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- (71) Applicant: Cognis IP Management GmbH 40589 Düsseldorf (DE)
- (72) Inventors:
 - Hinrichs, Klaus, Dr. 40789 Monheim (DE)

- Bigorra Liosas, Joaquin,Dr. 08201 Sabadell (ES)
- Hoffmann-Doerr, Simone 40597 Düsseldorf (DE)
- Köppl, Dietger 40169 Mönchengladbach (DE)
- (74) Representative: Fabry, Bernd et al Cognis GmbH Postfach 13 01 64 40551 Düsseldorf (DE)
- (54) Process for the flotation of non-sulfidic minerals and ores

(57) Suggested is a process for the flotation of nonsulfidic minerals or ores, in which crushed crude minerals or ores are mixed with water and a collector to form a suspension, air is introduced into the suspension in the presence of a reagent system and a floated foam containing said non-sulfidic mineral or ores formed therein along with a flotation residue comprising the gangue, wherein the improvement comprises using as the collector quaternised alkanolamine-monoesters.

Description

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Field of the invention

⁵ **[0001]** This invention relates to the flotation of non-sulfidic minerals and ores, and more particularly the use of certain cationic surfactants as collectors in a froth flotation process.

Background of the invention

[0002] Flotation is a separation technique commonly used in the dressing of minerals and crude ores for separating valuable materials from the gangue. Non-sulfidic minerals and ores in the context of the present invention include, for example calcite, apatite, fluorite, scheelite, baryta, iron oxides and other metal oxides, for example the oxides of titanium and zirconium, and also certain silicates and aluminosilicates. In dressing processes based on flotation, the mineral or ore is normally first subjected to preliminary size-reduction, dry-ground, but preferably wet-ground and suspended in water. Collectors are then normally added, often in conjunction with frothers and, optionally, other auxiliary reagents such as regulators, depressors (deactivators) and/or activators, in order to facilitate separation of the valuable materials from the unwanted gangue constituents of the ore in the subsequent flotation process. These reagents are normally allowed to act on the finely ground ore for a certain time (conditioning) before air is blown into the suspension (flotation) to produce a froth at its surface. The collector hydrophobicizes the surface of the minerals so that they adhere to the gas bubbles formed during the activation step. The valuable constituents are selectively hydrophobicized so that the unwanted constituents of the mineral or ore do not adhere to the gas bubbles. The valuable material-containing froth is stripped off and further processed. The object of flotation is to recover the valuable material of the minerals or ores in as high a yield as possible while at the same time obtaining a high enrichment level of the valuable mineral.

[0003] Surfactants and, in particular, anionic, cationic and ampholytic surfactants are used as collectors in the flotation-based dressing of minerals and ores, in particular of calcite which is of considerable value especially for the paper industry. Calcite represents an important filler with the ability for adjusting the whiteness and transparency of the paper. Calcite minerals, however, are often accompanied by silicates so that, to purify the calcite, the silicate - which is undesirable for many applications - has to be removed. Another problem which has a serious impact on the selectivity of the froth flotation process is related to the magnesium content of the minerals or ores. Magnesium salts seriously improve the stability of the froth, which collapses slowly and therefore increases the flotation time, while the selectivity drops. In order to overcome the disadvantages known from the state of the art, for example, international patent application WO 97/026995 (Henkel) suggests the use of readily biodegradable mixtures of quatemised mono- and diesters of fatty acids and triethanolamine (so-called mono/diesterquats). Although said esterquat mixtures show a superior biodegradability when compared with other cationic collectors, the products still do not lead to satisfactory recovery of the valuable material, in particular calcite minerals, when used in economically reasonable quantities.

[0004] Accordingly, an object of the present invention is to provide improved collectors which make flotation processes more economical, i.e. with which it is possible to obtain either greater yields of valuable material for the same quantities of collector and for the same selectivity or at least the same yields of valuable materials for reduced quantities of collector. A second object is to supply collectors which simultaneously meet the needs for high biodegradability.

Detailed description of the invention

[0005] The present invention refers to a process for the flotation of non-sulfidic minerals or ores, in which crushed crude minerals or ores are mixed with water and a collector to form a suspension, air is introduced into the suspension in the presence of a reagent system and a floated foam containing said non-sulfidic minerals or ores formed therein along with a flotation residue comprising the gangue, wherein the improvement comprises using quaternised alkanolamine-monoesters as the collector.

[0006] Surprisingly it has been observed that quaternised triethanolamine-monooleates are extremely effective as collectors for the flotation of non-sulfidic minerals and ores. In particular with respect to the presence of silicates and/or magnesium salts in the minerals or ores, the collectors according to the present invention have been found even more effective compared to conventional mono/diesterquat mixtures while exhibiting a similarly high degree of biodegradability. In particular, the products have been found rather useful for the separation of silicate minerals from calcite by froth flotation.

The collectors

[0007] Quaternised esters of alkanolamines and fatty acids are well known from the state of the art which may be obtained by the relevant methods of preparative organic chemistry. Reference is made in this connection to International patent application WO 91/01295 (Henkel), which is a very early reference disclosing this subject matter, according to

which triethanolamine is partly esterified with fatty acids in the presence of hypophosphorous acid, air is passed through and the resulting reaction mixture is quatemised with dimethyl sulfate or ethylene oxide. The document, of course, discloses mixtures of mono-, di- and triesterquats, but the skilled person would be able to modify the teaching of the document in order to end up with an esterquat showing a high content of monoester by simply reducing the amount of fatty acids in the esterification step. Alkanolamine esters with high content of monoesters can be found in the market, for example under the trademark Emulan[®] (BASF AG).

[0008] According to the present invention, suitable quatemised alkanolamine-monoesters derived from alkanolamines are derived from amines following general formula (I).

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$$R^3$$

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$$R^1-N-R^2$$
(I)

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in which R^1 represents a hydroxyethyl radical, and R^2 and R^3 independently from each other stand for hydrogen, methyl or a hydroxyethyl radical. Typical examples are methyldiethanolamin (MDA), monoethanolamine (MES), diethanolamine (DEA) and triethanolamine (TEA). In a preferred embodiment of the present invention, quatemised triethanolaminemonoesters are used.

[0009] With respect to the fatty acid moiety of the quaternised alkanolamine esters, the products are derived from fatty acids following general formula (II),

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in which R⁴CO stands for a linear or branched acyl radical having 8 to 22 carbon atoms, preferably 16 to 18 carbon atoms, and 0 or 1 to 3 double bonds. Typical examples are caprylic acid, caprinic acid, lauric acid, myristic acid, palmitic acid, palmoleic acid, stearic acid, isostearic acid, oleic acid, elaidinic acid, linoic acid, conjugated linoic acid (CLA), linoleic acid, ricinoleic acid, arachidonic acid, gadoleic acid, behenic acid, erucic acid and also technical grade fatty acids obtained from renewable resources. In a preferred embodiment of the present invention, the collectors are obtained from unsaturated fatty acids. In particular the preferred compounds are quaternised alkanolamine-monooleates.

[0010] The most preferred collectors, however, are quaternised alkanolamine-monoesters following general formula (III)

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in which R⁵CO represents the acyl residue of oleic acid.

Co-collectors

[0011] In certain cases it may be advantageous to modify, adjust or even support the properties of the quaternised alkanolamine-monoesters by adding defined co-collectors, such as, for example, cationic surfactants others than the quaternised alkanolamine-monoesters or amphotheric surfactants.

[0012] Where cationic surfactants are to be used as co-collectors in accordance with the invention, they may be selected in particular from

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- Primary aliphatic amines,
- Alkylenediamines substituted by alpha-branched alkyl radicals,
- Hydroxyalkyl-substituted alkylenediamines,
- Water-soluble acid addition salts of these amines and also

· Quaternary ammonium compounds.

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- Suitable primary aliphatic amines include, above all, the C₈-C₂₂ fatty amines derived from the fatty acids of natural fats and oils, for example n-octylamine, n-decylamine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, n-eicosylamine, n-docosylamine, n-hexadecenylamine and n-octadecenylamine. The amines mentioned may be individually used as co-collectors, although amine mixtures of which the alkyl and/or alkenyl radicals derive from the fatty acid component of fats and oils of animal or vegetable origin are normally used. It is known that amine mixtures such as these may be obtained from the fatty acids obtained by lipolysis from natural fats and oils via the associated nitriles by reduction with sodium and alcohols or by catalytic hydrogenation. Examples include tallow amines or hydrotallow amines of the type obtainable from tallow fatty acids or from hydrogenated tallow fatty acids via the corresponding nitriles and hydrogenation thereof.
- The alkyl-substituted alkylenediamines suitable for use as co-collectors correspond to formula (IV),

 $R^6CHR^7-NH-(CH_2)_nNH_2$ (IV)

in which R^6 and R^7 represent linear or branched alkyl or alkenyl radicals and in which n = 2 to 4. The production of these compounds and their use in flotation is described in East German Patent DD 64275.

The hydroxyalkyl-substituted alkylenediamines suitable for use as co-collectors correspond to formula (V),

OH | $R^{8}CH-CHR^{9}-NH-(CH_{2})_{n}NH_{2}$ (V)

in which R^8 and R^9 are hydrogen and/or linear alkyl radicals containing 1 to 18 carbon atoms, the sum of the carbon atoms in R^8+R^9 being from 9 to 18, and n = 2 to 4. The production of compounds corresponding to formula (V) and their use in flotation is described in German Patent DE-AS 2547987.

[0013] The amine compounds mentioned above may be used as such or in the form of their water-soluble salts. The salts are obtained in given cases by neutralization which may be carried out both with equimolar quantities and also with more than or less than equimolar quantities of acid. Suitable acids are, for example, sulfuric acid, phosphoric acid, acetic acid and formic acid.

The quaternary ammonium compounds suitable for use as co-collectors correspond to formula (VI),

 $[R^{10}R^{11}R^{12}R^{13}N^{+}]X^{-}$ (VI)

in which R^{10} is preferably a linear alkyl radical containing 1 to 18 carbon atoms, R^{11} is an alkyl radical containing 1 to 18 carbon atoms or a benzyl radical, R^{12} and R^{13} may be the same or different and each represent an alkyl radical containing 1 to 2 carbon atoms, and X is a halide anion, particularly a chloride ion. In preferred quaternary ammonium compounds, R^{10} is an alkyl radical containing 8 to 18 carbon atoms; R^{11} , R^{12} and R^{13} are the same and represent either methyl or ethyl groups; and X is a chloride ion.

[0014] The ampholytic surfactants used as co-collectors in accordance with the invention are compounds which contain at least one anionic and one cationic group in the molecule, the anionic groups preferably consisting of sulfonic acid or carboxyl groups, and the cationic groups consisting of amino groups, preferably secondary or tertiary amino groups. Suitable ampholytic surfactants include, in particular,

- · Sarcosides,
- · Taurides,
- N-substituted aminopropionic acids and
- N-(1,2-dicarboxyethyl)-N-alkylsulfosuccinamates..
 - The sarcosides suitable for use as co-collectors correspond to formula (VII),

in which R¹⁴ is an alkyl radical containing 7 to 21 carbon atoms, preferably 11 to 17 carbon atoms. These sarcosides are known compounds which may be obtained by known methods. Their use in flotation is described by H. Schubert in "Aufbereitung fester mineralischer Rohstoffe (Dressing of Solid Mineral Raw Materials)", 2nd Edition, Leipzig 1977, pages 310-311 and the literature references cited therein.

The taurides suitable for use as co-collectors correspond to formula (VIII),

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 CH_{3} | $R^{15}CO-N^{+}H-CH_{2}CH_{2}SO_{3}^{-}$ | | H(VIII)

in which R¹⁵ is an alkyl radical containing 7 to 21 carbon atoms, preferably 11 to 17 carbon atoms. These taurides are known compounds which may be obtained by known methods. The use of taurides in flotation is known, **cf. H. Schubert, loc. cit.**

N-substituted aminopropionic acids suitable for use as co-collectors correspond to formula (IX),

$$R^{16}(NHCH2CH2)nN+H2CH2CH2COO- (IX)$$

in which n may be 0 or a number from 1 to 4, while R¹⁶ is an alkyl or acyl radical containing from 8 to 22 carbon atoms. The afore-mentioned N-substituted aminopropionic acids are also known compounds obtainable by known methods. Their use as collectors in flotation is described by H. Schubert, loc. cit. and in Int. J. Min. Proc. 9 (1982), pp 353-384.

• The N-(1,2-dicarboxyethyl)-N-alkylsulfosuccinamates suitable for use as co-collectors according to the invention correspond to formula (X),

in which R¹⁷ is an alkyl radical containing 8 to 22 carbon atoms, preferably 12 to 18 carbon atoms, and M is a hydrogen ion, an alkali metal cation or an ammonium ion, preferably a sodium ion. The N-(1,2-dicarboxyethyl)-N-alkylsulfosuccinamates mentioned are known compounds which may be obtained by known methods. The use of these compounds as collectors in flotation is also known, **cf. H. Schubert, loc. cit.**

[0015] Said collectors and said co-collectors can be used in a weight ratio of about 10:90 to about 90:10, preferably about 25:75 to about 75:25, and most preferably about 40:60 to about 60:40. To obtain economically useful results in the flotation of non-sulfidic minerals or ores, the collectors or, respectively, the mixtures of collectors and co-collectors must be used in a certain minimum quantity. However, a maximum quantity of collectors/co-collectors should not be exceeded, because otherwise frothing is too vigorous and selectivity with respect to the valuable minerals decreases.

The quantities in which the collectors to be used in accordance with the invention are used are governed by the type of minerals or ores to be floated and by their valuable mineral content. Accordingly, the particular quantities required may vary within wide limits. In general, the collectors and collector/co-collector mixtures according to the invention are used in quantities of from 50 to 2000 g/metric ton, and preferably in quantities of from 100 to 1500 g/metric ton of crude ore.

The flotation process

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[0016] Typical steps in the process sequence are, generally, firstly the dry or preferably wet grinding of the minerals or ores, suspension of the resulting ground mineral or ore in water in the presence of the flotation aids and, preferably after a contact time of the collectors and optionally co-collectors present in the flotation aids to be determined in each individual case, injection of air into the plant. In the following the nature of the starting materials as well as the flotation aids is illustrated in more detail.

Non-sulfidic minerals and ores

Floatable minerals and ores may be divided into the two groups of polar and non-polar materials. Since non-polar minerals and ores are difficult to hydrate, these materials have to be classified as hydrophobic. Examples of non-polar minerals are graphite, molybdenite, diamond, coal and talcum which are all floatable in their naturally occurring state. By contrast, polar minerals and ores have strong covalent or ionic surface bonds which are accessible to rapid hydration by water molecules in the form of multi-layers, These starting materials include, for example, calcite, malachite, azurite, chrysocolla, wulfenite, cerrusite, whiterite, megnesite, dolomite, smithsonite, rhodochrosite, siderite, magnetite, monazite, hematite, goethite, chromite, pyrolusite, borax, wolframite, columbite, tantalite, rutile, zircon, hemimorphite, beryl, mica, biotite, quartz, feldspar, kyanite and garnet. The flotation of non-sulfidic, but polar minerals and ores is a preferred object of the present invention.

Particle size

The flotation behaviour of the individual mineral constituents can be controlled within certain limits through the particle size distribution of the ground mineral. Conversely, however, the use of the collector or collector/co-collector mixture is also influenced by the particle size so that both particle size and, for example, collector concentration may be determined in situ in a brief series of tests. Generally, however, it may be said that the particles have to increasingly be hydrophobicised with increasing particle size before flotation occurs. As a general rule, the ores should be so finely ground that the individual fine particles consist only of one type of mineral, namely either the valuable minerals or the impurities. The ideal particle size normally has to be determined in dependence upon the particular mineral. In the present case, however, a particle size distribution of around 5 to 500 µm has generally been found to be practicable, narrower distributions being of advantage in some cases. For example, silicate-rich ores can be separated by flotation with excellent results using the flotation aids according to the present invention providing less than 40 % b.w., preferably less than 30 % b.w., and more preferably less than 15 % b.w. of the total mineral or ore fraction has particle sizes of less than 250 µm. To enable the flotation process to be optimally carried out, it can be particularly preferred for the particles larger than 125 μm in size to make up less than 15 % b.w., or preferably less than 10 % b.w. or even 6 % b.w. The lower limit to the particle sizes is determined both by the possibility of size reduction by machine and also by handling properties of the constituents removed by flotation. In general, more than 20 % b.w. of the ground mineral or ore should be smaller than about 50 μm in size, a percentage of particles with this diameter of more than 30 or even 40 % b.w., for example, being preferred. According to the present invention it is of particular advantage for more than 40 % b.w. of the mineral or ore particles to be smaller than 45 µm in diameter.

In certain cases, it may be necessary and appropriate to divide the ground material into two or more fractions, for example three, four or five fractions differing in their particle diameter and separately to subject these fraction to separation by flotation. According to the present invention, the flotation aids may be used in only one separation step although, basically, they may even be used in several separation steps or in all necessary separation steps. The invention also encompasses the successive addition of several different flotation aids, in which case at least one or even more of the flotation aids must correspond to the invention. The fractions obtainable in this way may be further processes either together or even separately after the flotation process.

Technical parameters

The technical parameters of the flotation plant in conjunction with a certain flotation aid and a certain mineral or ore can influence the result of the flotation process within certain limits. For example, it can be of advantage to remove the froth formed after only a short flotation time because the content of floated impurities or floated valuable materials can change according to the flotation time. In this case, a relatively long flotation time can lead to a poorer result than a relatively short flotation time. Similarly, it can happen in the opposite case that the separation process leads to a greater purity or otherwise improved quality of the valuable-mineral fraction with increasing time. Optimising external parameters such as these is among the routine activities of the expert familiar with the technical specifications

of the particular flotation machine.

Surface modifiers as auxiliary agents

Reagents which modify surface tension or surface chemistry are generally used for flotation. They are normally classified as frothers, controllers, activators and depressants (deactivators), and of course (co-)collectors which already have been discussed above.

Frothers support the formation of froth which guarantees collectors with an inadequate tendency to froth a sufficiently high froth density and a sufficiently long froth life to enable the laden froth to be completely removed. In general, the use of the collectors or collector/co-collector systems mentioned above will eliminate the need to use other frothers. In special cases, however, it may be necessary or at least advantageous - depending on the flotation process used - to regulate the frothing behaviour. In this case, suitable frothers are, for example, alcohols, more particularly aliphatic C₅-C₈ alcohols such as, for example, n-pentanol, isoamyl alcohol, hexanol, heptanol, methylbutyl carbinol, capryl alcohol, 4-heptanol, which all have good frothing properties. Natural oils may also be used to support frothing. In particular, alcohols, ethers and ketones, for example, alpha-terpineol, borneol, fennel alcohol, piperitone, camphor, fenchol or 1,8-cineol, have both a collecting and a frothing effect. Other suitable frothers are non-ionic compounds, like, for example, polypropylene glycol ethers.

Depressants which may be effectively used for the purpose of the present invention include, for example, naturally occurring polysaccharides, such as guar, starch and cellulose. Quebracho, tannin, dextrin (white dextrin, British gum, and yellow dextrin) and other chemical derivatives may also be used, including in particular the derivatives of starch, guar and cellulose molecules of which the hydroxyl groups may be equipped with a broad range of anionic, cationic and non-ionic functions. Typical anionic derivatives are epoxypropyl trimethylammonium salts while methyl, hydroxyethyl and hydroxypropyl derivatives are mainly used as non-ionic compounds.

Solvents

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To adjust their rheological behaviour, the flotation aids according to the present invention may contain solvents in a quantity of 0.1 to 40 % b.w., preferably in a quantity of 1 to 30 % b.w., and most preferably in a quantity of 2 to 15 % b.w. Suitable solvents are, for example, the aliphatic alcohols mentioned above and other alcohols with shorter chain lengths. Thus the flotation aids according to the present invention may contain small quantities of glycols, for example, ethylene glycol, propylene glycol or butylene glycol, and also monohydric linear or branched alcohols, for example, ethanol, n-propanol or isopropanol.

[0017] As outlined above, flotation is carried out under the same conditions as state-of-the-art processes. Reference in this regard is made to the following literature references on the background to ore preparation technology: H. Schubert, Aufbereitung fester mineralischer Stoffe (Dressing of Solid Mineral Raw Materials), Leipzig 1967; B. Wills, Mineral Processing Technology Plant Design, New York, 1978; D. B. Purchas (ed.), Solid/Liquid Separation Equipment Scale-up, Croydon 1977; E. S. Perry, C. J. van Oss, E. Grushka (ed.), Separation and Purification Methods, New York, 1973 to 1978. As far as the process for conducting the froth flotation of non-sulfidic minerals and ores is concerned, their contents are incorporated by reference.

Industrial application

40 [0018] Another object of the present invention is the use of quaternised alkanolamine-monoesters as collectors for the froth flotation of non-sulfidic minerals or ores. The collectors to be used in accordance with the invention may be used with advantage in the dressing of such minerals or ores as a quartz, kaolin, mica, phlogopite, feldspar, silicates and iron ores.

45 Examples

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[0019] The following examples demonstrate the superiority of the quaternised alkanolamine-monoesters to be used in accordance with the invention over collector components known from the prior art, in particular compared to convention mono/di-esterquat mixtures. The tests were carried out under laboratory conditions, in some cases with increased collector concentrations considerably higher than necessary in practice. Accordingly, the potential applications and inuse conditions are not limited to separation exercises and test conditions described in the examples. The quantities indicated for reagents are all based on active substance.

Examples 1-3, Comparative Examples C1-C3

[0020] The following examples and comparative examples illustrate the effectiveness of the collectors according to the present invention compared to conventional mono/di-esterquat collectors in the flotation of silicate containing calcite minerals. The results are shown in Table 1.

Particle size distribution: > 40 μ m: > 50 % b.w.

Silicates: about 1.5 to 2.5 % b.w. Calcite: about 97.5 to 98.5 % b.w.

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Table 1 Calcite flotation

Composition	C1	C2	С3	1	2	3
Dehyquart® AU 46 ¹ [g*t ⁻¹]	660	560	320	-	-	-
Dehyquart® EQ ² [g*t ⁻¹]	-	-	-	350	300	250
OMC 6317 ³ [g*t ⁻¹]	100	100	85	-	-	-
Results						
Yield Floated Material [g]	39.8	75.4	59.7	20.6	23.4	18.0
Yield Residue [g]	383	361	438	420.7	494.9	571.8
Feed: HCl insoluble [%]	2.6	2.6	2.2	2.5	2.6	2.1
Floated Material : HCl insoluble [%]	25.7	13.6	18.4	52.8	55.8	57.4
Residue: HCl insoluble [%]	0.09	0.18	0.57	0,04	0,08	0,35
Calcite Loss [%]	7.2	15.3	10.0	2.2	2.0	1.3

¹ Methyl-quaternised Triethanolamine-mono/di-stearate, Methosulfate, 90 % b.w. AS (Cognis Iberia, ES)

Examples 4-5, Comparative Examples C4-C5

[0021] The following examples and comparative examples illustrate the effectiveness of the collectors according to the present invention compared to conventional mono/di-esterquat collectors under conditions of high magnesium concentrations. The foam height was measured according to the well known Ross-Miles method. The results are shown in Table 2:

Table 2 Foaming behaviour in the presence of magnesium chloride (AS = Active Substance)

Ex.	Product	Addition AS [% b.w.]	Quantity Product [g]	Test Solution	Foam height [ml]	Foam half life [min]
C4	Dehyquart® AU 46	1	2.25 2.29	2 % MgCl ₂ 2 % MgCl ₂	220 220	2:35 2:35
C5	Dehyquart [®] AU 46	1	2.27 2.54	5 % MgCl ₂ 5 % MgCl ₂	220 220	0:30 0:30
4	Dehyquart [®] EQ	1	2.25 2.29	2 % MgCl ₂ 2 % MgCl ₂	220 220	2:05 2:05
5	Dehyquart [®] EQ	1	2.27 2.54	5 % MgCl ₂ 5 % MgCl ₂	220 220	0:15 0:15

[0022] As one can see, the collectors according to the present invention lead to a faster collapse of the foam compared to the state of the art which is desirable in the flotation of minerals and ores.

Claims

1. In a process for the flotation of non-sulfidic minerals or ores, in which crushed crude minerals or ores are mixed with water and a collector to form a suspension, air is introduced into the suspension in the presence of a reagent

² Methyl-quaternised Triethanolamine-monooleate, Methosulfate, 90 % b.w. AS (Cognis Iberia, ES)

³ Frother (Cognis Deutschland GmbH & Co. KG, DE)

system and a floated foam containing said non-sulfidic minerals or ores formed therein along with a flotation residue comprising the gangue, wherein the improvement comprises using as the collector quatemised alkanolamine-monoesters.

2. Process according to Claim 1, **characterised in that** quaternised alkanolamine-monoesters derived from alkanolamines are used according to general formula (I).

$$R^{3}$$

$$|$$

$$R^{1}-N-R^{2}$$
(I)

in which R¹ represents a hydroxyethyl radical, and R² and R³ independently from each other stand for hydrogen, methyl or a hydroxyethyl radical.

- 3. Process according to Claims 1 and/or 2, characterised in that quaternised triethanolamine-monoesters are used.
- 4. Process according to any of Claims 1 to 3, **characterised in that** quaternised alkanolamine-monoesters derived from fatty acids are used according to general formula (II),

in which R⁴CO stands for a linear or branched acyl radical having 8 to 22 carbon atoms and 0 or 1 to 3 double bonds.

- **5.** Process according to any of Claims 1 to 4, **characterised in that** quaternised alkanolamine-monooleates are used.
- **6.** Process according to any of Claims 1 to 5, **characterised in that** quaternised alkanolamine-monoesters are used according to general formula (**III**)

- in which R⁵CO represents the acyl residue of oleic acid.
 - 7. Process according to any of Claims 1 to 6, **characterised in that** cationic surfactants other than the quaternised alkanolamine-monoesters or amphotheric surfactants as co-collectors are used.
- **8.** Process according to Claim 7, **characterised in that** said collectors and said co-collectors are used in a weight ratio of 10:90 to 90:10.
 - 9. Use of quaternised alkanolamine-monoesters as collectors for the froth flotation of non-sulfidic minerals or ores.
- 50 **10.** Use according to Claim 9, **characterised in that** calcite minerals are subjected to said froth flotation.

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EUROPEAN SEARCH REPORT

Application Number EP 07 00 1678

	DOCUMENTS CONSIDE	RED TO BE RELEVANT		
Category	Citation of document with ind of relevant passag		Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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