl moiety, or a C_{1-6} alkylcarbonyl group optionally substituted with an amino, hydroxy or phosphonyl moiety;

and X, a, b and n are as defined in claim 1.

3. A collector as claimed in claim 2 wherein R^1 is C_{2-14} hydrocarbyl; R^2 is C_{1-6} alkyl or C_{1-6} alkylcarbonyl; R^3 is hydrogen or C_{2-14} hydrocarbyl; a is the integer 0 or 1; b is the integer 1 or 2; and n is an integer of from 1 to 4.

4. A collector as claimed in claim 3 wherein R^1 is C_{4-11} hydrocarbyl; R^2 is C_{1-4} alkyl or C_{1-4} alkylcarbonyl; R^3 is hydrogen or C_{4-11} hydrocarbyl; n is the integer 2 or 3; and X is -S-, $-\overset{|}{N}-R^3$ or -O-.

5. A collector as claimed in claim 4 wherein X is -S- or $-\overset{|}{N}-R^3$.

6. A collector as claimed in claim 4 wherein X is -S-.

7. A collector as claimed in claim 1 which is an omega-(hydrocarbylthio)-alkylamine; an S-(omega-aminoalkyl) hydrocarbon thioate; an N-(hydrocarbyl)-alpha, omega-alkanediamine; an (omega-aminoalkyl) hydrocarbon amide; an omega-(hydrocarbyloxy-)-alkylamine; an omega-aminoalkyl hydrocarbonoate; or a mixture thereof.

8. A process for recovering metal values from a metal ore, comprising subjecting the metal ore, in the form of an aqueous pulp, to a froth flotation process in the presence of a flotation collector as claimed in claim 1 under conditions such that the metal values are recovered in the froth.

9. A process as claimed in claim 8, wherein the collector is as defined in any one of claims 2 to 7.

10. A process as claimed in claim 8 or claim 9

wherein the collector is added in an amount of from between 5 to 250 grams per metric ton of ore and/or the metal value recovered is a metal sulfide, metal oxide or precious metal.