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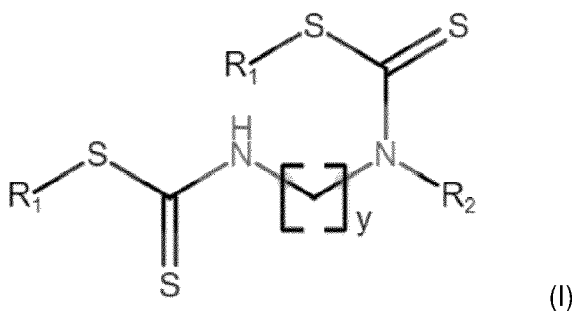
EP 4 438 184 A1

EUROPEAN PATENT APPLICATION

(22) Date of filing: **27.03.2023**

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(57) The present disclosure relates to a collector composition comprising at least one bis-dithiocarbamate compound of formula (I):



R₁ is H, a cationic counterion, or an alkyl group;
R₂ is a C₁₀-C₃₀ linear or branched, saturated or unsaturated alkyl; and
y is an integer from 2-10.

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5 **[0001]** The present disclosure relates to collector compositions comprising at least one bis-dithiocarbamate compound as defined herein and the use of said collector compositions in mineral flotation methods.

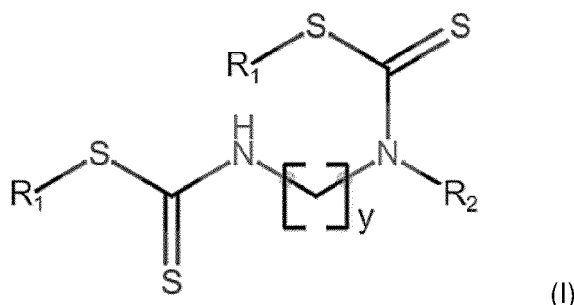
10 **[0002]** Froth flotation is a physico-chemical process used to separate mineral particles considered economically valuable from those considered waste. It is based on the ability of air bubbles to selectively attach to those particles that were previously rendered hydrophobic. The particle-bubble combinations then rise to the froth phase from where the flotation cell is discharged, whilst the hydrophilic particles remain in the flotation cell. Particle hydrophobicity is, in turn, induced by special chemicals called collectors. In direct flotation systems, it is the economically valuable minerals which
15 are rendered hydrophobic by the action of the collector. Similarly, in reverse flotation systems, the collector renders hydrophobicity to those mineral particles considered waste. Frothers are well-known class of reagents used in mineral flotation. Commonly, the frother is added in a step after the pulp ore was conditioned with the collector. Frothers help optimize and control such important froth characteristics as volume (height) and stability.

[0004] One class of metal ore that continues to receive much attention are the sulfide minerals. It is well known that xanthates are good collectors for metallic sulphides (flotation agents known as "collectors" are generally used to facilitate the separation of a particular ore). Methyl isobutyl carbinol (MIBC) is the most commonly used frother in flotation of sulfide minerals. Other types of frothers are also used. However, whilst the xanthates may provide acceptable recovery of the metal component, there is room to improve with respect to sulfur recovery, which can be rather poor for the xanthate collectors.

[0006] US4702821 and US4554068 disclose carboxyalkyl dithiocarbamate salts for suppressing Cu, Fe, and Pb in the flotation of Mo.

[0008] There is a continued need for sustainable flotation systems that are more efficient in separating desired components and impurities.

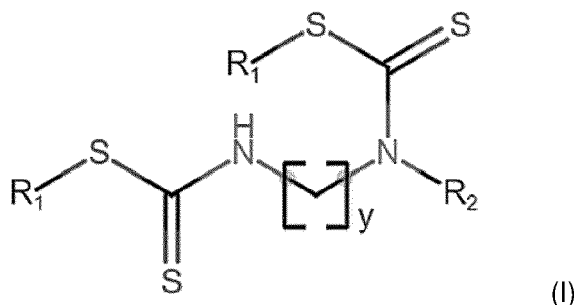
40 [0009] It has now been found that compounds of formula (I) are excellent collectors for sulfide minerals:



55 R₁ is H, a cationic counterion, or an alkyl group (such as a C1-C6 alkyl);
R₂ is a C10-C30 linear or branched, saturated or unsaturated alkyl; and
y is an integer from 2-10.

[0010] These collector compounds have been found to not only improve recovery for a range of metals, but also improve sulfur recovery at the same time. As shown in the worked examples, these collector compounds outperform the standard xanthates in both aspects.

[0011] Accordingly, in a first aspect, the present disclosure relates to a collector composition comprising at least one bis-dithiocarbamate compound of formula (I):



wherein:

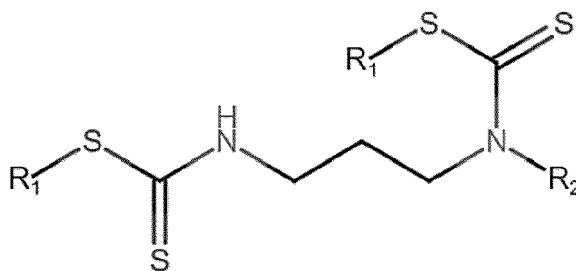
R_1 is H, a cationic counterion, or an alkyl group (such as a C1-C6 alkyl);
 R_2 is a C10-C30 linear or branched, saturated or unsaturated alkyl; and
 y is an integer from 2-10.

[0012] Preferably, R_1 is H or a cationic counterion, and more preferably R_1 is a cationic counterion. R_1 may be any suitable cationic counterion that is capable of forming a stable salt with the dithiocarbamate moiety. Preferred cationic counterions include, but are not limited to, alkali(ne) metal cations, such as Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and ammonium cations, such as those of the formula $NR_1R_2R_3R_4$, wherein each of R_1 , R_2 , R_3 , and R_4 is independently selected from H or C₁-C₁₂ alkyl.

[0013] Preferably, R_2 is a C12-C20 linear or branched, saturated or unsaturated alkyl, most preferably a C12-C18 linear or branched, saturated or unsaturated alkyl. These fatty compounds may originate from a renewable natural source, such as, but not limited to, coconut oil or tallow.

[0014] In a preferred embodiment, y is an integer from 2-6, preferably from 2-4, and most preferably y is 3.

[0015] In a preferred embodiment, the bis-dithiocarbamate compound of formula (I) is



wherein:

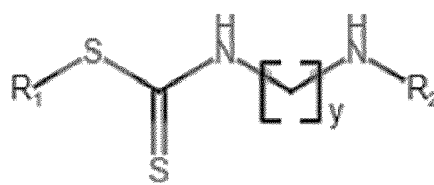
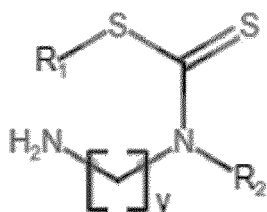
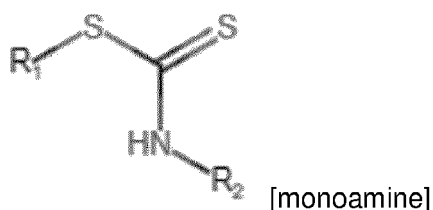
R_1 is H or a cationic counterion, preferably a cationic counterion, more preferably an alkali(ne) metal cation or an ammonium cation of the formula $NR_1R_2R_3R_4$, wherein each of R_1 , R_2 , R_3 , and R_4 is independently selected from H or C₁-C₁₂ alkyl; and

R_2 is a C10-C30 linear or branched, saturated or unsaturated alkyl, preferably a C12-C20 linear or branched, saturated or unsaturated alkyl, most preferably a C12-C18 linear or branched, saturated or unsaturated alkyl.

[0016] The collector composition may contain the at least one bis-dithiocarbamate compound of formula (I) in an amount of from 1-100% relative to the total weight of the collector composition, preferably in an amount of at least 5 wt.%. In a preferred embodiment, the collector composition may be in the form of an aqueous or aqueous-alcoholic composition comprising from 5-50 wt.%, preferably from 10-45 wt.%, preferably from 15-40 wt.% of the bis-dithiocarbamate compound of formula (I).

[0017] Certain impurities may also be present in the collector composition, such as the monoamine dithiocarbamate

or the mono-substituted dithiocarbamate:



[R₁, R₂ and y are as defined above]

[0018] The impurities originate from the synthesis of the compounds of formula (I) and are typically present in a total amount of less than 15 wt.% relative to the amount of the at least one compound of formula (I). If desired, these impurities can be removed by standard purification techniques, however it has been found that their removal is not essential for achieving the beneficial effects provided by the at least one compound of formula (I) (i.e., the presence of the impurities is not detrimental to the performance of the compounds of formula (I)).

[0019] In addition to the above compounds of formula (I), the collector compositions of the present invention may further comprise one or more collector compounds. It should be understood, however, that the compounds of formula (I) may be successfully used in flotation methods without necessarily requiring an additional collector compound. For the avoidance of any doubt, it should be understood that the optional collector compound is different to the bis-dithiocarbamate compounds of formula (I).

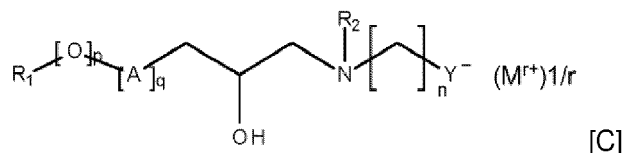
[0020] Thus, the collector compositions disclosed herein comprise:

- (i) at least one bis-dithiocarbamate compound of formula (I) as defined above;
- (ii) optionally, one or more collector compounds different to (i).

[0021] The optional collector compound(s) (ii) is not particularly limited. As noted above, flotation agents known as "collectors" are well-known to the skilled person and are generally used to facilitate the separation of a particular ore. Any such collector compounds are envisaged herein.

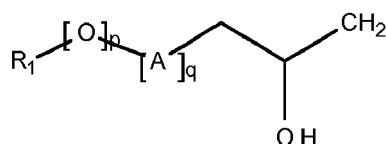
[0022] Preferred collector compound(s) (ii) are the surfactants, such as cationic surfactants, anionic surfactants, non-ionic surfactants, amphoteric surfactants, or a mixture of two or more of these. Below some examples of surfactants are given, but these should only be considered as suitable for the invention and are not to be regarded as limiting.

[0023] Suitable amphoteric surfactants include, but are not limited to, those of the formula [C]:

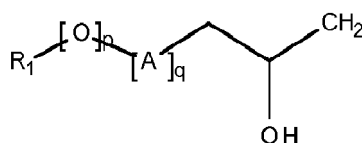


wherein R₁ is a hydrocarbyl group with 8-22, preferably 12-18, carbon atoms; A is an alkyleneoxy group having 2-4, preferably 2, carbon atoms; p is a number 0 or 1; q is a number

from 0 to 5, preferably 0; R₂ is a hydrocarbyl group having 1-4 carbon atoms, preferably 1, or R₂ is the group

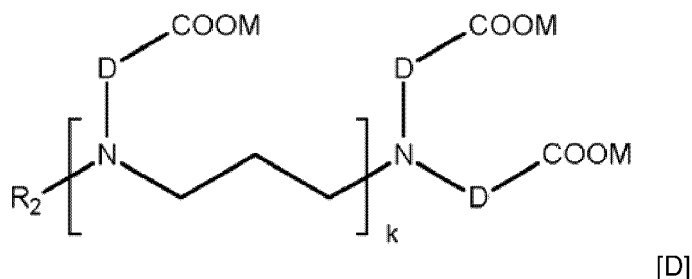


wherein R_1 , A, p and q have the same meaning as above; Y^- is selected from the group consisting of COO^- and SO_3^- , preferably COO^- ; n is a number 1 or 2, preferably 1; M is a cation, which may be monovalent or divalent, and inorganic or organic, and r is a number 1 or 2. The amphoteric surfactant of formula [C] may also be used in its acid form, where the nitrogen is protonated and no external cation is needed. The compounds according to formula [C] can easily be produced in high yield from commercially available starting materials using known procedures. US 4,358,368 discloses some ways to produce the compounds where R_1 is a hydrocarbyl group with 8-22 carbon atoms (col 6, line 9 - col 7, line 52), and in US 4,828,687 (col 2, line 2 - col 2, line 31) compounds where R_2 is



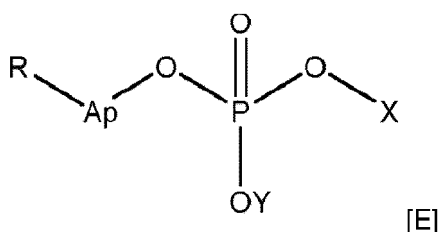
attached to the compound of formula [C] via the methylene group, are described.

[0025] Further suitable amphoteric surfactants have the formula [D]:

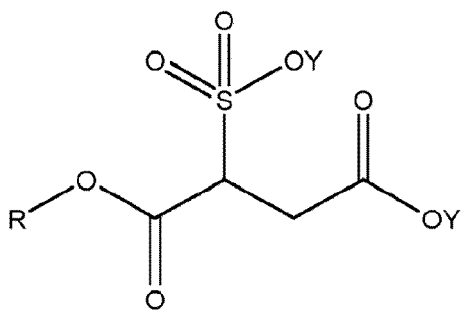


wherein R_2 is a hydrocarbyl group with 8-22, preferably 12-18, carbon atoms, D is $-CH_2-$ or $-CH_2CH_2-$, k is 0-4, preferably 0-3, and most preferably 0-2, and M is hydrogen or a cation, such as sodium or potassium. These products are well known and are produced commercially by methods well known in the art. The products where D is $-CH_2-$ are prepared by the reaction between a fatty amine and chloroacetic acid or its salts, and the products where D is $-CH_2CH_2-$ are prepared by the reaction between a fatty amine and acrylic acid or esters thereof, in the latter case the reaction is followed by hydrolysis.

[0026] Suitable anionic surfactants include, but are not limited to, fatty acids (such as those with an C8 to C22 acyl group), alkylphosphates, such as those of formula [E],

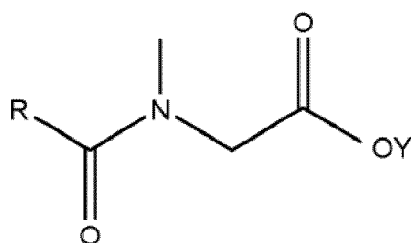


alkylsulfosuccinates, such as those of formula [F],



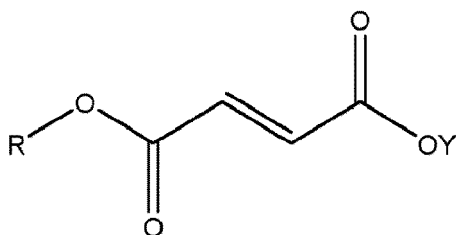
[F]

alkylsarcosinates, such as those of formula [G],



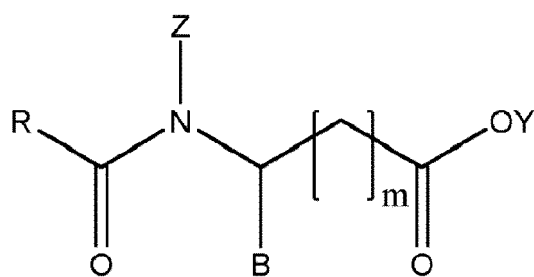
[G]

alkylmaleates, such as those of formula [H],



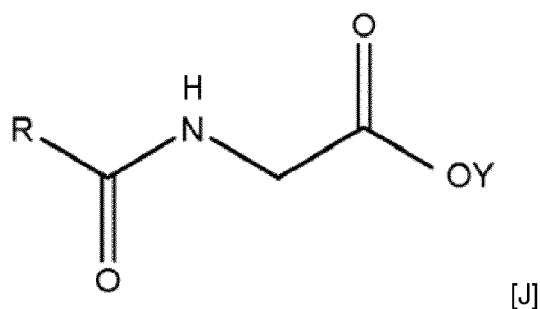
[H]

alkylamidocarboxylates, such as those of formula [I],

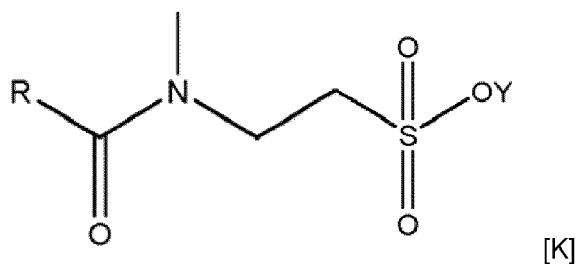


[I]

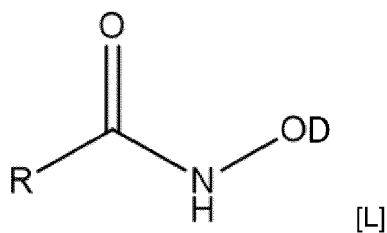
alkylglycinates, such as those of formula [J],



alkyltaurates, such as those of formula [K],



alkylhydroxamates, such as those of formula [L],



35 wherein for each of formulae [E]-[L]:

R is linear or branched, saturated or unsaturated hydrocarbon group containing 1 to 24 carbon atoms;

A is an alkylene oxide unit;

Y is H, Na, K or an ammonium or alkylated ammonium;

p is 0 - 25;

X is chosen from the same groups as R-Ap or Y;

m is 0-7;

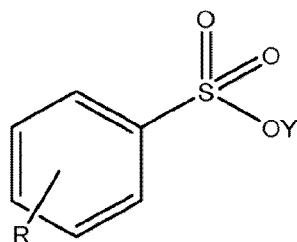
B is -H, -CH₃, -CH(CH₃)₂, -CH₂CH(CH₃)₂, -CH(CH₃)CH₂CH₃;

Z is -H, -CH₃ or -CH₂CH₃; and

D is an alkali(ne) metal counterion, preferably Na⁺, K⁺, Ca²⁺, or Mg²⁺.

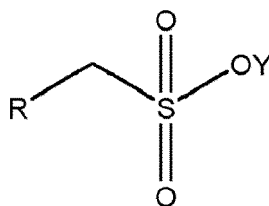
[0027] Esters of the above alkylamidocarboxylates are also contemplated (preferably following the formula [I] of the alkylamidocarboxylates compounds, wherein Y is an alcohol derived hydrocarbon group, such as also described in US20160129456),

[0028] Further examples of suitable anionic surfactants include sulphonated fatty acids, alkylbenzenesulphonates, such as those of formula [M],



[M]

and alkylsulfonates, such as those of formula [N],



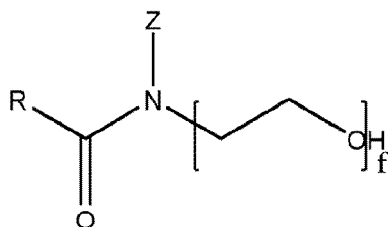
[N]

wherein in formulae [M] and [N]:

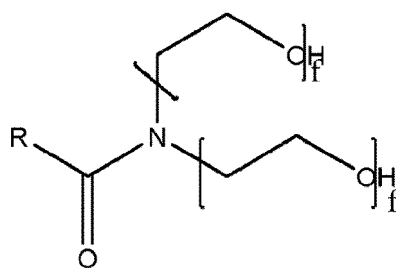
R is linear or branched, saturated or unsaturated hydrocarbon group containing 1 to 24 carbon atoms; and

Y is H, Na, K or an ammonium or alkylated ammonium.

[0029] Suitable nonionic surfactants include alcohols and alkoxylates (such as alkoxylated fatty alcohols $RO(A)_nH$, alkoxylated fatty acids $RC(O)O(A)_nH$), or alkyl glycosides (e.g., $R(C_6O_6H_{11})_k$), or alkylethanolamides, such as those of the formulae [O] or [P],



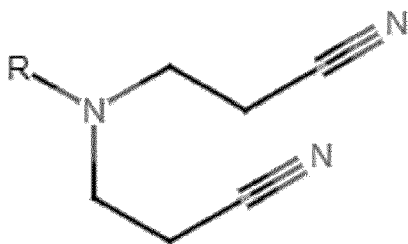
[O]



[P]

wherein R is linear or branched, saturated or unsaturated hydrocarbon group containing 1 to 24 carbon atoms; A is an alkylene oxide unit; n is from 0 to 50; Y is H, Na, K or an ammonium or alkylated ammonium; Z is -H, -CH₃ or -CH₂CH₃; f is 1-25, preferably f is 1-15, and most preferable 1-10 and each f is independently 1 to 25; k is 1 or more, preferably about 1-5.

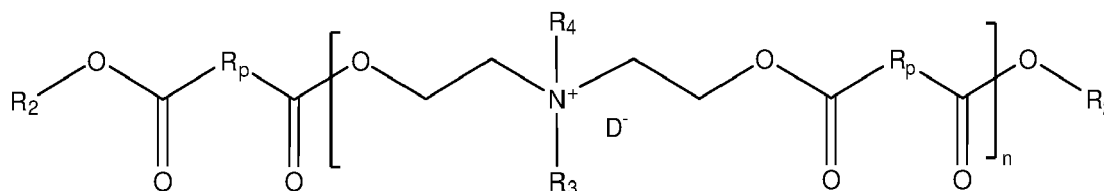
[0030] Further examples of suitable nonionic surfactants include alkyl nitrites, such as those of formulae [Q₁] and [Q₂],

[Q₁][Q₂]

wherein, for each of formulae Q₁ and Q₂, R is a linear or branched, substituted or unsubstituted, saturated or unsaturated, C10-C30 alkyl. The compounds of formula [Q₂] may also be in dimeric form (such as when the R group is an unsaturated alkyl), one nonlimiting example of which is (7Z)-9,10-dinonyloctadec-7-enedinitrile (CAS No. 68606-80-4).

[0031] Suitable cationic surfactants include, but are not limited to, fatty amines (preferably C8-C22, linear or branched alkylamines), fatty diamines (preferably C8-C22, linear or branched), alkyl etheramines (preferably C8-C22, linear or branched alkyl etheramines), alkyl etherdiamines (preferably C8-C22, linear or branched alkyl etherdiamines), alkyl esteramines (preferably C8-C22, linear or branched alkyl esteramines), quaternary ammonium surfactants, polyester polyamines (PEPA), and polyester polyquats (PEPQ).

[0032] The terms PEPA or PEPQ are related to polymeric components containing multiple amine or quaternary ammonium centres, respectively. Commonly, PEPA and PEPQ are obtained from reaction of an amine, dicarboxylic acid and hydrophobic precursor (for example, fatty acid or fatty alcohol). Preferred PEPA and PEPQ cationic surfactants include, but are not limited to:



wherein:

R is a linear or branched, saturated or unsaturated, C2-C20 alkyl;

R₂ is a linear or branched, saturated or unsaturated, C1-C20 alkyl;

D is a halogen counterion (preferably Cl⁻, I⁻, Br or F⁻) or an organic counterion (preferably sulfate, sulfonate, phosphate, phosphonate, carboxylate with C1-C10 alkyl);

p is 0 or 1;

n is 1 to 10;

R₃ and R₄ are each independently:

For PEPA: H, or a linear or branched, saturated or unsaturated, substituted or unsubstituted C1-C20 alkyl (preferably CH₃ or CH₂CH₂OH),

For PEPQ: a linear or branched, saturated or unsaturated, substituted or unsubstituted C1-C20 alkyl (preferably CH₃ or CH₂CH₂OH).

[0033] Further preferred PEPQ cationic surfactants include:



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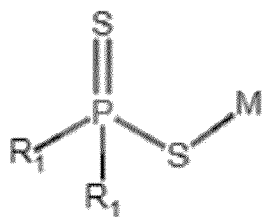
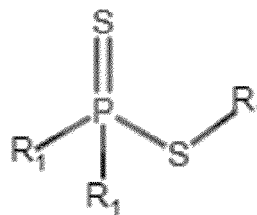
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[U₁][U₂]

wherein, for each of formulae [R]-[U],

R₁ is a linear or branched, substituted or unsubstituted, saturated or unsaturated, C1-C20 alkyl;

R₂ is a linear or branched, substituted or unsubstituted, saturated or unsaturated, C1-C20 alkyl; and

R₃ is H or a linear or branched, substituted or unsubstituted, saturated or unsaturated, C1-C20 alkyl

M is H or a suitable cationic counterion that is capable of forming a stable salt with the respective compound of formulae [Q]-[T]. Preferred cationic counterions include, but are not limited to, alkali(ne) metal cations, such as Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, and ammonium cations, such as those of the formula NR₁R₂R₃R₄, wherein each of R₁, R₂, R₃, and R₄ is independently selected from H or C₁-C₁₂ alkyl.

[0036] For embodiments of the collector composition of the present disclosure that comprise one or more collector compounds (ii), the weight ratio of the one or more collector compounds (ii) to component (i) (the at least one bis-dithiocarbamate compound of formula (I) as defined above) in the collector composition is preferably from about 15:85 to 99:1, preferably about 20:80 to 98:2, preferably about 25:75 to 95:5.

[0037] Preferably, the collector composition of the present disclosure comprises component (i) and optional component (ii) in a total amount of about 15 wt.% to about 100 wt.% (relative to the total weight of the collector composition), preferably in the above weight ratio (ii) to (i).

[0038] The collector compositions described above may further comprise a solvent. Preferred solvents include, but are not limited to, water, alcohol(s), and mixtures thereof. Preferred alcohols are the C1-C20 mono or polyhydric alcohols, such as, but not limited to, isopropyl alcohol, propylene glycol, polyethylene glycol, ethylene glycol, diethylene glycol, triethylene glycol, hydrocarbon oils, C6-C18 mono- and polyhydric alcohols, and mixtures thereof. If a solvent is used, then the collector composition preferably comprises at least 50 wt.%, more preferably at least 60 wt.%, and most preferably at least 65 wt.% of the solvent (relative to the total weight of the collector composition).

[0039] In a second aspect, the present invention relates to a flotation method using the collector composition as described in detail above. The collector composition is particularly suitable for treating sulfidic ores, such as copper-containing ores (e.g., chalcopyrite, chalcocite, bornite, malachite), zinc-containing ores (e.g., sphalerite), lead-containing ores (e.g., galena), nickel-containing ores (e.g., pentlandite, millerite), gold-containing ores (calaverite and electrum or gold is associated with pyrite, pyrrhotite, arsenopyrite, chalcopyrite, chalcocite, bornite, galena etc.), silver-containing ores (e.g., argentite or silver associated with pyrite, pyrrhotite, arsenopyrite, chalcopyrite, chalcocite, bornite, galena etc.), and iron/sulfur containing ores (e.g., pyrrhotite, pyrite, arsenopyrite).

[0040] The collector composition disclosed herein is particularly suitable for:

(1) direct flotation of valuable elements and metals from all sulfidic minerals mentioned above.

(2) direct flotation of sulphurous constituents (pyrite/pyrrhotite/arsenopyrite) from ores and tailings. For the case (2) the ores to be floated can be either sulfidic (as mentioned above) or non-sulfidic - for example: phosphates (igneous and sedimentary ores) or iron ores (hematite, magnetite, goethite etc.). For the case (2) the tailings to be floated can be generated either by main operations of flotation of sulfidic ores or by flotation or non-sulfidic ores.

[0041] The collector composition disclosed herein may be used in following flotation circuits and operations: Rougher, Scavenger, Cleaner flotation using mechanical, penumatic, froth separational or column flotation machines. Additionally and/or alternatively, the collector composition disclosed herein may be added directly to the milling stage of the ore before the actual conditioning or flotation stage.

[0042] The amount of collector composition added to the ore will in general be in the range of from about 5 to about 1000 g/ton dry ore, preferably in the range of from about 10 to about 500 g/ton dry ore, more preferably from about 15 to about 400 g/ton dry ore, more preferably from about 20 to about 200 g/ton dry ore. It should be understood that these values relate to the grams of actives content of the collector composition per ton of dry ore. For example, adding 100g of a 50% actives content collector composition (e.g., collector composition consisting of 50% actives and 50% solvent) to 1 ton of dry ore would result in a dosing of 50 g/ton collector composition.

[0043] Other additives can be also involved in the flotation process together with the collector composition of the current invention. These reagents can be added either at the same time or, preferably, separately during the process and can include depressants, such as a polysaccharide, alkalized starch or dextrin, extender oils, frothers/froth regulators, such as pine oil, MIBC (methylisobutyl carbinol) and alcohols such as hexanol and alcohol ethoxylates/propoxylates, inorganic dispersants, such as silicate of sodium (water glass), calcium oxide and soda ash, and pH-regulators.

[0044] The process to treat ores according to the present disclosure preferably comprises the steps of:

- grinding the ore and water to produce the pulp with the desired average particle size.
- conditioning of the mixture of a pulped mineral ore under stirring in aqueous solution.
- adding a flotation depressant, flotation activator or flocculant to the mixture with further conditioning (optional).
- adjusting the pH of the mixture with further conditioning (optional).
- adding the collector composition of the invention with further conditioning.
- adding a frother to the mixture with further conditioning (optional).
- performing a froth flotation by introducing air into the mixture. The froth is skimmed off to recover targeted minerals.

[0045] It is noted that various elements of the present invention, including but not limited to preferred ranges for the various parameters, can be combined unless they are mutually exclusive.

Worked Examples

[0046] The invention will be elucidated by the following examples without being limited thereto or thereby.

Example 1 - synthesis of compounds of formula (I)

Example 1A ($R_2 = 12$)

[0047] A 2 L round bottomed flask equipped with agitator, temperature controller/heating mantle, and condenser was charged with 435 g of water, 56 g of propylene glycol, and 183 g of 30 % NaOH. 180 g of N-coco-1,3-diaminopropane (pre-melted in a laboratory oven) was added from a beaker to the reactor through a neck using a glass funnel, followed by 50 g of propylene glycol and 40 g of water to ensure a quantitative transfer from the beaker to the reactor. 104 g of carbon disulfide was added to the reactor by slow-addition over 1.5 hr. at a temperature of 40 to 45 deg C using a reciprocating laboratory pump. The reactor solution was then held at 40 to 45 deg C for a final reaction/cook period. The reaction product was cooled, and the final pH was adjusted to a range of 12 to 13 using 50 % NaOH. The product was a clear, orange/red, low viscosity liquid with 30 % actives content.

Example 1B ($R_2 = 12$)

[0048] The experiment described in Example 1A was repeated, but with propylene glycol replaced by isopropyl alcohol. The product was a clear, orange/red, low viscosity liquid with 30 % actives content.

Example 1C ($R_2 = 18$)

[0049] A 1 L round bottomed flask equipped with agitator, temperature controller/heating mantle, and condenser was charged with 247 g of water, 35 g of isopropyl alcohol, and 88 g of 30 % NaOH. 110 g of N-tallow-1,3-diaminopropane (pre-melted in a laboratory oven) was added from a beaker to the reactor through a neck using a glass funnel, followed by 25 g of isopropyl alcohol and 30 g of water to ensure a quantitative transfer from the beaker to the reactor. 51 g of carbon disulfide was added to the reactor by slow-addition over 1.5 hr. at a temperature of 40 to 45 deg C using a reciprocating laboratory pump. The reactor solution was then held at 40 to 45 deg C for a final reaction/cook period. The reaction product was cooled, and the final pH was adjusted to a range of 12 to 13 using 50 % NaOH. The product was a clear, orange/red, low viscosity liquid with 30 % actives content.

Example 2 - Flotation of real and synthetic ores

Flotation of real ores

Chalcopyrite flotation method:

[0050]

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- 500 g ore + 500 g tap H₂O was grinded with stainless still rods to get the pulp with p80 -52 μm .
- Transfer of the pulp to 1.3L flotation cell.
- 5 • Conditioning with CaO (1%) at pH 9.0 (2 min).
- Conditioning with 20 g/t collector [actives content] (Example 1A) (1 min, pH 9).
- Rougher 1 (8 min, natural pH). 15 g/t MIBC frother added.
- 10 • Conditioning with 3 g/t of collector [actives content] (Example 1A) (1 min, pH 9).
- Rougher 2 (5 min, natural pH). 5 g/t MIBC added.
- 15 • Conditioning with 3 g/t collector [actives content] (Example 1A) (1 min, pH 9).
- Rougher 3 (4 min, natural pH). 5 g/t MIBC added.
- Conditioning with 3 g/t collector [actives content] (Example 1A) (1 min, pH 10.5).
- 20 • Cleaner 1 and 2 (7 and 4 min, respectively). 5 g/t MIBC added to each stage.

Gold ore flotation method:

25 [0051]

- 500 g ore + 500 g tap H₂O was grinded with stainless still rods to get the pulp with p80 -140 μm .
- Transfer of the pulp to 2.5L flotation cell.
- 30 • Conditioning with 20 g/t collector [actives content] (Example 1A) (4 min, pH 7.5).
- Rougher 1 (1 min, natural pH). 10 g/t MIBC added.
- 35 • Agitation (1 min).
- Rougher 2 (2 min, natural pH). 15 g/t MIBC added.
- Conditioning with 30 g/t collector [actives content] (Example 1A) (4 min, pH 7.5).
- 40 • Rougher 3 (6 min, natural pH). 20 g/t MIBC added.
- Conditioning with 20 g/t collector [actives content] (Example 1A) (4 min, pH 7.5).
- 45 • Rougher 4 (16 min, natural pH). 20 g/t MIBC added.

[0052] The results are set out in the following table.

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Ore type / Collector			Xanthate (PAX*)	C12 diamine dithiocarbamate	C12 monoamine dithiocarbamate
Real ores	1: Cu ore (chalcopyrite - 0.74%/ bornite - 0.12%)	Cu grade, %	25.3	16.2	17.5
		Cu recovery, %	59.9	73.9	69.1
	2: Au-S ore (gold - 0.3-1.5 ppm/ pyrite - 2-5%)	Au grade, ppm	11.6	12.1	---
		Au recovery, %	93.4	96.9	---
		S recovery, %	93.1	95.4	---

*PAX = potassium amyl xanthate

Flotation of synthetic ores

[0053] The following synthetic ores were prepared:

- Pure chalcopryrite, chalcocite, bornite or malachite was mixed with silica sand to receive the feed with 0.2% Cu.
- Pure galena or sphalerite was mixed with silica sand to receive the feed with 0.1% Pb or Zn, respectively.
- Pure pyrrhotite was mixed with silica sand to receive the feed with 1% S.

[0054] Flotation method:

- 500 g of the ore + 500 g H₂O was grinded with stainless steel rods to p80 -75.
- Transfer of the pulp to 1.3L flotation cell.
- Agitation at required pH* controlled with CaO (1%) (2 min).
- Conditioning with 20 g/t of collector [actives content] (Example 1A) (2 min).
- Rougher flotation (5 min). 20 g/t MIBC added.

*pH for flotation of chalcopryrite, chalcocite, malachite, sphalerite, pyrrhotite was 10.5.

*pH for flotation of galena and bornite was 9.0.

[0055] The results are provided in the following table.

Ore type / Collector			Xanthate		C12 diamine dithiocarbamate	C12 monoamine dithiocarbamate
			Type	Performance		
Synthetic ores	4: Cu (chalcopyrite)	Cu grade, %	PAX*	2.1	2.4	3.0
		Cu recovery, %		99.9	99.9	94.7
	5: Cu (chalcocite)	Cu grade, %	PAX	6.7	6.2	2.9
		Cu recovery, %		96.8	97.3	97.0
	6: Cu (Bornite)	Cu grade, %	PAX	1.7	1.8	0.9
		Cu recovery, %		90.0	90.6	87.6
	7: Cu (malachite)	Cu grade, %	PAX	0.3	0.1	---
		Cu recovery, %		44.1	52.8	---
	8: Zn (Sphalerite)	Zn grade, %	PAX	1.0	1.7	---
		Zn recovery, %		41.5	92.3	---
	9: S ore (Pyrrhotite)	S recovery, %	PAX	46.7	69.3	44.2
	10: Pb (Galena)	Pb grade, %	SIPX**	5.2	7.2	2.3
		Pb recovery, %		77.8	80.2	93.7

*PAX = potassium amyl xanthate

**SIPX = sodium isopropyl xanthate

[0056] The performance benefits provided by the compounds of formula (I) are summarized below.

- At the same actives content (g/ton), compounds of formula (I) demonstrated following recovery improvements in comparison with xanthate collector:
 - +14% (real Cu chalcopyrite ore),
 - +2.3 (real S pyrite ore),
 - +3.5% (real Au ore),

- +0.5% (synthetic Cu chalcocite and bornite ores),
 - +8.7% (synthetic Cu malachite ore),
 - +50.8% (synthetic Zn sphalerite ore),
 - +22.7% (synthetic S pyrrhotite ore),
 - +2.4% (synthetic Pb galena ore).
- Compounds of formula (I) showed higher recovery of S ores vs fully substituted dithiocarbamate of coco fatty monoamine:
 - + 25.1% (synthetic S pyrrhotite ore).

Example 3

[0057] The following collector compounds were tested in the flotation of chalcopyrite/pyrite ore:

	Collector Compound
Example 3A	
Example 3B	
Example 3C	

The ore characteristics were as follows:

S deportment was essentially split between pyrite and chalcopyrite, with almost 75% of the S deportment hosted within pyrite and 25% of the S deportment hosted within chalcopyrite.

Chalcopyrite was the only host of Cu. The major gangue minerals were plagioclase, feldspar, quartz, mica and biotite. Cu grade in the feed was -0.2%.

[0058] The following protocol was used in the flotation tests: 500 g of the ore was ground with 500 g of tap water in 6.4 kg stainless steel media during 4 min. This allowed to obtain the feed pulp with particle size distribution of p80 -150 μm . The pulp was transferred to the flotation cell of 1.4 L. The pulp was conditioned with 1% CaO solution at pH 10.5 during 2 min. The pulp was conditioned with 20 g/t of the collector (Example 1A) during 2 min. The pulp was conditioned with 20 g/t of 0.5% solution of MIBC frother during 10 sec before the actual flotation. Rougher flotation was performed

during 5 min (the pH was controlled at 10.5 with CaO). The air flow was 3.5 L/min with 1000 rpm.

[0059] The results from the flotation of chalcopyrite/pyrite are shown in Table below.

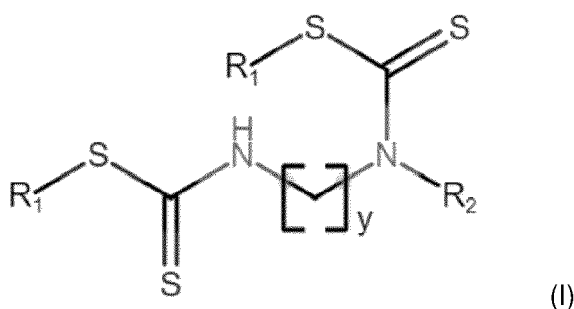
Performance: Cu ore (Chalcopyrite / Pyrite)		Example 3A	Example 3B	Example 3C
	Cu grade, %	3.5	4.5	2.0
	Cu recovery, %	92.4	92.4	80.9
	S recovery, %	89.2	66.9	Not analyzed

[0060] The results mirror those of Example 2, wherein, overall, the compounds of formula (I) (Ex. 3A) outperformed the monoamine dithiocarbamate (Ex. 3B) and the mono-substituted dithiocarbamate of diamine (Ex. 3C). For completeness, these results were replicated exactly when using the C18 equivalent compound of formula (I) (Example 1C, R₂ = 18; the recovery results matched those of Example 3A).

[0061] In this specification, unless expressly otherwise indicated, the word 'or' is used in the sense of an operator that returns a true value when either or both of the stated conditions is met, as opposed to the operator 'exclusive or' which requires that only one of the conditions is met. The word 'comprising' is used in the sense of 'including' rather than to mean 'consisting of'. All prior teachings acknowledged above are hereby incorporated by reference. No acknowledgement of any prior published document herein should be taken to be an admission or representation that the teaching thereof was common general knowledge in Europe or elsewhere at the date hereof.

Claims

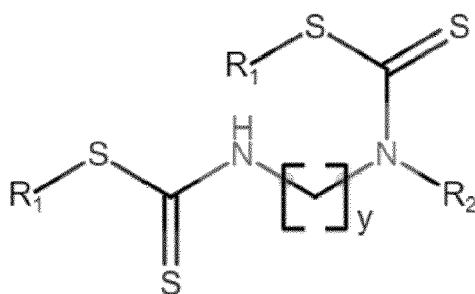
1. A collector composition comprising at least one bis-dithiocarbamate compound of formula (I):



wherein:

- R₁ is H, a cationic counterion, or an alkyl group;
 - R₂ is a C10-C30 linear or branched, saturated or unsaturated alkyl; and
 - y is an integer from 2-10.
2. The collector composition of claim 1, wherein R₁ is H or a cationic counterion.
3. The collector composition of claims 1 or 2, wherein R₁ is a cationic counterion selected from alkali(ne) metal cations, preferably Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, or ammonium cations, preferably those of the formula NR₁R₂R₃R₄, wherein each of R₁, R₂, R₃, and R₄ is independently selected from H or C₁-C₁₂ alkyl.
4. The collector composition of any one of claims 1 to 3, wherein R₂ is a C12-C20 linear or branched, saturated or unsaturated alkyl.
5. The collector composition of any one of claims 1 to 4, wherein R₂ is a C12-C18 linear or branched, saturated or unsaturated alkyl.
6. The collector composition of any one of claims 1 to 5, wherein y is an integer from 2 to 6.

7. The collector composition of any one of claims 1 to 6, wherein y is 3.
8. The collector composition of any one of claims 1 to 7, wherein:
 - R₁ is a cationic counterion;
 - R₂ is a C12-C18 linear or branched, saturated or unsaturated alkyl; and
 - y is 3.
9. The collector composition of any one of claims 1 to 8, further comprising at least one collector compound different to the at least one bis-dithiocarbamate compound of formula (I).
10. The collector composition of claim 9, wherein the at least one collector compound different to the at least one bis-dithiocarbamate compound of formula (I) is a surfactant.
11. The collector composition of claims 9 or 10, wherein the at least one collector compound different to the at least one bis-dithiocarbamate compound of formula (I) is selected from one or more of the following:
 - anionic surfactants;
 - nonionic surfactants;
 - cationic surfactants;
 - amphoteric surfactants;
 - xanthates;
 - dithiophosphates;
 - thionocarbamates; and/or
 - dithiophosphinates.
12. The collector composition of any one of claims 1 to 11, wherein the collector composition further comprises a solvent, preferably selected from water, alcohol(s), and mixtures thereof.
13. A mineral ore flotation method comprising the use of a collector composition according to any one of claims 1 to 12.
14. The mineral ore flotation method of claim 13, wherein the mineral ore is a sulfidic ore.
15. Use of a compound of formula (I) for improving the flotation recovery of valuable minerals and sulfur from valuable mineral-containing sulfidic ores:



(I)

wherein:

- R₁ is H, a cationic counterion, or an alkyl group;
- R₂ is a C10-C30 linear or branched, saturated or unsaturated alkyl; and
- y is an integer from 2-10.



EUROPEAN SEARCH REPORT

Application Number

EP 23 16 4423

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EPO FORM 1503 03.82 (P04C01)

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X	US 5 013 451 A (THOMPSON NEIL E S [US] ET AL) 7 May 1991 (1991-05-07)	1-6, 13	
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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 6 September 2023	Examiner Retucci, Lisa
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category 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	

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