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

(57) A flotation process is disclosed wherein the selectivity to the valuable mineral is improved by the depression of silica or siliceous gangue by the use of a hydroxy-containing compound such as an alkanol amine. The process is useful in the flotation of oxide minerals as well as in sulfide flotation.

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This invention is related to the recovery of minerals 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 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 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 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 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 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 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.

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.

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.

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 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.

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

The present invention is 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 wherein the flotation of the silica or siliceous gangue is depressed by the use of an effective amount of a hydroxy-containing compound selected from the group comprising ethanol amine, propanol amine, butanol amine, lactic acid, glycolic acid, ß-hydroxy-1-propane sulfonic acid, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, glycerol, trihydroxy benzoic acid, hydroxy benzoic acid, butylene glycol, dibutylene glycol, diethanol amine, dipropanol amine, tripropanol amine, triethanol amine and simple sugar alcohols such as sucrose, glucose and dextrose and mixtures thereof. Additionally, the froth flotation process of this invention utilizes collectors, frothers and other flotation reagents known in the art.

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 (CuS), chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), vallerite ($Cu_2Fe_4S_7$ or $Cu_3Fe_4S_7$), tetrahedrite (Cu_3SbS_2), enargite ($Cu_3(As_2Sb)S_4$), tennantite ($Cu_{12}As_4S_{13}$), cubanite ($Cu_2SFe_4S_5$), brochantite ($Cu_4(OH)_6SO_4$), antlerite ($Cu_3SO_4(OH)_4$), famatinite ($Cu_3(SbAs)S_4$), and bournonite ($PbCuSbS_3$); lead-bearing minerals such as galena (PbS); antimony-bearing minerals such as stibnite (Sb_2S_3); zinc-bearing minerals such as sphalerite (ZnS); silver-bearing minerals such as stephanite (Ag_5SbS_4) and argentite (Ag_2S); chromium-bearing minerals such as daubreelite ($FeSCrS_3$); nickel-bearing minerals such as pentlandite [$(FeNi)_9S_8$]; molybdenum-bearing minerals such as molybdenite (MoS_2); and platinum- and palladium-bearing minerals such as cooperite [$Pt(AsS)_2$]. Preferred metal-containing sulfide minerals include molybdenite (MoS_2), chalcopyrite ($CuFeS_2$), chalcocite (Cu_2S), galena (Pbs), sphalerite (ZnS), bornite (Cu_5FeS_4), and pentlandite [$(FeNi)_9S_8$].

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 ($Cu_2(OH)_2CO_3$), azurite ($Cu_3(OH)_2(CO_3)_2$), cuprite (Cu_2O), atacamite ($Cu_2Cl(OH)_3$), tenorite (CuO), chrysocolla ($CuSiO_3$); aluminum-bearing minerals such as corundum; zinc-containing minerals such as zincite (ZnO) and smithsonite ($ZnCO_3$); tungsten-bearing minerals such as wolframite [$(Fe_2Mn)WO_4$]; nickel-bearing minerals such as bunsenite (NiO); molybdenum-bearing minerals such as wulfenite ($PbMoO_4$) and powellite ($CaMoO_4$); iron-containing minerals such as hematite and magnetite; chromium-containing minerals such as chromite ($FeOCr_2O_3$); 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 ($U_2O_5(U_3O_8)$) and gummite (UO_3nH_2O).

Other metal-containing minerals for which the use of thiol collectors in this process is useful include gold-bearing minerals such as sylvanite ($AuAgTe_2$) and calaverite ($AuTe$); platinum- and palladium-bearing minerals such as sperrylite ($PtAs_2$); and silver-bearing minerals such as hessite ($AgTe_2$). 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-

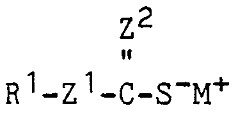
naphthalene sulfonic acid, sodium lauryl sulfate, sodium stearate, dodecane sodium sulfonic acid, hexadecyl sulfonic acid, dodecyl sodium sulfate, dodecyl phosphate, chloride derivative of dodecyl phosphonic acid, 2-naphthoic acid, pimelic acid, and dodecyl benzene sulfonate and mixtures thereof.

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, thiocarbanilides, thiophosphates, thiophosphinates, mercaptans, xanthogen formates, xanthic esters and mixtures thereof.

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



$$R^1-Z^1-\overset{\overset{\displaystyle Z^2}{\|}}{C}-S^-M^+$$

wherein

R^1 is independently a C_{1-20}, preferably C_{2-16}, more preferably C_{3-12} alkyl group;

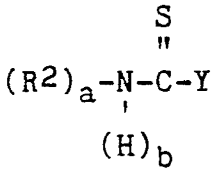
Z^1 and Z^2 are independently a sulfur or oxygen atom; and

M^+ is an alkali metal cation.

The compounds represented by this formula include the alkyl thiocarbonates (both Z^1 and Z^2 are oxygen), alkyl dithiocarbonates (Z^1 is O, Z^2 is S) and the alkyl trithiocarbonates (both Z^1 and Z^2 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:



$$(R^2)_a-\underset{\underset{\displaystyle (H)_b}{|}}{N}-\overset{\overset{\displaystyle S}{\|}}{C}-Y$$

wherein

each R^2 is independently a C_{1-10}, preferably a C_{1-4}, more preferably a C_{1-3}, alkyl group;

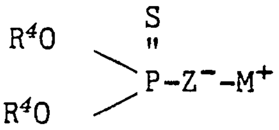
Y is $-S^-M^+$ or $-OR^3$, wherein R^3 is a C_{1-10}, preferably a C_{2-6}, more preferably a C_{3-4}, alkyl group;

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^-M^+) and alkyl thionocarbamates ($a=1$, $b=1$ and Y is $-OR^3$). 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:

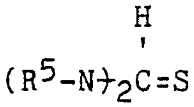


wherein each R^4 is independently hydrogen or a C_{1-10} alkyl, preferably a C_{2-8} alkyl, or an aryl, preferably an aryl group having from 6-10 carbon atoms, more preferably cresyl; Z is oxygen or sulfur; and M is an alkali metal cation.

Of the thiophosphates, those preferably employed include the monoalkyl dithiophosphates (one R^4 is hydrogen and the other R^4 is a C_{1-10} alkyl and Z is S), dialkyl dithiophosphates (both R^4 are C_{1-10} alkyl and Z is S) and dialkyl monothiophosphate (both R^4 are a C_{1-10} 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.

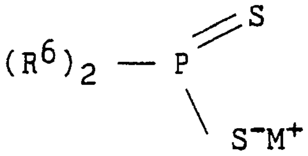
Thiocarbanilides (dialkyl thioureas) are represented by the general structural formula:



$$(R^5-\overset{H}{N})_2C=S$$

wherein each R^5 is individually H or a C_{1-6}, preferably a C_{1-3}, hydrocarbyl.

Thiophosphinates are represented by the general structural formula:



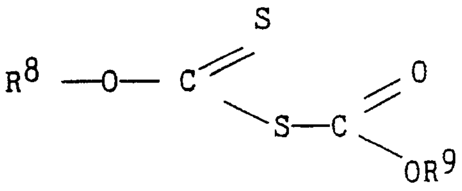
wherein M^+ is as hereinbefore described and each R^6 is independently an alkyl or aryl group, preferably an alkyl group having from 1 to 12, more preferably an alkyl group having from 1 to 8 carbon atoms. Most preferably, each R^6 is isobutyl.

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

R^7-S-H

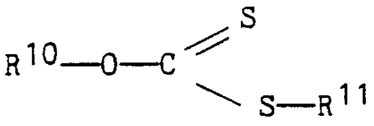
wherein R^7 is an alkyl group, preferably an alkyl group having at least 10, more preferably from 10 to 16, carbon atoms.

Xanthogen formates are represented by the general structural formula:



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:



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.

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 compounds useful in the practice of this invention comprises compounds containing at least one -OH moiety. This hydroxy compound is selected to be essentially non-frothing under the conditions of use. For purposes of this invention, non-frothing compounds are those which have minimal frothing action under the conditions of use. As is well recognized by those skilled in the art, when considering simple hydroxy-containing compounds such as alcohols, their frother power generally increases with the number of carbon atoms in the alcohol up to about six or seven. When the number of carbon atoms reaches this point, the effectiveness of the alcohol as a frother drops. Thus, under some conditions of use, monohydric alcohols such as octanol, nonanol, decanol, undecanol and dodecanol may be useful as non-frothing hydroxy-containing compounds. Laboratory scale flotation work using relatively pure water has shown that these alcohols may be non-frothing and useful in the practice of this invention. However, under most practical conditions of use, these alcohols demonstrate sufficient frothing so that their use is not preferred.

The hydroxy-containing compound used in the practice of this invention is ethanolamine, propanolamine, butanolamine, lactic acid, glycolic acid, beta-hydroxy-l-propane sulfonic acid, ethylene glycol, diethylene glycol, glycerol, trihydroxybenzoic acid, hydroxybenzoic acid, butylene glycol, ditbutylene glycol, diethanolamine, dipropanolamine, tripropanolamine, triethanolamine or a simple sugar alcohol such as sucrose, glucose or dextrose, or a mixture of two or more thereof.

In a more preferred embodiment, the hydroxy-containing compounds is ethanol amine, propanol amine, butanol amine, diethanol amine, dipropanol amine, tripropanol amine, triethanol amine or a mixture of two or more thereof.

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 degress of purity. For example, diethanol amine may contain varying amounts of ethanol amine and/or triethanol amine. 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 bing 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 preferably added to the flotation system separately from the collector. They are also preferably added prior to the addition of the collector. For example, 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, 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 additivies 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_{5-8} alcohols, pine oils, cresols, C_{1-6} alkyl ethers of polypropylene glycols, dihyroxylates 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.

The following examples include work involving Hallimond tube flotation and flotation done in laboratory scale flotation cells. It should be noted that Hallimond tube flotation is a simple way to screen collectors, but does not necessarily predict the success of collectors in actual flotation. Hallimond tube flotation does not involve the shear or agitation present in actual flotation and does not measure the effect of frothers. Thus, while a collector must be effective in a Hallimond tube flotation if it is to be effective in actual flotation, a collector effective in Hallimond tube flotation will not necessarily be effective in actual flotation. It should also be noted that experience has shown that collector dosages required to obtain satisfactory recoveries in a Hallimond tube are often substantially higher than those required in a flotation cell test. Thus, the Hallimond tube work cannot precisely predict dosages that would be required in an actual flotation cell.

Example 1 - Hallimond Tube Flotation of Malachite and Silica

In this example, the effect of various collectors on the flotation of copper was determined using a

Hallimond tube. About 1.1 g of (1) malachite, a copper oxide mineral having the approximate formula $Cu_2CO_3(OH)_2$, or (2) silica was sized to about -60 to +120 U.S. mesh and placed in a small bottle with about 20 ml of deionized water. The mixture was shaken 30 seconds and then the water phase containing some suspended fine solids or slimes was decanted. This desliming step was repeated several times.

A 150-ml portion of deionized water was placed in a 250-ml glass beaker. Next, 2.0 ml of a 0.10 molar solution of potassium nitrate was added as a buffer electrolyte. The pH was adjusted to about 10.0 with the addition of 0.10 N HCl and/or 0.10 N NaOH. Next, a 1.0-g portion of the deslimed mineral was added along with deionized water to bring the total volume to about 180 ml. The collector and hydroxy-containing compound, as identified in the various runs reported in Table I below, were added and allowed to condition with stirring for 15 minutes. The pH was monitored and adjusted as necessary.

The slurry was transferred into a Hallimond tube designed to allow a hollow needle to be fitted at the base of the 180-ml tube. After the addition of the slurry to the Hallimond tube, a vacuum of 5 in (12.7 cm) of mercury was applied to the opening of the tube for a period of 10 minutes. This vacuum allowed air bubbles to enter the tube through the hollow needle inserted at the base of the tube. During flotation, the slurry was agitated with a magnetic stirrer set at 200 revolutions per minute (RPM).

The floated and unfloated material was filtered out of the slurry and oven dried at 100 ° C. Each portion was weighed. After each test, all equipment was washed with concentrated HCl and rinsed with 0.10 N NaOH and deionized water before the next run.

The results obtained using the above-described procedure and varying the identity of the collector and hydroxy-containing compound are reported in Table I following. The recovery of malachite and silica, respectively, reported is that fractional portion of the original mineral placed in the Hallimond tube that is recovered. Thus, a recovery of 1.00 indicates that all of the material was recovered. It should be noted that although the recovery of copper and silica, respectively, is reported for each run, the data is actually collected in two separate experiments done under identical conditions. It should further be noted that a low silica recovery suggests a selectivity to the copper. The values given for copper recovery generally are correct to ±0.05 and those for silica recovery are generally correct to ±0.03.

TABLE I

Run	Collector	Dosage (kg/kg)	Fractional Cu Recovery	Fractional Silica Recovery
1①	Oleic acid	0.024	0.860	0.096
2①	Lauric acid	0.024	0.786	0.154
3①	Octanoic acid	0.024	0.228	0.354
4①	Linoleic acid	0.024	0.982	0.120
5①	2-naphthalene sulfonic acid	0.024	0.073	0.000
6①	Sodium lauryl sulfate	0.024	0.971	0.106
7①	Dodecyl sodium sulfonate	0.024	0.223	0.212
8①	Dodecyl phosphonic acid	0.024	0.910	0.071
9①	1,2-dodecanediol	0.024	0.255	0.210
10	1,2-dodecanediol Oleic acid	0.012 0.012	0.938	0.154
11①	Benzoic acid	0.024	0.058	0.000
12	Benzoic acid Oleic acid	0.012 0.012	0.592	0.071

TABLE I (Cont'd.)

Run	Collector	Dosage (kg/kg)	Fractional Cu Recovery	Fractional Silica Recovery
13①	Hydroxy benzoic acid	0.024	0.072	0.246
14	Hydroxy benzoic acid Oleic acid	0.012 0.012	0.732	0.191
15①	Trihydroxy benzoic acid	0.024	0.068	0.113
16	Trihydroxy benzoic acid Oleic acid	0.012 0.012	0.816	0.089
17①	Phenol	0.024	0.059	0.137
18	Phenol Oleic acid	0.012 0.012	0.389	0.099
19①	Potassium salt of dodecyl xanthate	0.024	0.962	0.137
20①	$C_6H_9(CH_2)_2OCS_2K$	0.024	0.170	0.165
21①	Linolenic acid	0.024	0.973	0.243
22①	Stearic acid	0.024	1.000	0.122
23①	Palmitic acid	0.024	1.000	0.082
24①	Glycerol	0.024	0.038	0.380
25	Glycerol Oleic acid	0.012 0.012	0.748	0.283

TABLE I (Cont'd.)

Run	Collector	Dosage (kg/kg)	Fractional Cu Recovery	Fractional Silica Recovery
26①	Ethanol amine	0.024	0.435	0.261
27	Ethanol amine Oleic acid	0.012 0.012	0.963	0.105
28①	2-propanol amine	0.024	0.541	0.294
29	2-propanol amine Oleic acid	0.012 0.012	0.993	0.117
30①	Glycolic acid	0.024	0.116	0.049
31	Glycolic acid Oleic acid	0.012 0.012	0.904	0.047
32①	β-hydroxy propionic acid	0.024	0.247	0.061
33	β-hydroxy propionic acid Oleic acid	0.012 0.012	0.933	0.060
34①	Lactic acid	0.024	0.094	0.035
35	Lactic acid Oleic acid	0.012 0.012	0.893	0.031
36①	3-hydroxy-1-propane sulfonic acid	0.024	0.513	0.119
37	3-hydroxy-1-propane sulfonic acid Oleic acid	0.012 0.012	0.971	0.090

TABLE I (Cont'd.)

Run	Collector	Dosage (kg/kg)	Fractional Cu Recovery	Fractional Silica Recovery
38①	Propylene glycol	0.024	0.344	0.149
39	Propylene glycol Oleic acid	0.012 0.012	0.967	0.077
40	Propylene glycol Lauric acid	0.012 0.012	0.917	0.051
41	Propylene glycol Octanoic acid	0.012 0.012	0.855	0.099
42	Propylene glycol Linoleic acid	0.012 0.012	0.979	0.019
43	Propylene glycol 2-naphthalene sulfonic acid	0.012 0.012	0.391	0.020
44	Propylene glycol Sodium lauryl sulfate	0.012 0.012	0.994	0.068
45	Propylene glycol Dodecyl sodium sulfonate	0.012 0.012	0.844	0.092
46	Propylene glycol Potassium salt of dodecyl xanthate	0.012 0.012	0.998	0.088
47	Propylene glycol $C_6H_9(CH_2)_2OCS_2K$	0.012 0.012	0.773	0.061
48	Propylene glycol Linolenic acid	0.012 0.012	1.000	0.067
49	Propylene glycol Stearic acid	0.012 0.012	1.000	0.099

TABLE I (Cont'd.)

Run	Collector	Dosage (kg/kg)	Fractional Cu Recovery	Fractional Silica Recovery
50	Propylene glycol Palmitic acid	0.012 0.012	1.000	0.049
51	Propylene glycol Dodecyl benzene sulfonic acid	0.012 0.012	0.818	0.043
52①	Diethanol amine	0.024	0.389	0.147
53	Diethanol amine Oleic acid	0.012 0.012	1.000	0.071
54	Diethanol amine Linoleic acid	0.012 0.012	0.991	0.023
55	Diethanol amine Dodecyl sodium sulfonate	0.012 0.012	0.791	0.097
56	Diethanol amine Dodecyl benzene sulfonic acid	0.012 0.012	0.801	0.047
57①	Amino decanol	0.024	0.197	0.071
58	Amino decanol Oleic acid	0.012 0.012	0.731	0.047

① Not an embodiment of the invention.

The data in the table above indicates the broad effectiveness of the present invention in a Hallimond tube. It also indicates that the hydroxy-containing compound alone generally functions poorly as a collector.

Example 2 -Hallimond Tube Flotation of Chrysocolla and Silica

The procedure outlined for Example 1 is followed with the exception that chrysocolla ($Cu_2H_2Si_2O_5(OH)_4$) is used in place of malachite. In addition, in some cases different collectors and hydroxy-containing compounds are used. The results obtained are set out in Table II following.

TABLE II

Run	Collector	Dosage (kg/kg)	Fractional Cu Recovery	Fractional Silica Recovery
1①	Oleic acid	0.024	0.950	0.137
2①	Dodecyl benzene sulfonic acid	0.024	0.363	0.163
3①	Propylene glycol	0.024	0.227	0.146
4①	Diethanol amine	0.024	0.191	0.151
5	Propylene glycol Oleic acid	0.012 0.012	0.999	0.094
6	Propylene glycol Dodecyl benzene sulfonic acid	0.012 0.012	0.844	0.101
7	Diethanol amine Oleic acid	0.012 0.012	0.986	0.096
8	Diethanol amine Dodecyl benzene sulfonic acid	0.012 0.012	0.773	0.119

① Not an embodiment of the invention.

The data in Table II above demonstrates the general effectiveness of the present invention in the recovery of copper from chrysocolla in Hallimond tube flotation within the limitations discussed relating to Example 1. These runs demonstrate that the use of the hydroxy-containing compound and anionic surfactant results in increased copper recovery, decreased silica recovery or both when compared to identical runs using either component alone.

Example 3 - Flotation of Mixed Copper Oxide Ore

In this example, the effect of different collectors and hydroxy-containing compounds on the flotation of copper ore in laboratory flotation cells was examined. Samples of copper ore from Central Africa containing 500 g per sample were prepared. The ore contained about 76 percent by weight malachite and the remainder was made up of chrysocolla and chalcocite. A 500-g portion of the ore was ground with 257 g deionized water in a rod mill at about 60 RPM for two minutes.

The resulting pulp was next deslimed. The pulp was placed in a flotation cell. The cell was filled with water, the slurry pH adjusted to 9.2 with sodium carbonate and then stirred for 5 minutes. The solids in the cell were allowed to settle for 120 seconds and then the water phase containing finely divided solids was decanted. This process was repeated four times. This deslimed pulp was used in Run 8. In Runs 1-7, the desliming steps were omitted.

The pulp was transferred to a 1500-ml Agitair Flotation cell outfitted with an automatic paddle removal system. The pH of the slurry was adjusted to 9.2 by the addition of sodium carbonate, if necessary. The collectors and hydroxy-containing compounds specified in Table III were added separately to the slurry in the amounts specified in Table III and the slurry was allowed to condition for one minute after the addition of each. A polyglycol ether frother, in the amount of 40 g per ton of dry ore, was then added and the slurry allowed to condition for one additional minute.

The flotation cell was agitated at 1150 RPM and air introduced at a rate of 4.5 liters per minute. Samples of the froth concentrate were collected at 1.0 and 6.0-minute intervals after the air was first introduced into the cell. Samples of the tailings and concentrate were dried, weighed, and pulverized for analysis. After being pulverized, they were dissolved with the use of acid and the copper content determined using a DC Plasma spectrometer. The assay data was used to determine fractional recoveries and grades using standard mass balance formulas.

The data obtained is shown in Table III following.

TABLE III

Run	Collector	Dosage (kg/metric ton)	Copper Recovery and Grade					
			0-1 Minute		1-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
1⊙	NaSH $C_5H_{11}OCS_2K$	0.5 0.2	0.156	0.091	0.085	0.048	0.241	0.076
2⊙	Diethanol amine	0.2	--	--	--	--	0.061	0.057
3	Diethanol amine Oleic acid	0.1 0.1	0.508	0.061	0.117	0.029	0.625	0.055
4⊙	Ethanol amine	0.2	--	--	--	--	0.044	0.058
5	Ethanol amine Oleic acid	0.1 0.1	0.463	0.072	0.096	0.037	0.559	0.066

TABLE III (Cont'd)

Run	Collector	Dosage (kg/metric ton)	Copper Recovery and Grade					
			0-1 Minute		1-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
6⊙	2-propanol amine	0.2	--	--	--	--	0.056	0.048
7	2-propanol amine Oleic acid	0.1 0.1	0.510	0.059	0.084	0.030	0.594	0.055
8⊙	Oleic acid	0.2	0.549	0.058	0.021	0.009	0.570	0.056

⊙ Not an embodiment of the invention.

The data in Table III above demonstrates the effectiveness of this invention under conditions approximating actual flotation conditions. Run 1, which is not an example of the invention, approximates current industry practice. Runs 3, 5, and 7, which are examples of the invention, demonstrate the effectiveness of the process of this invention in the recovery of copper.

Example 4 - Flotation of Chrysocolla Ore

A series of samples containing 500 g of ore from Central Africa were prepared. The ore contained greater than 90 percent chrysocolla and the remainder comprised additional copper oxide minerals and gangue. A 500-g sample was ground with 257 g of deionized water in a rod mill at about 60 RPM for six minutes. The resulting pulp was transferred to an Agitair 1500 ml flotation cell outfitted with an automated paddle removal system. The pH of the slurry was adjusted by the addition of either sodium carbonate or HCl. The natural ore pH in slurry form was 7.8. After addition of the hydroxy-containing compounds as shown in Table IV, the slurry was allowed to condition for one minute. The collector was then added followed by an additional minute of conditioning. A polyglycol ether frother was added in an amount of 20 g per ton of dry ore followed by an additional minute of conditioning.

The float cell was agitated at 1150 RPM and air is introduced at a rate of 4.5 liters per minute. Samples of the froth concentrate were collected at 1.0 and 6.0 minute intervals after the air was first introduced. The samples of the concentrates and the tailings were dried, weighed, pulverized for analysis and dissolved with the use of acid. The copper content was determined by the use of DC Plasma Spectrometer. Using the assay data, fractional recoveries and grades were calculated using standard mass balance formulas. The results obtained are shown in Table IV following.

TABLE IV

Run	Collector	Dosage (kg/metric ton)	pH	Copper Recovery and Grade					
				0-1 Minute		1-6 Minutes		Total	
				Rec	Gr	Rec	Gr	Rec	Gr
1①	Oleic acid	0.2	9.5	0.257	0.088	0.164	0.061	0.421	0.077
2①	NaSH $C_5H_{11}OCS_2K$	0.25 0.2	9.5	0.123	0.050	0.302②	0.072	0.425②	0.065
3	Diethanol amine Oleic acid	0.100 0.100	9.5	0.457	0.141	0.136	0.067	0.593	0.124
4①	Diethanol amine	0.100	9.5	---	---	---	---	0.118	0.071
5	Propylene glycol Oleic acid	0.100 0.100	9.5	0.437	0.130	0.111	0.056	0.548	0.115
6①	Propylene glycol	0.200	9.5	---	---	---	---	0.097	0.0099

① Not an embodiment of the invention.

② Flotation time is expanded to 11 minutes rather than 6 minutes. The frother dosage required is 3 times that of other runs.

The data in Table IV generally demonstrates the effectiveness of the collector composition of the present invention. Run 2 approximates current industry standards.

Example 5 - Flotation of Iron Oxide Ore

A series of 600-g samples of iron oxide ore from Michigan were prepared. The ore contained a mixture of hematite, martite, goethite and magnetite mineral species. Each 600-g sample was ground along with 400 g of deionized water in a rod mill at about 60 RPM for 10 minutes. The resulting pulp was transferred to an Agitair 3000 ml flotation cell outfitted with an automated paddle removal system. The pH of the slurry was adjusted from a natural pH of 7.3 to a pH of 8.5 using sodium carbonate. The hydroxy-containing compound, if used, was added and the slurry allowed to condition for one minute. This was followed by the addition of the collector, followed by an additional minute of conditioning. Next, an amount of a polyglycol ether frother equivalent to 40 g per ton of dry ore was added followed by another minute of conditioning.

The float cell was agitated at 900 RPM and air introduced at a rate of 9.0 liters per minute. Samples of the froth concentrate were collected at 1.0 and 6.0 minutes after the start of the air flow. Samples of the froth concentrate and the tailings were dried, weighed and pulverized for analysis. They were then dissolved in acid, and the iron content determined by the use of a D.C. Plasma Spectrometer. Using the assay data, the fractional recoveries and grades were calculated using standard mass balance formulas. The results are shown in Table V following.

TABLE V

Run	Collector	Dosage (kg/metric ton)	Iron Recovery and Grade					
			0-1 Minute		1-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
1①	Oleic acid	0.200	0.388	0.369	0.262	0.266	0.650	0.327
2①	Propylene glycol	0.200	0.034	0.361	0.039	0.340	0.073	0.342
3	Propylene glycol Oleic acid	0.050 0.050	0.444	0.441	0.081	0.438	0.525	0.441
4①	Oleic acid	0.100	0.165	0.313	0.145	0.287	0.310	0.301
5	Propylene glycol Oleic acid	0.100 0.100	0.587	0.421	0.055	0.358	0.642	0.416
6	Diethylene glycol Oleic acid	0.100 0.100	0.484	0.460	0.075	0.428	0.559	0.456
7	Diethanol amine Oleic acid	0.100 0.100	0.421	0.471	0.072	0.457	0.493	0.469

TABLE V (Cont'd.)

Run	Collector	Dosage (kg/metric ton)	Iron Recovery and Grade					
			0-1 Minute		1-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
8①	Diethanol amine	0.200	--	--	--	--	0.141	0.458②
9①	Ethanol amine	0.200	--	--	--	--	0.074	0.376②
10	Ethanol amine Oleic acid	0.100 0.100	0.298	0.357	0.089	0.396	0.387	0.366

①Not an embodiment of the invention.
②Only one concentrate sample collected.

The data in Table V above demonstrates the effectiveness of the present invention in obtaining good recoveries of high grade iron.

Example 6 - Flotation of Arizona Copper Oxide Ore

A series of 30-g samples of -60 mesh copper ore from Arizona were prepared. It should be noted that this ore is very fine and, thus, very difficult to float. The make-up of the valuable components of the ore was about 60 percent azurite [$Cu_3(CO_3)(OH)_2$], 35 percent malachite [$Cu_2CO_3(OH)_2$], and 5 percent chalcocite [Cu_2S]. Each sample of ore was ground with 15 g of deionized water in a rod mill (2.5 inch diameter with 0.5 inch rods)(6.35 cm dia. with 1.27 cm 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 unless otherwise noted. After addition of the hydroxy-containing compound as shown in Table VI, the slurry was allowed to condition for one minute. Next, the collector was added with an additional minute of conditioning. Next, the frother, a polyglycol ether, was added in an amount equivalent to 0.050 g per ton of dry ore and the slurry allowed to condition an additional minute.

The float cell was agitated at 1800 RPM and air introduced at a rate of 2.7 liters per minute. Samples of the froth concentrate were collected by standard hand paddling at 1.0 and 6.0 minutes after the start of the introduction of air into the cell. Samples of the concentrate and the tailings were dried and analyzed as described in the previous examples. The results obtained are presented in Table VI following.

TABLE VI

Run	Collector	Dosage (kg/metric ton)	Copper Recovery and Grade					
			0-1 Minute		1-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
1①	Oleic acid	0.450	0.097	0.078	0.158	0.069	0.255	0.072
2①	Oleic acid	2.400	0.307	0.080	0.231	0.065	0.538	0.074
3	Propylene glycol Oleic acid	1.200 1.200	0.220	0.094	0.198	0.078	0.418	0.086
4	Dipropylene glycol Oleic acid	1.200 1.200	0.225	0.094	0.232	0.080	0.457	0.087
5②	Propylene glycol Oleic acid	1.200 0.600	0.153	0.081	--	--	--	--
	Oleic acid	0.600	--	--	0.354	0.084	0.507	0.083
6①②	Propylene glycol	2.400	--	--	--	--	0.091	0.035
7①③	Dipropylene glycol	2.400	--	--	--	--	0.113	0.038

TABLE VI (Cont'd)

Run	Collector	Dosage (kg/metric ton)	Copper Recovery and Grade					
			0-1 Minute		1-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
8①	Dodecyl benzene sulfonic acid	2.400	0.213	0.063	0.147	0.053	0.360	0.059
9	Propylene glycol Dodecyl benzene sulfonic acid	1.200 1.200	0.233	0.074	0.172	0.070	0.405	0.072
10①②	No collector	--	--	--	--	--	0.087	0.021
11①	Triethanol amine	2.400	--	--	--	--	0.144	0.078
12	Triethanol amine Oleic Acid	1.200 1.200	0.374	0.083	0.216	.069	0.590	0.078

TABLE VI (Cont'd)

Run	Collector	Dosage (kg/metric ton)	Copper Recovery and Grade					
			0-1 Minute		1-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
13①	Sucrose	2.400	--	--	--	--	0.091	0.068
14①	Trihydroxy benzoic acid	2.400	--	--	--	--	0.148	0.071
15	Sucrose Oleic acid	1.200 1.200	0.297	0.084	0.163	0.067	0.460	0.078
16	Trihydroxy benzoic acid Oleic acid	1.200 1.200	0.337	0.082	0.140	0.071	0.477	0.075

① Not an embodiment of the invention.
② The second 0.600 portion of oleic acid was added after collection of the 0-1 minute fraction.
③ Two concentrates were combined and analyzed as one.

The data in Table VI demonstrates the effectiveness of the collector composition of the present invention in the flotation of difficult to float Arizona copper oxide ore.

Example 7 - Flotation of Mixed Oxide/Sulfide Copper Ore

A series of 30-g samples of -10 mesh copper ore from Canada were prepared. The make-up of the valuable portion of the ore was approximately 50 percent malachite [$Cu_2CO_3(OH)_2$] and 50 percent chalcopyrite [$CuFeS_2$]. Each sample was ground along with 15 grams of deionized water in a rod mill (2.5 inch diameter with 0.5 inch rods) for 1000 revolutions. The resulting pulp was transferred to a 300 ml flotation cell. The pH of the slurry was adjusted to 9.0 by the addition of sodium carbonate. The hydroxy-containing compound, collector and frother were added as described in the previous examples.

The float cell was operated and samples were prepared and analyzed as described in Example 6. The results obtained are given in Table VII following.

TABLE VII

Run	Collector	Dosage (kg/metric ton)	pH	Copper Recovery and Grade					
				0-1 Minute		1-6 Minutes		Total	
				Rec	Gr	Rec	Gr	Rec	Gr
1	Diethanol amine Oleic acid②	0.100 0.100	9.0	0.457	0.090	0.079	0.080	0.536	0.089
2①	Diethanol amine③	0.200	9.0	--	--	--	--	0.111	0.089
3	Ethanol amine Oleic acid②	0.100 0.100	9.0	0.279	0.106	0.215	0.076	0.494	0.093
4①	Ethanol amine③	0.200	9.0	--	--	--	--	0.089	0.092
5	Ethanol amine Oleic acid②	0.100 0.100	9.0	0.243	0.097	0.099	0.079	0.342	0.097
6①	Oleic acid	0.200	9.0	0.218	0.090	0.058	0.065	0.376	0.062

①Not an embodiment of the invention.

The data in Table VII above generally demonstrate the effectiveness of this invention in the flotation of mixed copper oxide/sulfide ores.

Example 8 - Flotation of Corundum

A series of 30-g samples of a -10 mesh mixture of corundum (Al_2O_3) and silica (SiO_2) were prepared. Each sample was ground and transferred to a 300 ml flotation cell as described in Example 7 with the exception that the sample was ground 2000 revolutions. The pH of the slurry was left at the natural pH of 7.4. Collector, hydroxy compound and frother were added and the float cell operated as described in Example 7. Samples were obtained as described in Example 7 and were dried, weighed, pulverized and the aluminum content determined by X-ray fluorescence. The results obtained are shown in Table VIII following.

TABLE VIII

Run	Collector	Dosage (kg/metric ton)	Aluminum Recovery and Grade					
			0-1 Minute		1-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
1①	Oleic acid	0.200	0.331	0.160	0.013	0.080	0.344	0.157
2①	Propylene glycol	0.200	---	---	---	---	0.118	0.086
3	Propylene glycol Oleic acid	0.100 0.100	0.513	0.194	0.071	0.152	0.584	0.188
4①	Diethanol amine	0.200	---	---	---	---	0.146	0.104
5	Diethanol amine Oleic acid	0.100 0.100	0.466	0.205	0.044	0.171	0.490	0.202

①Not an embodiment of the invention.

The data shown in Table VIII above demonstrates the effectiveness of the present invention in the separation of aluminum from silica by flotation.

Example 9 - Flotation of Various Oxide Ores

The general procedure described in Example 1 were followed with the exception that various oxide ores were used in place of the copper ore of Example 1. The results obtained are shown in Table IX following.

TABLE IX

Recoveries of Different Minerals as a Function of pH and Collector Composition Using Propylene Glycol and Oleic Acid at a Dosage of .012 kg/kg Each

MINERAL	pH 10.00
Pyrite, FeS_2	1.000
Silica, SiO_2	0.086
Bauxite, $Al(OH)_3$	0.913
Cassiterite, SnO_2	1.000
Hematite, Fe_2O_3	1.000
Corundum, Al_2O_3	0.798
Calcite, $CaCo_3$	1.000
Rutile, TiO_2	1.000
Chromite, $FeCr_2O_4$	1.000
Dolomite, $CaMg(CO_3)_2$	1.000
Apatite, $Ca_5(Cl_1F)[PO_4]_3$	1.000
Galena, PbS	1.000
Chalcopyrite, $CuFeS_2$	1.000
Chalcocite, Cu_2S	1.000
Sphalerite, ZnS	1.000
Sylvite①	0.703
Pentlandite, Ni(FeS)②	1.000
Nickel Oxide (NiO)	0.911

① Process carried out in saturated KCl solution at pH 12.1.

② Sample includes some pyrrhotite.

This example demonstrates the efficacy of the present invention in floating a broad range of oxide and sulfide minerals. Also demonstrated is the ability to distinguish these various minerals from silica, the major gangue constituent found with these minerals in natural ores.

Example 10

This example used the general Hallimond tube procedure outlined in Example 1 except that instead of using only pure mineral specimens in each run, a specific test consisted of running a pre-mixed sample of 10 percent malachite (or 10 percent chrysocolla) along with 90 percent silica. Copper assays were performed on flotation concentrate and flotation tailings using the acid dissolution procedure and D.C. plasma spectrometry as discussed in Example 3. The results are shown in Table Xa for malachite and Table Xb for chrysocolla. All runs were determined at a pH of 10.0 with the collector dosages as indicated.

TABLE Xa

Malachite/Silica Mixture Separation

Collector	Dosage (kg/kg)	Cu Recovery	Cu Grade
Oleic acid①	0.024	0.971	0.191
Oleic acid①	0.012	0.963	0.169
Propylene glycol①	0.024	0.212	0.712
Propylene glycol Oleic acid	0.012 0.012	0.892	0.387
Propylene glycol Oleic acid	0.012 0.006	0.944	0.325
Propylene glycol Oleic acid	0.012 0.003	0.971	0.248
Dodecyl benzene sulfonic acid①	0.024	0.927	0.178
Propylene glycol Dodecyl benzene sulfonic acid	0.012 0.012	0.961	0.355
Dipropylene glycol①	0.024	0.438	0.133
Dipropylene glycol Oleic acid	0.012 0.012	1.000	0.184
Ethylene glycol①	0.024	0.114	0.579
Ethylene glycol Oleic acid	0.012 0.012	0.944	0.255
Trihydroxy benzoic acid①	0.024	0.167	0.326
Trihydroxy benzoic acid Oleic acid	0.012 0.012	0.659	0.219

①Not an embodiment of the invention.

TABLE Xa (Cont'd.)

Malachite/Silica Mixture Separation

Collector	Dosage (kg/kg)	Cu Recovery	Cu Grade
Diethylene glycol①	0.024	0.183	>0.900
Diethylene glycol Oleic acid	0.012 0.012	1.000	0.401
Glucose①	0.024	0.154	>0.900
Glucose Oleic acid	0.012 0.012	0.886	0.442
Ethanol amine①	0.024	0.078	0.799
Ethanol amine Oleic acid	0.012 0.012	0.990	0.309
Diethanol amine①	0.024	0.050	>0.900
Diethanol amine Oleic acid	0.012 0.012	0.892	0.404
Glycerol①	0.024	0.359	0.721
Glycerol Oleic acid	0.012 0.012	0.775	0.407
Sucrose	0.024	0.316	>0.900
Sucrose Oleic acid	0.012 0.012	0.943	0.501

①Not an embodiment of the invention.

TABLE Xb

Chrysocolla/Silica Mixture Separation

Collector	Dosage (kg/kg)	Cu Recovery	Cu Grade
Oleic acid①	0.024	0.672	0.187
Oleic acid①	0.012	0.389	0.324
Propylene glycol①	0.024	0.255	>0.900
Dodecyl benzene sulfonic acid①	0.024	0.370	0.232
Propylene glycol Oleic acid	0.012 0.012	0.691	0.533
Propylene glycol Dodecyl benzene sulfonic acid	0.012 0.012	0.676	0.337

①Not an embodiment of the invention.

It is apparent from Tables Xa and Xb that a number of hydroxy-containing compounds are effective in decreasing the amount of silica gangue floated and generally resulting in increased recovery and grade.

Example 11

A series of samples containing 30 g of a -10 mesh (U.S.) mixture of 10 percent rutile (TiO_2) and 90 percent silica (SiO_2) were prepared. The remainder of the procedure was exactly the same as that used in Example 6.

TABLE XI

Rutile and Silica Mixture

Run	Collector	Dosage (kg/metric ton)	Titanium Recovery and Grade					
			0-1 Minute		1-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
1①	Propylene glycol	0.400	0.044	0.066	0.012	0.021	0.056	0.054
2	Propylene glycol Oleic acid	0.400 0.100	0.674	0.099	0.062	0.014	0.736	0.092
3①	Diethanol amine	0.400	0.048	0.045	0.027	0.020	0.075	0.036
4	Diethanol amine Oleic acid	0.400 0.100	0.771	0.103	0.033	0.046	0.804	0.101
5①	Oleic acid	0.100	0.449	0.075	0.061	0.025	0.510	0.069

①Not an embodiment of the invention.

The data in Table XI above demonstrates the effect of the present invention in increasing titanium grade and recovery.

Example 12 - Separation of Apatite and Silica

A series of 30-g samples of a -10 mesh (U.S.) mixture of 10 percent apatite ($Ca_5(Cl,F)[PO_4]_3$) and 90 percent silica (SiO_2) were prepared. The remainder of the procedure was exactly the same as that used in Example 6. The natural ore slurry pH is 7.1.

TABLE XII

Apatite and Silica Mixture

Run	Collector	Dosage (kg/metric ton)	Phosphorus Recovery and Grade					
			0-1 Minute		1-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
1	Propylene glycol	0.200	0.923	0.056	0.044	0.005	0.967	0.052
	Oleic acid	0.200						
2	Diethanol amine	0.200	0.841	0.041	0.124	0.002	0.965	0.036
	Oleic acid	0.200						
3	Diethylene glycol	0.200	0.929	0.038	0.030	0.002	0.959	0.038
	Oleic acid	0.200						

TABLE XII

Apatite and Silica Mixture

Run	Collector	Dosage (kg/metric ton)	Phosphorus Recovery and Grade					
			0-1 Minute		1-6 Minutes		Total	
			Rec	Gr	Rec	Gr	Rec	Gr
4①	Oleic acid	0.200	0.801	0.039	0.145	0.013	0.946	0.035
5①	Propylene glycol	0.200	---	---	---	---	0.361	0.031
6①	Diethanol amine	0.200	---	---	---		0.397	0.033
7①	Diethylene glycol	0.200	---	---	---	---	0.304	0.028

① Not an embodiment of the invention.

The data presented above demonstrates that the use of hydroxy-containing compounds of this invention with oleic acid (which is a recognized collector for the flotation of apatite) gives better grade and faster flotation kinetics than the oleic acid alone. The recoveries of apatite with all collectors was quite high although slight improvements were observed in all cases using the hydroxy-containing compounds of this invention. Likewise, grade was improved in each case with substantial improvement being shown in Run 1.

Example 13 - Flotation of Chalcopyrite Copper Ore

In this example, the effect of different alkanol amines on the flotation of copper ore in laboratory flotation cells was examined. Samples of copper ore from Western Canada containing 500 g per sample were prepared. The ore was relatively high grade and also contained significant amounts of silica gangue. A

500-g portion of the ore was ground with 257 g deionized water in a rod mill having 2.5 cm rods at about 60 revolutions per minute (RPM) for about 7 minutes. This produced a size distribution of 25 percent less than 100 mesh. Except as indicated in Table I, the alkanol amine was added to the mill prior to the grinding step. Lime was also added to the mill to produce the desired pH for the subsequent flotation.

The pulp was transferred to a 1500-ml Agitair Flotation cell outfitted with an automatic paddle removal system. The cell was agitated at 1150 RPM. The, pH of the slurry adjusted to 8.5 by the addition of additional lime, if necessary. The collector, potassium amyl xanthate, unless specified otherwise in Table XIII, was added to the slurry at a dosage of 8 g per ton and the slurry allowed to condition for one minute. A polyglycol ether frother, in the amount of 18 g per ton of dry ore, was then added and the slurry allowed to condition for one additional minute.

The flotation cell was agitated at 1150 RPM and air introduced at a rate of 4.5 liters per minute. Samples of the froth concentrate were collected for a period of eight minutes after the air was first introduced into the cell. These samples of the tailings and concentrate were dried overnight in an oven, weighed, and pulverized for analysis. After being pulverized, they were dissolved with the use of acid and the copper content determined using a DC Plasma spectrometer. The assay data was used to determine fractional recoveries and grades using standard mass balance formulas. The recoveries represent the fractional amount of the specified mineral present that was recovered. Selectivity was determined by dividing the copper recovery by the silica gangue recovery.

The data obtained is shown in Table XIII following.

TABLE XIII

Run	Alkanol Amine	Dosage (kg/metric ton)	Copper Recovery	Silica Recovery	Selectivity
1①	None	--	0.654	0.135	4.8
2	Ethanol amine	0.020	0.663	0.114	5.8
3	Diethanol amine	0.020	0.677	0.087	7.8
4	Triethanol amine	0.020	0.669	0.096	7.0
5	Propanol amine	0.020	0.673	0.118	5.7
6	Dipropanol amine	0.020	0.683	0.093	7.3
7	Isopropanol amine	0.020	0.668	0.107	6.2
8	Butanol amine	0.020	0.682	0.127	5.4
9	Diethanol amine	0.040	0.648	0.079	8.2
10	Diethanol amine	0.080	0.617	0.074	8.4
11②	Diethanol amine	0.020	0.668	0.093	7.2
12②	Diethanol amine	0.040	0.627	0.089	7.2
13③	Diethanol amine	0.020	0.597	0.105	5.7
14③	Diethanol amine	0.040	0.544	0.095	5.8

TABLE XIII, Continued

Run	Alkanol Amine	Dosage (kg/metric ton)	Copper Recovery	Silica Recovery	Selectivity
15①②	None	--	0.660	0.137	4.8
16①③	None	--	0.582	0.128	4.5
17④	Diethanol amine	0.020	0.658	0.100	6.6
18④	Diethanol amine	0.040	0.644	0.088	7.3
19	Isopropanol amine	0.040	0.649	0.095	6.8
20⑤	Diethanol amine	0.020	0.658	0.117	5.6

① Not an embodiment of the invention.

② N-ethyl isopropyl thionocarbamate used as collector.

③ Sec-butyl dithiophosphate used as collector.

④ In this run, the amine was added to the flotation cell rather than grinding mill.

⑤ In this run, the amine and collector were added to the flotation cell concurrently.

The data in Table XIII demonstrates that the practice of this invention is effective in decreasing the recovery of silica gangue and thus increasing the selectivity of the flotation process. The data also demonstrates that the practice of this invention can result in lower recovery of the desired copper mineral values. A comparison of Runs 3, 17 and 20 shows that addition of the amine in the grinding stage rather than in the flotation cell or concurrently with collector results in the highest recovery of high grade copper.

Example 14 - Flotation of Mixed Copper Ore

A series of 30-g samples of mixed copper sulfide ore from Nevada were prepared. The make-up of the valuable components of the ore was about 0.25 weight percent copper, about 0.004 weight percent molybdenum and about 4 g/metric ton gold. Each sample of ore was ground dry for about 20 seconds in a swing mill to about 12 percent greater than 100 mesh. The resulting ore was transferred to a 300 ml flotation cell and diluted with water.

The pH of the slurry was adjusted to 8.5 with lime. The alkanol amine as specified in Table XIV was added and the slurry allowed to condition for one minute. Next, a first portion of the collector, sodium isopropyl xanthate, (0.050 kg/metric ton of ore) was added with an additional minute of conditioning. Next, the frother, a polyglycol ether, was added in an amount equivalent to 0.020 g per ton of dry ore and the slurry allowed to condition an additional minute.

The float cell was agitated at 1800 RPM and air introduced at a rate of 2.7 liters per minute. Samples of the froth concentrate were collected by standard hand paddling at 2.0 minutes after the start of the introduction of air into the cell. Next, a second dose of collector (0.025 kg/metric ton of ore) was added with one minute of conditioning and a six minute concentrate collected. Samples of the concentrate and the tailings were combined and then dried and analyzed as described in the previous examples. The results obtained are presented in Table XIV following. In each case, the copper, gold, molybdenum and silica recoveries represent the total amount recovered at the 2 and 6 minute intervals.

TABLE XIV

Run	Alkanol Amine	Dosage (kg/metric ton)	Copper Recovery	Gold Recovery	Molybdenum Recovery	Silica Recovery
1	Diethanol amine	0.100	0.658	0.552	0.529	0.197
2	Diethanol amine	0.050	0.671	0.583	0.541	0.217
3	Diethanol amine	0.200	0.614	0.529	0.498	0.183
4	Monoethanol amine	0.100	0.647	0.541	0.511	0.209
5	Triethanol amine	0.100	0.653	0.557	0.518	0.213
6	Isopropanol amine	0.100	0.651	0.549	0.523	0.217
7①	None	--	0.624	0.533	0.489	0.250

① Not an embodiment of the invention.

The data shown above demonstrates the effectiveness of the process of the present invention in increasing the grade of recovered mineral values.

Example 15 - Flotation of Mixed Sulfide/Oxide Copper Ore

The general procedure outlined in Example 13 was followed using a southern Africa mixed sulfide/oxide copper ore. The sulfide copper ore was floated by the practice of this invention and the remaining oxide ore recovered in a subsequent step such as leaching or oxide flotation. The sulfide minerals contained in this ore was quite small, less than about 0.22 weight percent of the total ore.

One modification to the procedure outlined in Example 13 was that the ore was ground for 700 revolutions to produce a size distribution of 13 percent greater than 100 mesh. The collector used was potassium amyl xanthate at a concentration of 0.025 kg/metric ton of ore. In each case, the alkanol amine used was diethanol amine in the amounts specified. The results obtained are shown in Table XV following.

TABLE XV

Run	Dosage (kg/metric ton)	Copper Recovery	Lead Recovery	Zinc Recovery	Silica Recovery
1①	None	0.704	0.835	0.491	0.317
2	0.025	0.714	0.831	0.486	0.273
3	0.050	0.693	0.824	0.480	0.246
4	0.100	0.650	0.791	0.452	0.209
5	0.200	0.589	0.746	0.396	0.152

① Not an embodiment of the invention.

The data above again show that the practice of the present invention results in decreasing recoveries of silica gangue. With this particular ore, the recovery of the desired mineral values of lead and zinc also declined even at the lowest dosage of the alkanol amine.

Example 16 - Effect of Order and Manner of Addition of Collector and Hydroxy-Containing Compound

The procedure outlined in Example 6 was followed with the exception that the apatite used was from a different source and contained about 30 percent apatite and about 70 percent silica. The hydroxy-containing compound used in each case was diethanol amine and the anionic collector oleic acid. In each run, the manner in which the diethanol amine and oleic acid were added to the flotation system varied. In Run 1, diethanol amine 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, diethanol amine 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, diethanol amine 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 diethanol amine available commercially as M-210 from The Dow Chemical Company was used in place of unreacted oleic acid and diethanol amine. In Runs 6 and 7, oleic acid was used alone. The results obtained are shown in Table XVI following.

TABLE XVI

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 Oleic acid	0.100 0.100	0.908	0.124	0.020	0.067	0.928	0.124
2	Oleic acid Diethanol amine	0.100 0.100	0.876	0.126	0.042	0.083	0.918	0.124
3	Diethanol amine Oleic acid	0.100 0.100	0.803	0.133	0.016	0.057	0.819	0.132
4①	Diethanol amine/Oleic acid salt	0.200	0.703	0.126	0.024	0.94	0.727	0.115
5①	Condensate	0.200	0.060	0.066	0.015	0.034	0.075	0.060
6①	Oleic acid	0.200	0.881	0.089	0.033	0.027	0.904	0.087
7①	Oleic acid	0.100	0.687	0.113	0.115	0.061	0.802	0.105

① Not an embodiment of the invention.

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/diethanol amine condensate is ineffective in this process.

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 wherein the flotation of the silica or siliceous gangue is depressed by a hydroxy-containing compound, which is ethanolamine, propanolamine, butanolamine,

lactic acid, glycolic acid, beta-hydroxy-l-propane sulfonic acid, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, glycerol, trihydroxybenzonic acid, hydroxybenzoic acid, butylene glycol, dibutylene glycol, diethanolamine, dipropanolamine, tripropanolamine, triethanolamine, a simple sugar alcohol, such as sucrose, glucose or dextrose, or a mixture of two or more such hydroxy-containing compounds.

2. The process of Claim 1, wherein the hydroxy containing compound is ethanolamine, propanolamine, butanolamine, diethanolamine, dipropanolamine, dibutanolamine, triethanolamine, tripropanolamine, tributanolamine or a mixture of two or more thereof.

3. The process of Claim 1, wherein the hydroxy-containing compound is an alkylene glycol or a mixture of two or more thereof.

4. The process of Claim 3, wherein the alkylene glycol is ethylene glycol, diethylene glycol, propylene glycol or a mixture of two or more thereof.

5. The process of any one of the preceding claims, including an anionic collector derived from a carboxylic, sulfonic, sulfuric, phosphoric or a phosphonic acid.

6. The process of Claim 5, 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.

7. The process of Claim 5, 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.

8. The process of Claim 5, 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-naphthalenic sulfonic acid, dodecane sodium 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.

9. The process of any one of the preceding claims, including a thiol collector which is a thiocarbonate, a thionocarbamate, a thiocarbanilide, a thiophosphate, a thiophosphinate, a mercaptan, a xanthogen, a formate, a xanthic ester, or a mixture of two or more thereof.

European
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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 4633

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 213 942 (E.W.J. THORNTON) * Column 1, line 26 - column 2, line 45 * – – –	1,5,8	B 03 D 1/008 B 03 D 1/01 B 03 D 1/012
A	US-A-4 220 525 (U. PETROVICH) * Column 1, lines 6-25; column 3, lines 39-67; column 4, table 2 * – – –	1,5,8	
A	GB-A-1 456 392 (IMPERIAL CHEMICAL INDUSTRIES) * Page 1, lines 9-72 * – – –	1,5,8,9	
A	US-A-2 070 076 (E.H. BROWN) * Page 1, left-hand column, lines 43-51 * – – –	1	
A	US-A-2 019 306 (R.S. HANDY) * Page 1, left-hand column, lines 13-38; page 2, right-hand column, lines 54-59 * – – –	1	
A	US-A-4 437 983 (U. PETROVICH) * The whole document * – – –	1	
A	SOVIET INVENTIONS ILLUSTRATED, week B46, 2nd January 1980, no. 83749B/46, Derwent Publications Ltd, London, GB; & SU-A-649 469 (NON-FERRORE ENRICH) 08-02-1979 – – –	1	TECHNICAL FIELDS SEARCHED (Int. Cl.5) B 03 D
A	SOVIET INVENTIONS ILLUSTRATED, week 8533, 26th September 1985, no. 85=201864/33, Derwent Publications Ltd, london, GB; & SU-A-1135 497 (BELORUSS KIROV TECHN. INS.) 23-01-1985 – – –	1	
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The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	10 December 90	LAVAL J.C.A

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
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P: intermediate document
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EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	SOVIET INVENTIONS ILLUSTRATED, week 84/27, 15th August 1984, no. 84-170196/27, Derwent Publications Ltd, London, GB; & JP-A-1050 751 (NOW-FERR METAL INST.) 30-10-1983 – – –	1	
A	SOVIET INVENTIONS ILLUSTRATED, week 8530, 5th September 1985, no. 85-182285/30, Derwent Publications Ltd, London, GB; & SU-A-1003 431 (KURKOV AV) 07-02-1985 – – – – –	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	10 December 90	LAVAL J.C.A

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document