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Europäisches Patentamt  
European Patent Office  
Office européen des brevets



11 Publication number:

**0 453 677 B1**

12

**EUROPEAN PATENT SPECIFICATION**

- 49 Date of publication of patent specification: **09.08.95** 51 Int. Cl.<sup>8</sup>: **B03D 1/008**, B03D 1/01,  
B03D 1/012
- 21 Application number: **90304633.2**
- 22 Date of filing: **27.04.90**

54 **Depression of the flotation of silica or siliceous gangue in mineral flotation.**

43 Date of publication of application:  
**30.10.91 Bulletin 91/44**

45 Publication of the grant of the patent:  
**09.08.95 Bulletin 95/32**

84 Designated Contracting States:  
**DE ES GB GR SE**

56 References cited:  
**GB-A- 1 456 392           US-A- 2 019 306**  
**US-A- 2 070 076           US-A- 4 213 942**  
**US-A- 4 220 525           US-A- 4 437 983**

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B46, 2nd January 1980, no. 83749B/46, Der-  
went Publications Ltd, London, GB; & SU-  
A-649 469 (NON-FERRORE ENRICH)  
08-02-1979**

**SOVIET INVENTIONS ILLUSTRATED, week  
8533, 26th September 1985, no. 85=201864/33,  
Derwent Publications Ltd, London, GB; & SU-  
A-1135 497 (BELORUSS KIROV TECH. INS.)  
23-01-1985**

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**EP 0 453 677 B1**

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**SOVIET INVENTIONS ILLUSTRATED**, week  
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A-1003 431 (KURKOV AV) 07-02-1985

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## Description

This invention is related to the recovery of minerals by froth flotation.

5 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 the solids is separated from other finely divided mineral solids, e.g., silica, siliceous gangue, clays and other like materials present in the ore, by introducing a gas (or providing a gas *in situ*) in the liquid to produce a frothy mass containing certain of the solids on the top of the liquid, and leaving suspended (unfrothed) other solid components of the ore. Flotation is based on the principle that introducing a gas into a liquid containing solid particles of different materials suspended  
10 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, these particles rise to the top of the liquid to form a froth.

The minerals and their associated gangue which are treated by froth flotation generally do not possess sufficient hydrophobicity or hydrophilicity to allow adequate separation. Therefore, various chemical  
15 reagents are often employed in froth flotation to create or enhance the properties necessary to allow separation. Collectors are used to enhance the hydrophobicity and thus the floatability of different mineral values. Collectors must have the ability to (1) attach to the desired mineral species to the relative exclusion of other species present; (2) maintain the attachment in the turbulence or shear associated with froth flotation; and (3) render the desired mineral species sufficiently hydrophobic to permit the required degree  
20 of separation.

A number of other chemical reagents are used in addition to collectors. Examples of types of additional reagents used include frothers, depressants, pH regulators, such as lime and soda, dispersants and various promoters and activators. Depressants are used to increase or enhance the hydrophilicity of various mineral species and thus depress their flotation. Frothers are reagents added to flotation systems to promote the  
25 creation of a semi-stable froth. Unlike both depressants and collectors, frothers need not attach or adsorb on mineral particles.

Froth flotation has been extensively practiced in the mining industry since at least the early twentieth century. A wide variety of compounds are taught to be useful as collectors, frothers and other reagents in froth flotation. For example, xanthates, simple alkylamines, alkyl sulfates, alkyl sulfonates, carboxylic acids  
30 and fatty acids are generally accepted as useful collectors. Reagents useful as frothers include lower molecular weight alcohols such as methyl isobutyl carbinol and glycol ethers. The specific additives used in a particular flotation operation are selected according to the nature of the ore, the conditions under which the flotation will take place, the mineral sought to be recovered and the other additives which are to be used in combination therewith.

35 While a wide variety of chemical reagents are recognized by those skilled in the art as having utility in froth flotation, it is also recognized that the effectiveness of known reagents varies greatly depending on the particular ore or ores being subjected to flotation as well as the flotation conditions. It is further recognized that selectivity or the ability to selectively float the desired species to the exclusion of undesired species is a particular problem.

40 Minerals and their associated ores are generally categorized as sulfides or oxides, with the latter group including carbonates, hydroxides, sulfates and silicates. While a large proportion of the minerals existing today are contained in oxide ores, the bulk of successful froth flotation systems is directed to sulfide ores. The flotation of oxide minerals is recognized as being substantially more difficult than the flotation of sulfide minerals and the effectiveness of most flotation processes in the recovery of oxide ores is limited.

45 A major problem associated with the recovery of minerals, both oxides and sulfides, is selectivity. Some of the recognized collectors such as the carboxylic acids, alkyl sulfates and alkyl sulfonates discussed above are taught to be effective collectors for oxide mineral ores. Certainly, existing collectors are known to be useful in sulfide flotation. However, while the use of these collectors can result in acceptable recoveries, it is recognized that the selectivity to the desired mineral value may not be as high as desired and, in the  
50 case of oxide flotation, is typically quite poor. That is, the grade or the percentage of the desired mineral contained in the recovered mineral is unacceptably low.

A publication in "Soviet Inventions Illustrated" number 83749B/46, dated 2nd January 1980 discloses the use of an emulsion comprising an industrial oil, oleic acid and triethanolamine in the flotation of non-ferrous metal ores. It is observed in this reference that the emulsion does not separate under significant  
55 dilution. The oleic acid and triethanolamine are thus added to the flotation system as a pre-mix system.

A publication in Soviet Inventions Illustrated, number 85-201864/33, published 26th September 1985 concerns the use of monoethanolamine and an ethoxylated alcohol as a collector for a clay carbonate gangue. The reference indicates that the combination of ethanolamine/ethoxylated alcohol may be used to

float the clay carbonate gangue away from the sulfide ore which is then recovered in a separate step. Thus, the material which is floated is the gangue material, rather than the mineral to be recovered. The reference does not suggest the use of an anionic collector.

Thus, a need remains for methods of increasing selectivity in the flotation of both sulfide and oxide ores.

The present invention provides a process for the recovery of mineral values by froth flotation comprising subjecting a particulate ore, which contains silica or siliceous gangue and is in an aqueous slurry, to froth flotation under conditions such that the minerals to be recovered are floated and the flotation of the silica or siliceous gangue is depressed, wherein the flotation is carried out in the presence of an anionic collector and a hydroxy-containing compound, which is ethanolamine, propanolamine, butanolamine, diethanolamine, dipropanolamine, dibutanolamine, triethanolamine, tripropanolamine, tributanolamine, or a mixture of two or more such hydroxy-containing compounds, characterised in that the hydroxy-containing compound is added to the flotation system separately from the anionic collector.

By improved selectivity, it is meant that the total amount of mineral recovered and/or the grade of the mineral recovered is increased while the amount of silica or siliceous gangue not recovered, i.e. remaining in the aqueous phase, is also increased. Thus, by the process of this invention, the ability to separate silica and/or siliceous gangue from desirable mineral values is enhanced. That is, the tendency of the silica or siliceous gangue to float is depressed.

The flotation process of this invention is useful in the recovery of various minerals, including oxide minerals, by froth flotation.

The flotation process of this invention is useful in the recovery of mineral values from a variety of ores. An ore herein refers to the mineral as it is taken out of the ground and includes the mineral-containing species intermixed with gangue. Gangue are those materials which are of little or no value and need to be separated from the mineral values. In this invention, gangue specifically includes silica and siliceous materials.

As is well recognized by one skilled in the art, different types of collectors are effective with different types of ores. Certain anionic collectors, described below and useful in the present invention, have been found to be surprisingly effective in the flotation of oxide ores. The oxide minerals which can be treated by the practice of this invention include carbonates, sulfates and silicates as well as oxides. In addition to its effectiveness in the flotation of oxide ores, it has also been found that the anionic collectors in the flotation process of this invention are also effective in the flotation of sulfide ores and mixed oxide/sulfide ores.

Non-limiting examples of oxide ores which can be floated using the practice of this invention preferably include iron oxides, nickel oxides, phosphorus oxides, copper oxides and titanium oxides. Other types of oxygen-containing minerals which can be floated using the practice of this invention include carbonates such as calcite or dolomite and hydroxides such as bauxite.

The process of this invention using the anionic collectors described below is also useful in the flotation of various sulfide ores. Non-limiting examples of sulfide ores which can be floated by the process of this invention include those containing chalcopyrite, chalcocite, galena, pyrite, sphalerite and pentlandite.

Noble metals such as gold and silver and the platinum group metals wherein platinum group metals comprise platinum, ruthenium, rhodium, palladium, osmium, and iridium, can also be recovered by the practice of this invention. For example, such metals are sometimes found associated with oxide and/or sulfide ores. For example, platinum is sometimes found associated with troilite. By the practice of the present invention, such metals can be recovered in good yield.

Non-limiting examples of oxide ores which can be subjected to froth flotation using the process of this invention are those including cassiterite, hematite, cuprite, vallerite, calcite, talc, kaolin, apatite, dolomite, bauxite, spinel, corundum, laterite, azurite, rutile, magnetite, columbite, ilmenite, smithsonite, anglesite, scheelite, chromite, cerussite, pyrolusite, malachite, chrysocolla, zincite, massicot, bixbyite, anatase, brookite, tungstite, uraninite, gummite, brucite, manganite, psilomelane, goethite, limonite, chrysoberyl, microlite, tantalite and samarskite. One skilled in the art will recognize that the froth flotation process of this invention will be useful for the processing of additional ores including oxide ores wherein oxide is defined to include carbonates, hydroxides, sulfates and silicates as well as oxides and sulfide ores.

Ores for which the process of this invention using anionic thiol collectors are useful include sulfide mineral ores containing copper, zinc, molybdenum, cobalt, nickel, lead, arsenic, silver, chromium, gold, platinum, uranium and mixtures thereof. Examples of metal-containing sulfide minerals which can be concentrated by froth flotation using the composition and process of this invention include copper-bearing minerals such as covellite ( $\text{CuS}$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), chalcopyrite ( $\text{CuFeS}_2$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), vallerite ( $\text{Cu}_2\text{Fe}_4\text{S}_7$  or  $\text{Cu}_3\text{Fe}_4\text{S}_7$ ), tetrahedrite ( $\text{Cu}_3\text{SbS}_2$ ), enargite ( $\text{Cu}_3(\text{As}_2\text{Sb})\text{S}_4$ ), tennantite ( $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ ), cubanite ( $\text{Cu}_2\text{SFe}_4\text{S}_5$ ), brochantite ( $\text{Cu}_4(\text{OH})_6\text{SO}_4$ ), antlerite ( $\text{Cu}_3\text{SO}_4(\text{OH})_4$ ), famatinite ( $\text{Cu}_3(\text{SbAs})\text{S}_4$ ), and

bournonite ( $\text{PbCuSbS}_3$ ); lead-bearing minerals such as galena ( $\text{PbS}$ ); antimony-bearing minerals such as stibnite ( $\text{Sb}_2\text{S}_3$ ); zinc-bearing minerals such as sphalerite ( $\text{ZnS}$ ); silver-bearing minerals such as stephanite ( $\text{Ag}_5\text{SbS}_4$ ) and argentite ( $\text{Ag}_2\text{S}$ ); chromium-bearing minerals such as daubreelite ( $\text{FeSCrS}_3$ ); nickel-bearing minerals such as pentlandite [ $(\text{FeNi})_9\text{S}_8$ ]; molybdenum-bearing minerals such as molybdenite ( $\text{MoS}_2$ ); and platinum- and palladium-bearing minerals such as cooperite [ $\text{Pt}(\text{AsS})_2$ ]. Preferred metal-containing sulfide minerals include molybdenite ( $\text{MoS}_2$ ), chalcopyrite ( $\text{CuFeS}_2$ ), chalcocite ( $\text{Cu}_2\text{S}$ ), galena ( $\text{PbS}$ ), sphalerite ( $\text{ZnS}$ ), bornite ( $\text{Cu}_5\text{FeS}_4$ ), and pentlandite [ $(\text{FeNi})_9\text{S}_8$ ].

Sulfidized metal-containing oxide minerals are minerals which are treated with a sulfidization chemical, so as to give such minerals sulfide mineral characteristics. The minerals so treated can then be recovered in froth flotation using collectors which recover sulfide minerals. Sulfidization results in oxide minerals having sulfide mineral characteristics. Oxide minerals are sulfidized by contact with compounds which react with the minerals to form a sulfur bond or affinity. Such methods are well known in the art. Such compounds include sodium hydrosulfide, sulfuric acid and related sulfur-containing salts such as sodium sulfide.

Sulfidized metal-containing oxide minerals and oxide minerals for which this process utilizing the thiol collectors described below is useful include oxide minerals containing copper, aluminum, iron, titanium, magnesium, chromium, tungsten, molybdenum, manganese, tin, uranium, and mixtures thereof. Examples of metal-containing minerals which may be sulfidized by froth flotation using the thiol collectors described below include copper-bearing minerals such as malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ), azurite ( $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ ), cuprite ( $\text{Cu}_2\text{O}$ ), atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ), tenorite ( $\text{CuO}$ ), chrysocolla ( $\text{CuSiO}_3$ ); aluminum-bearing minerals such as corundum; zinc-containing minerals such as zincite ( $\text{ZnO}$ ) and smithsonite ( $\text{ZnCO}_3$ ); tungsten-bearing minerals such as wolframite [ $(\text{Fe}_2\text{Mn})\text{WO}_4$ ]; nickel-bearing minerals such as bunsenite ( $\text{NiO}$ ); molybdenum-bearing minerals such as wulfenite ( $\text{PbMoO}_4$ ) and powellite ( $\text{CaMoO}_4$ ); iron-containing minerals such as hematite and magnetite; chromium-containing minerals such as chromite ( $\text{FeOCr}_2\text{O}_3$ ); iron- and titanium-containing minerals such as ilmenite; magnesium- and aluminum-containing minerals such as spinel; titanium-containing minerals such as rutile; manganese-containing minerals such as pyrolusite; tin-containing ores; minerals such as cassiterite; and uranium-containing minerals such as uraninite, pitchblende ( $\text{U}_2\text{O}_5(\text{U}_3\text{O}_8)$ ) and gummite ( $\text{UO}_3\text{nH}_2\text{O}$ ).

Other metal-containing minerals for which the use of thiol collectors in this process is useful include gold-bearing minerals such as sylvanite ( $\text{AuAgTe}_2$ ) and calaverite ( $\text{AuTe}$ ); platinum- and palladium-bearing minerals such as sperrylite ( $\text{PtAs}_2$ ); and silver-bearing minerals such as hessite ( $\text{AgTe}_2$ ). Also included are metals which occur in a metallic state, e.g., gold, silver and copper.

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

Ores do not always exist purely as oxide ores or as sulfide ores. Ores occurring in nature may comprise both sulfur-containing and oxygen-containing minerals as well as, in some cases, noble metals. Metals may be recovered from the oxides found in such ores by the practice of this invention. This may be done in a two-stage flotation where one stage comprises conventional sulfide flotation to recover primarily sulfide minerals and the other stage of the flotation utilizes the process of the present invention using the anionic collectors described below to recover primarily the oxide minerals. Alternatively, the various types of minerals may be recovered simultaneously by the practice of this invention.

In addition to the flotation of ores found in nature, the flotation process of this invention is useful in the flotation of oxides and sulfides from other sources. For example, the waste materials from various processes such as heavy media separation, magnetic separation, metal working and petroleum processing often contain oxides and/or sulfides that may be recovered using the flotation process of the present invention.

A wide variety of anionic collectors are useful in the practice of the present invention. The anionic portion of the anionic collector is preferably derived from carboxylic, sulfonic, sulfuric, phosphoric or phosphonic acids. The anionic collector is also hydrophobic. Its hydrophobicity is derived from a saturated or unsaturated hydrocarbyl or saturated or unsaturated substituted hydrocarbyl moiety. Examples of suitable hydrocarbyl moieties include straight or branched alkyl, arylalkyl and alkylaryl groups. Non-limiting examples of substituents for the hydrocarbyl group include alkoxy, ether, amino, hydroxy and carboxy. When the hydrocarbyl moiety is unsaturated, it is preferably ethylenically unsaturated. It should also be recognized that the anionic surfactant may be a mixture of compounds.

The anionic collector may be used in acid form or in salt form, depending on which is soluble under conditions of use. The appropriate form of the anionic collector will vary depending on the particular

collector used and other conditions present in the flotation process. One skilled in the art will recognize that some of the anionic collectors useful in the present invention will be soluble in the acid form under conditions of use while others will be soluble in the salt form. For example, oleic acid is preferably used in the acid form and saturated carboxylic acids are preferably used in salt form. When the anionic collectors of the present invention are used in salt form, the counter ion may be a calcium ion, a magnesium ion, a sodium ion, a potassium ion or an ammonium ion. As discussed above, the choice of an appropriate counter ion depends on the particular anionic collector used and its solubility. It is generally preferred that the counter ion be a sodium ion, a potassium ion or an ammonium ion.

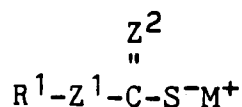
Non-limiting examples of suitable anionic collectors include linolenic acid, oleic acid, lauric acid, linoleic acid, octanoic acid, capric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, 2-naphthalene sulfonic acid, sodium lauryl sulfate, sodium stearate, dodecane sodium sulfonic acid, hexadecyl sulfonic acid, dodecyl sodium sulfate, dodecyl phosphate, chloride derivative of dodecyl phosphonic acid, 2-naphthoic acid, pimelic acid, and dodecyl benzene sulfonate and mixtures thereof.

Preferred anionic collectors include those derived from carboxylic acids and sulfonic acids. In the case of the anionic surfactants derived from carboxylic acids, the unsaturated acids such as oleic acid, linoleic acid and linolenic acids or mixtures thereof are preferred. Examples of mixtures of these carboxylic acids include tall oil and coconut oil.

When the anionic collector is derived from sulfonic acids, it is preferred to use alkyl or alkylaryl sulfonic acids. Examples of preferred species include dodecyl benzene sulfonic acid, dodecyl sulfonic acid, alkylated diphenyl oxide monosulfonic acid and salts thereof.

The thiol collectors of this invention are compounds selected from the group consisting of thiocarbonates, thionocarbamates, thiocarbamides, thiophosphates, thiophosphinates, mercaptans, xanthogen formates, xanthic esters and mixtures thereof.

Preferred thiocarbonates are the alkyl thiocarbonates represented by the structural formula:



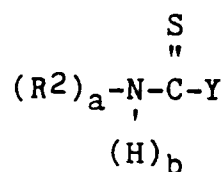
wherein

- R<sup>1</sup> is independently a C<sub>1-20</sub>, preferably C<sub>2-16</sub>, more preferably C<sub>3-12</sub> alkyl group;  
 Z<sup>1</sup> and Z<sup>2</sup> are independently a sulfur or oxygen atom; and  
 M<sup>+</sup> is an alkali metal cation.

The compounds represented by this formula include the alkyl thiocarbonates (both Z<sup>1</sup> and Z<sup>2</sup> are oxygen), alkyl dithiocarbonates (Z<sup>1</sup> is O, Z<sup>2</sup> is S) and the alkyl trithiocarbonates (both Z<sup>1</sup> and Z<sup>2</sup> are sulfur).

Examples of preferred alkyl monothiocarbonates include sodium ethyl monothiocarbonate, sodium isopropyl monothiocarbonate, sodium isobutyl monothiocarbonate, sodium amyl monothiocarbonate, potassium ethyl monothiocarbonate, potassium isopropyl monothiocarbonate, potassium isobutyl monothiocarbonate and potassium amyl monothiocarbonate. Preferred alkyl dithiocarbonates include potassium ethyl dithiocarbonate, sodium ethyl dithiocarbonate, potassium amyl dithiocarbonate, sodium amyl dithiocarbonate, potassium isopropyl dithiocarbonate, sodium isopropyl dithiocarbonate, sodium sec-butyl dithiocarbonate, potassium sec-butyl dithiocarbonate, sodium isobutyl dithiocarbonate, potassium isobutyl dithiocarbonate, and the like. Examples of alkyl trithiocarbonates include sodium isobutyl trithiocarbonate and potassium isobutyl trithiocarbonate. It is often preferred to employ a mixture of an alkyl monothiocarbonate, alkyl dithiocarbonate and alkyl trithiocarbonate.

Preferred thionocarbamates correspond to the formula:



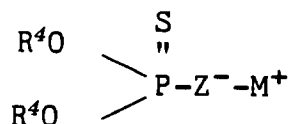
wherein

- each R<sup>2</sup> is independently a C<sub>1-10</sub>, preferably a C<sub>1-4</sub>, more preferably a C<sub>1-3</sub>, alkyl group;  
 Y is -S<sup>-</sup>M<sup>+</sup> or -OR<sup>3</sup>, wherein R<sup>3</sup> is a C<sub>1-10</sub>, preferably a C<sub>2-6</sub>, more preferably a C<sub>3-4</sub>, alkyl group;  
 5 a is the integer 1 or 2; and  
 b is the integer 0 or 1, wherein a + b must equal 2.

Preferred thionocarbamates include dialkyl dithiocarbamates (a=2, b=0 and Y is S<sup>-</sup>M<sup>+</sup>) and alkyl thionocarbamates (a=1, b=1 and Y is -OR<sup>3</sup>). Examples of preferred dialkyl dithiocarbamates include methyl butyl dithiocarbamate, methyl isobutyl dithiocarbamate, methyl sec-butyl dithiocarbamate, methyl propyl dithiocarbamate, methyl isopropyl dithiocarbamate, ethyl butyl dithiocarbamate, ethyl isobutyl dithiocarbamate, ethyl sec-butyl dithiocarbamate, ethyl propyl dithiocarbamate, and ethyl isopropyl dithiocarbamate. Examples of preferred alkyl thionocarbamates include N-methyl butyl thionocarbamate, N-methyl isobutyl thionocarbamate, N-methyl sec-butyl thionocarbamate, N-methyl propyl thionocarbamate, N-methyl isopropyl thionocarbamate, N-ethyl butyl thionocarbamate, N-ethyl isobutyl thionocarbamate, N-ethyl sec-butyl thionocarbamate, N-ethyl propyl thionocarbamate, and N-ethyl isopropyl thionocarbamate. Of the foregoing, N-ethyl isopropyl thionocarbamate and N-ethyl isobutyl thionocarbamate are most preferred.

Thiophosphates useful herein generally correspond to the formula:

20



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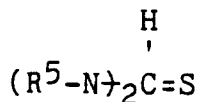
wherein each R<sup>4</sup> is independently hydrogen or a C<sub>1-10</sub> alkyl, preferably a C<sub>2-8</sub> alkyl, or an aryl, preferably an aryl group having from 6-10 carbon atoms, more preferably cresyl; Z is oxygen or sulfur; and M is an alkali metal cation.

30 Of the thiophosphates, those preferably employed include the monoalkyl dithiophosphates (one R<sup>4</sup> is hydrogen and the other R<sup>4</sup> is a C<sub>1-10</sub> alkyl and Z is S), dialkyl dithiophosphates (both R<sup>4</sup> are C<sub>1-10</sub> alkyl and Z is S) and dialkyl monothiophosphate (both R<sup>4</sup> are a C<sub>1-10</sub> alkyl and Z is O).

Examples of preferred monoalkyl dithiophosphates include ethyl dithiophosphate, propyl dithiophosphate, isopropyl dithiophosphate, butyl dithiophosphate, sec-butyl dithiophosphate, and isobutyl dithiophosphate. Examples of dialkyl or aryl dithiophosphates include sodium diethyl dithiophosphate, sodium di-sec-butyl dithiophosphate, sodium diisobutyl dithiophosphate, and sodium diisoamyl dithiophosphate. Preferred monothiophosphates include sodium diethyl monothiophosphate, sodium di-sec-butyl monothiophosphate, sodium diisobutyl monothiophosphate, and sodium diisoamyl monothiophosphate.

Thiocarbamides (dialkyl thioureas) are represented by the general structural formula:

40

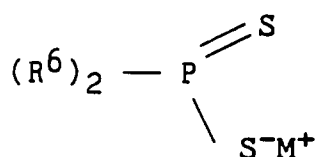


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wherein each R<sup>5</sup> is individually H or a C<sub>1-6</sub>, preferably a C<sub>1-3</sub>, hydrocarbyl.

Thiophosphinates are represented by the general structural formula:

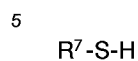
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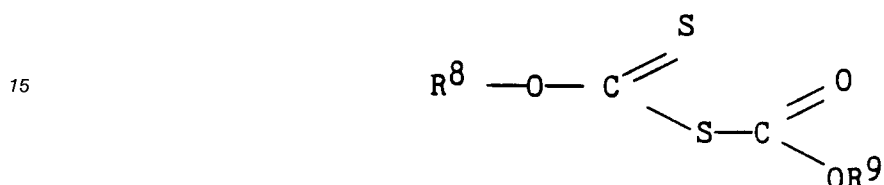
wherein  $M^+$  is as hereinbefore described and each  $R^6$  is independently an alkyl or aryl group, preferably an alkyl group having from 1 to 12, more preferably an alkyl group having from 1 to 8 carbon atoms. Most preferably, each  $R^6$  is isobutyl.

Mercaptan collectors are preferably alkyl mercaptans represented by the general structural formula:



wherein  $R^7$  is an alkyl group, preferably an alkyl group having at least 10, more preferably from 10 to 16, carbon atoms.

10 Xanthogen formates are represented by the general structural formula:



20 wherein  $R^8$  is an alkyl group having from 1 to 7, preferably from 2 to 6 carbon atoms and  $R^9$  is an alkyl group having 1 to 6, preferably 2 to 4, more preferably 2 or 3, carbon atoms.

Xanthic esters are preferably compounds of the general structural formula:



30 wherein  $R^{10}$  is an allyl group and  $R^{11}$  is an alkyl group having from 1 to 7 carbon atoms.

Preferred thiol compounds for use as a collector are the thiocarbonates, thionocarbamates and the thiophosphates due to the surprisingly high recoveries and selectivities towards mineral values which can be achieved.

35 As will be recognized by one skilled in the art, the thiol collectors described above are particularly useful in the flotation of sulfide minerals or sulfidized oxide minerals. The other anionic collectors described above are useful in the flotation of certain sulfide minerals, but are also surprisingly useful in the flotation of oxide minerals.

The hydroxy-containing compound used in the practice of this invention is ethanolamine, propanolamine, butanolamine, diethanolamine, dipropanolamine, tripropanolamine, triethanolamine, or a mixture of two or more thereof.

40 The alkanol amines useful in the practice of this invention are available commercially. As will be recognized by one skilled in the art, commercially available alkanol amines will have varying degrees of purity. For example, diethanol amine may contain varying amounts of ethanol amine and/or triethanol amine. 45 Such alkanol amines are suitable in the practice of the present invention.

The hydroxy-containing compounds may be added directly to the float cell or may be added to the grinding stage. The preferred time of addition will vary depending on the particular ore being floated, the other reagents present and the processing system being used. The hydroxy-containing compounds are not pre-mixed with the collector prior to addition to the flotation process. They are added to the flotation system separately from the collector. They are preferably added prior to the addition of the collector. For example, 50 the hydroxy-containing compounds may be added to the grinding stage.

The collector 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 mineral to be recovered, the grade of the ore to be subjected to the froth flotation process and the desired quality of the mineral to be recovered. Additional factors to be considered in determining dosage levels include the amount of surface area of the ore to be treated. As will be recognized by one skilled in the art, the smaller the particle size, 55 the greater the amount of collector reagents needed to obtain adequate recoveries and grades.

Preferably, the concentration of the collector is at least about 0.001 kg/metric ton, more preferably at least about 0.005 kg/metric ton. It is also preferred that the total concentration of the collector is no greater than about 5.0 kg/metric ton and more preferred that it is no greater than about 2.5 kg/metric ton. It is more preferred that the concentration of the collector is at least about 0.005 kg/metric ton and no greater than about 0.100 kg/metric ton. It is generally preferred to start at the lower concentration range and gradually increase the concentration to obtain optimum performance.

The concentration of the hydroxy-containing compounds useful in this invention is preferably at least about 0.001 kg/metric ton and no greater than about 5.0 kg/metric ton. A more preferred concentration is at least about 0.005 kg/metric ton and no more than about 0.500 kg/metric ton. As discussed above, it is generally preferred to start at the lower concentration range and gradually increase the concentration to obtain optimum performance. This is particularly important when thiol collectors are used in the flotation of sulfide minerals since the general trend is that selectivity is increased at the expense of overall recovery.

It has been found advantageous in the recovery of certain minerals to add the collector to the flotation system in stages. By stage addition, it is meant that a part of the total collector dose is added; froth concentrate is collected; an additional portion of the collector is added; and froth concentrate is again collected. This staged addition can be repeated several times to obtain optimum recovery and grade. The number of stages in which the collector is added is limited only by practical and economic constraints. Preferably, no more than about six stages are used.

In addition to the hydroxy-containing compounds employed in the process of this invention, other conventional additives may be used in the flotation process, including other collectors than those mentioned above. Examples of such additives include depressants and dispersants. In addition to these additives, frothers may be and preferably are also used. Frothers are well-known in the art and reference thereto is made for the purposes of this invention. Non-limiting examples of useful frothers include C<sub>5-8</sub> alcohols, pine oils, cresols, C<sub>1-6</sub> alkyl ethers of polypropylene glycols, dihydroxylates of polypropylene glycols, glycol fatty acids, soaps, alkylaryl sulfonates and mixtures thereof.

When anionic collectors are used, pH is believed to play a role in the flotation process. The nature of the anionic collectors of the present invention is related to the charge characteristics of the particular oxide mineral to be recovered. Thus, pH plays an important role in the froth flotation process of the present invention. While not wishing to be bound by any particular theory, it is assumed that the anionic collector attaches to the oxide at least in part through charge interaction with the mineral surface. Thus, pH conditions under which the charge of the oxide mineral is suitable for attachment are required in the practice of this invention.

The pH in flotation systems may be controlled by various methods known to one skilled in the art. A common reagent used to control pH is lime. However, in the practice of this invention, it is preferred to use reagents such as potassium hydroxide, sodium hydroxide and sodium carbonate and other reagents having monovalent cations to regulate pH. Reagents having divalent cations such as magnesium hydroxide and calcium hydroxide may be used, but are not preferred since their use results in the need to use larger dosages of the collector. It should be noted that when the anionic collector is derived from sulfonic and sulfuric acids, the presence of divalent and/or metal cations is not as detrimental.

The following examples are provided to illustrate the invention and should not be interpreted as limiting it in any way. Unless stated otherwise, all parts and percentages are by weight.

#### Example 1

A series of 30g samples of apatite ore containing about 30 percent apatite and about 70 percent silica were prepared. The hydroxy-containing compound used in each case was diethanolamine and the anionic collector oleic acid. Each sample of ore was ground with 15g of deionized water in a rod mill (2.5 inch diameter with 0.5 inch rods)(6.35 cm dia. with 1.27cm rods) for 240 revolutions. The resulting pulp was transferred to a 300 ml flotation cell. The pH of the slurry was left at natural ore pH of 8.0.

In each run, the manner in which diethanolamine and oleic acid were added to the flotation system varied. In Run 1, diethanolamine was added to the cell and allowed to condition for one minute. This was followed by the addition of the oleic acid followed by an additional minute of conditioning. In Run 2, the order of addition is reversed. In Run 3, diethanolamine and oleic acid were each added to the cell at the same time and in approximately the same physical location and allowed to condition for one minute. In Run 4, diethanolamine and oleic acid were mixed in a separate container and a salt was formed as indicated by the evolution of heat. This was added to the flotation cell and then conditioned for one minute. In Run 5, a condensate of excess fatty acids and diethanolamine available commercially as M-210 from The Dow Chemical Company was used in place of unreacted oleic acid and diethanolamine. In Runs 6 and 7, oleic

acid was used alone. The recovery reported is that fractional portion of the original mineral that is recovered. Thus, a recovery of 1.00 indicates that all of the material was recovered. The results obtained are shown in Table I.

Runs 1-3, embodiments of this invention, clearly demonstrate its effectiveness. Run 4 shows that when the components of the invention are pre-mixed, the recovery of phosphorus obtained is substantially less than when oleic acid is used alone. Run 5 shows that a fatty acid/diethanolamine condensate is ineffective in this process. A number of additional Examples of the invention are given in the published text of EP-A-0453677.

TABLE I  
Apatite and Silica Mixture

Run	Collector	Dosage (kg/metric ton)	Phosphorus Recovery and Grade					
			0-2 Minute		2-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
1	Diethanol amine	0.100	0.908	0.124	0.020	0.067	0.928	0.124
	Oleic acid	0.100						
2	Oleic acid	0.100	0.876	0.126	0.042	0.083	0.918	0.124
	Diethanol amine	0.100						
3	Diethanol amine	0.100	0.803	0.133	0.016	0.057	0.819	0.132
	Oleic acid	0.100						
4 <sup>ⓐ</sup>	Diethanol amine/Oleic acid salt	0.200	0.703	0.126	0.024	0.94	0.727	0.115
5 <sup>ⓐ</sup>	Condensate	0.200	0.060	0.066	0.015	0.034	0.075	0.060
6 <sup>ⓐ</sup>	Oleic acid	0.200	0.881	0.089	0.033	0.027	0.904	0.087
7 <sup>ⓐ</sup>	Oleic acid	0.100	0.687	0.113	0.115	0.061	0.802	0.105

<sup>ⓐ</sup> Not an embodiment of the invention.

**Claims**

1. A process for the recovery of mineral values by froth flotation comprising subjecting a particulate ore, which contains silica or siliceous gangue and is in an aqueous slurry, to froth flotation under conditions such that the minerals to be recovered are floated and the flotation of the silica or siliceous gangue is depressed, wherein the flotation is carried out in the presence of an anionic collector and a hydroxy-containing compound, which is ethanolamine, propanolamine, butanolamine, diethanolamine, dipropanolamine, dibutanolamine, triethanolamine, tripropanolamine, tributanolamine, or a mixture of two or more such hydroxy-containing compounds,  
 characterised in that the hydroxy-containing compound is added to the flotation system separately from the anionic collector.
2. The process of Claim 1, wherein the anionic collector is derived from a carboxylic, sulfonic, sulfuric, phosphoric or a phosphonic acid.
3. The process of Claim 2, wherein the anionic collector comprises an alkyl sulfonic acid or salt thereof, an alkylaryl sulfonic acid or salt thereof, or a mixture of two or more thereof.
4. The process of Claim 2, wherein the anionic collector is an alkylated benzene sulfonic acid or salt thereof, an alkylated sulfonic acid or salt thereof, an alkylated diphenyl oxide monosulfonic acid or a salt thereof, or a mixture of two or more thereof.
5. The process of Claim 2, wherein the anionic collector is linolenic acid, oleic acid, lauric acid, linoleic acid, octanoic acid, capric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, behenic acid, 2-naphthyl sulfonic acid, dodecane sulfonic acid, chloride derivative of dodecyl phosphonic acid, 2-naphthoic acid, pimelic acid, 11-aminododecanoic acid, dodecyl benzyl sulfonic acid, hexadecyl sulfonic acid, a salt of any of the aforesaid acids, sodium lauryl sulfate, sodium stearate, dodecyl sodium sulfate dodecyl phosphate, or a mixture of two or more thereof.
6. The process of any one of the preceding claims, including a thiol collector which is a thiocarbonate, a thiocarbamate, a thiocarbanilide, a thiophosphate, a thiophosphinate, a mercaptan, a xanthogen formate, a xanthic ether, or a mixture of two or more thereof.

**Patentansprüche**

1. Verfahren zur Gewinnung von Mineralwertstoffen durch Schaumflotation, umfassend das Unterwerfen eines teilchenförmigen Erzes, das Kieselerde oder kieselerdehaltige Gangart enthält und in einer wässrigen Aufschlämmung vorliegt, der Schaumflotation unter solchen Bedingungen, daß die zu gewinnenden Mineralstoffe flотиert werden und die Flotation von Kieselerde oder kieselerdehaltiger Gangart unterdrückt wird, worin die Flotation in Anwesenheit eines anionischen Kollektors und einer hydroxy-haltigen Verbindung, welche Ethanolamin, Propanolamin, Butanolamin, Diethanolamin, Dipropanolamin, Dibutanolamin, Triethanolamin, Tripropanolamin, Tributanolamin oder eine Mischung von zwei oder mehreren solcher hydroxy-haltiger Verbindungen ist, durchgeführt wird, dadurch gekennzeichnet, daß die hydroxy-haltige Verbindung zu dem Flotationssystem getrennt von dem anionischen Kollektor zugesetzt wird.
2. Verfahren nach Anspruch 1, worin der anionische Kollektor von einer Carbonsäure, Sulfonsäure, Schwefelsäure, Phosphorsäure oder Phosphonsäure abstammt.
3. Verfahren nach Anspruch 2, worin der anionische Kollektor eine Alkylsulfonsäure oder ein Salz hiervon, eine Alkylarylsulfonsäure oder ein Salz hiervon oder eine Mischung von zwei oder mehreren hiervon umfaßt.
4. Verfahren nach Anspruch 2, worin der anionische Kollektor eine alkylierte Benzolsulfonsäure oder ein Salz hiervon, eine alkylierte Sulfonsäure oder ein Salz hiervon, eine alkylierte Diphenyloxid-monosulfonsäure oder ein Salz hiervon oder eine Mischung von zwei oder mehreren hiervon ist.

5. Verfahren nach Anspruch 2, worin der anionische Kollektor Linolensäure, Ölsäure, Laurinsäure, Linoleinsäure, Octancarbonsäure, Caprinsäure, Myristinsäure, Palmitinsäure, Stearinsäure, Arachidinsäure, Behensäure, 2-Naphthylsulfonsäure, Dodecansulfonsäure, Chloridderivat von Dodecylphosphonsäure, 2-Naphthoesäure, Pimelinsäure, 11-Aminododecancarbonsäure, Dodecylbenzylsulfonsäure, Hexadecylsulfonsäure, ein Salz irgendeiner der zuvorgenannten Säuren, Natriumlaurylsulfat, Natriumstearat, Dodecylnatriumsulfat, Dodecylsulfat oder eine Mischung von zwei oder mehreren hiervon ist.
6. Verfahren nach einem der vorhergehenden Ansprüche, einschließend einen Thiol-Kollektor, der ein Thiocarbonat, ein Thiocarbamat, ein Thiocarbanilid, ein Thiophosphat, ein Thiophosphinat, ein Mercaptan, ein Xanthogenformiat, ein Xanthogenatether oder eine Mischung von zwei oder mehreren hiervon ist.

### Revendications

1. Procédé de récupération de minéraux de valeur par flottation par écumage, comprenant le fait de soumettre un minerai particulier, qui contient de la silice ou une gangue siliceuse et se trouve en suspension aqueuse, à une flottation par écumage effectuée dans des conditions telles que les minéraux que l'on veut récupérer flottent et que la silice ou la gangue siliceuse est empêchée de flotter, cette flottation étant effectuée en présence d'un agent collecteur anionique et d'un composé hydroxylé qui est de l'éthanolamine, de la propanolamine, de la butanolamine, de la diéthanolamine, de la dipropanolamine, de la dibutanolamine, de la triéthanolamine, de la tripropanolamine, de la tributanolamine, ou un mélange de deux de ces composés hydroxylés ou plus, caractérisé en ce que le composé hydroxylé et l'agent collecteur anionique sont introduits séparément dans le système de flottation.
2. Procédé conforme à la revendication 1, dans lequel l'agent collecteur anionique est un dérivé d'un acide carboxylique, d'un acide sulfonique, de l'acide sulfurique, d'un acide phosphorique ou d'un acide phosphonique.
3. Procédé conforme à la revendication 2, dans lequel l'agent collecteur anionique est un acide alkylsulfonique ou un sel d'un tel acide, un acide alkarylsulfonique ou un sel d'un tel acide, ou un mélange de deux de ces composés ou plus.
4. Procédé conforme à la revendication 2, dans lequel l'agent collecteur anionique est un acide alkylbenzènesulfonique ou un sel d'un tel acide, un acide sulfonique alkylé ou un sel d'un tel acide, un acide monosulfonique dérivé d'un oxyde de diphenyle alkylé ou un sel d'un tel acide, ou un mélange de deux de ces composés ou plus.
5. Procédé conforme à la revendication 2, dans lequel l'agent collecteur anionique est de l'acide linoléique, de l'acide oléique, de l'acide laurique, de l'acide linoléique, de l'acide octanoïque, de l'acide caprique, de l'acide myristique, de l'acide palmitique, de l'acide stéarique, de l'acide arachidique, de l'acide béhénique, de l'acide 2-naphtalènesulfonique, de l'acide dodécanesulfonique, un dérivé chlorure de l'acide dodécylphosphonique, de l'acide 2-naphtoïque, de l'acide pimélique, de l'acide 11-aminododécanoïque, de l'acide dodécylbenzènesulfonique, de l'acide hexadécanesulfonique un sel de n'importe lequel de ces acides, du laurylsulfate de sodium, du stearate de sodium, du dodécylsulfat de sodium du phosphate de dodécyle, ou un mélange de deux de ces composés ou plus.
6. Procédé conforme à l'une des revendications précédentes, dans lequel on emploie un agent collecteur de type thiol, qui est un thiocarbonate, un thionocarbamate, un thiocarbanilide, un thiophosphate, un thiophosphinate, un mercaptan, un xanthogénoformiate, un éther xanthique ou un mélange de deux de ces composés ou plus.