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FLOTATION OF MINERALS WITH HYDROPEROXIDE FROTHERS

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This invention relates to a process for beneficiating ores and, more particularly, to a process for concentrating ores by froth flotation.

Reagents used in the flotation of ores are of three general types; namely, frothing agents, collecting agents, and modifying agents. Frothing agents depress the surface tension of the water employed and thus facilitate the formation of air bubbles when the water is aerated. Collectors serve to modify the surfaces of the ore particles and cause them to adhere to the air bubbles which are formed in the water. Modifying agents are used to modify the ore pulp so that the desired minerals will be collected into the froth and the remainder will not. The action of modifying agents is supplementary to that of the collectors. This invention comprises a froth flotation process which is carried out in the presence of new frothing agents.

Frothers heretofore employed in the flotation of minerals include pine oil, cresylic acid, creosotes, aliphatic alcohols, soaps, and, in a few instances, sulfonated organic compounds. For various reasons these reagents have not proved entirely satisfactory. For example, some frothers are characterized by collecting properties as well as frothing properties or are affected by the condition of the ore pulp, the pH of the flotation mixture, the presence of other conventional flotation reagents, or a combination of these factors. Furthermore, some frothers exhibit an inhibiting reaction on the flotation of the desired mineral. In addition, many desirable frothing agents have been commercially unfeasible as a consequence of their high cost.

Particularly is it desirable that a frother be characterized by a lack of collecting properties. If a substance possesses both frothing and collection properties, the intensity of one property cannot be changed with fluctuations in the ore character without simultaneous changes in the other property. The result is a very undesirable curtailment in reagent control and a consequent decrease in mill performance in the treatment of complex ores.

Now in accordance with this invention, it has been found that ores may be advantageously and economically concentrated by subjecting a pulp or slurry of the ground ores to froth flotation in the presence of an organic hydroperoxide. The organic hydroperoxides of this invention are secondary cyclic hydroperoxides and preferably those secondary cyclic hydroperoxides having between 8 and 13 carbon atoms, although secondary

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cyclic hydroperoxides having between 6 and 15 carbon atoms are operable.

The secondary cyclic hydroperoxides used in accordance with this invention have the structural formula $>CH-OOH$ where C is a carbon atom in the carbon ring of a cyclic compound. Cyclic terpenes having a nonconjugated ring structure are illustrative of the organic compounds which may be oxidized to give these hydroperoxides and the cyclic terpenes referred to include not only those compounds having the empirical formula $C_{10}H_{18}$ but also those compounds having the empirical formulas $C_{10}H_{16}$ and $C_{10}H_{20}$ which are known as dihydro- and tetrahydroterpenes, respectively. Both monocyclic and dicyclic terpenes are operable. As illustrative of the cyclic terpenes which may be oxidized, dipentene, carvomenthene and α -pinene may be particularly mentioned. However, a great number of other cyclic terpenes may also be oxidized to produce operable terpene hydroperoxides. Some of the better known of these terpenes are terpinolene, ψ -limonene, critmene, 2-menthene, 3-menthene, dihydroterpinolene, β -pinene, camphane, bornylene, and the like.

A variety of cyclic compounds other than terpenes may also be oxidized to the hydroperoxides of this invention. For example, compounds such as tetrahydronaphthalene, decahydronaphthalene and cyclohexene may be oxidized to give the corresponding secondary hydroperoxides. Solid compounds are dissolved in suitable solvents during the oxidation. The cyclic radicals may be substituted with alkyl groups such as methyl, ethyl, propyl, butyl, isobutyl, tert-butyl, or higher alkyl groups to give alkaryl and substituted cycloparaffin radicals as the case may be.

The organic hydroperoxides of this invention exhibit substantially no collecting properties and are attended by none of the other aforementioned disadvantages which characterize the frothers known to the prior art. These organic hydroperoxides can be used either alone or in conjunction with standard frothers heretofore employed. Likewise the hydroperoxides may be employed in conjunction with collecting and modifying agents customarily utilized in the flotation art.

Having thus indicated in a general way the nature and purpose of this invention, the following examples are offered to illustrate the practice thereof. All parts are by weight unless otherwise indicated.

Examples I, II, III and IV

One thousand twenty g. of a lead ore was

ground for 14 min. in a ball mill with 1020 ml. of water. The lead ore contained about 1.2% Pb, chiefly in the form of galena, contained in a gangue composed of dolomite. The ground ore was screened through a 48-mesh screen and then transferred to a 1000-g. Denver flotation machine. The pulp was diluted to about 25% solids with water and then 0.15 lb. Na₂S/ton of ore, 0.10 lb. potassium isopropyl xanthate/ton of ore, and the frothers listed below were added. A concentrate was removed for 10 min. The results are shown in the following table.

Example	Frother	Lb./Ton of Ore	Per cent Pb in Tailing	Per cent Pb in Concentrate	Per cent Pb Recovery
I.....	dipentene hydroperoxide ¹ ...	0.12	0.13	30.7	89.6
II.....	carvomenthene hydroperoxide ² ...	0.12	0.14	33.1	89.2
III.....	α -tetrahydronaphthalene hydroperoxide, ³ 90.2%.	0.12	0.14	40.3	86.5
IV.....	standard frother (3 parts wood creosote, 1 part Pentasol 124E).	0.18	0.13	37.5	88.7

¹ The dipentene hydroperoxide was prepared by the air oxidation of dipentene and contained 29% dipentene hydroperoxide, the remaining 71% consisting of a mixture of dipentene peroxide, alcohols, and ketones.

² The carvomenthene hydroperoxide was prepared by the air oxidation of carvomenthene and contained 47% carvomenthene hydroperoxide, the remaining 53% consisting of unreacted carvomenthene.

³ Added as a solution of 20 g. of the hydroperoxide in 100 cc. benzene.

Example V

One thousand twenty g. of a zinc ore was ground for 11 min. in a ball mill with 1020 ml. of water. The zinc ore contained about 10% Zn in the form of sphalerite (ZnS). Pyrite and siliceous gangue were also present. The ground ore was screened through a 48-mesh screen, the oversize discarded, and the feed of less than 48-mesh transferred to a 1000-g. Denver flotation machine. The pulp was diluted to about 25% solids and conditioned for 10 min. with 2.0 lb. of lime, 1.4 lb. CuSO₄·5H₂O and 0.04 lb. of KCN, all weights based upon 1 ton of ore. After this conditioning period 0.10 lb. of potassium ethyl xanthate/ton of ore and the dipentene hydroperoxide of Example I were added to the pulp. A zinc concentrate was removed for 10 min. The following results were obtained.

Example	Frother	Lb./Ton of Ore	Per cent Zn in Tailing	Per cent Zn in Concentrate	Per cent Zn Recovery
V.....	dipentene hydroperoxide.....	0.20	0.50	32.7	96.6

Example VI

Four hundred g. of a high ash (25–28%) content coal of about 28- to 200-mesh size which was obtained from the wash water of a coal breaker, was transferred to a 500-g. flotation machine. The coal was floated from the ash in tap water of pH 8.2 with 1.0 lb. fuel oil/ton of coal and 0.3 lb. dipentene hydroperoxide/ton of coal.

The froth was removed until all the material had floated and the following results were obtained.

	Per cent Total Weight of Ore	Per cent Ash Contained in Various Fractions	Per cent Distribution of Ash in the Various Fractions
Float.....	67.4	12.1	30.9
Tail.....	32.6	55.1	69.1
Feed.....	100.0	26.4	100.0

Thus a satisfactory coal of 12.1% ash was recovered from this waste product by flotation with the above reagents.

Example VII

Five hundred fifty g. of an iron ore was ground for 15 min. in a ball mill with 550 ml. of water. The ore contained hematite and magnetite in a siliceous gangue, and the total iron content was 32–35% Fe. The ground ore was then deslimed and about 13% of the total weight was removed as slimes. The deslimed ore was then trans-

ferred to a 500-g. Denver flotation machine, diluted with tap water of pH 8.2, and the following reagents added in the order given:

0.60 lb. gum starch per ton of ore
0.10 lb. dipentene hydroperoxide per ton of ore
0.10 lb. dehydrogenated rosin amine acetate per ton of ore

A froth was removed until practically all the minerals had floated, which took about 5 min. The results were as follows:

	Per Cent Total Weight of Ore	Per Cent Iron Contained in Various Fractions	Per Cent Iron Recovered in Various Fractions
Float.....	44.7	12.1	15.2
Tail.....	55.3	54.6	84.8
Feed.....	100.0	35.5	100.0

In the beneficiation of minerals by the froth flotation process, the ore or mineral to be concentrated is first finely ground in the presence of water to the proper particle size for the purpose of liberating the gangue from the metalliferous or mineral components. The ground material is screened to remove the oversized particles. The resultant pulp may then be treated in any of the various types of machines which have been developed for the purpose. Thus, vortex, supraeration, and pneumatic machines of the air-jet type may be employed. Customarily, the value mineral; i. e., the product which it is desired to recover, is floated. However, the procedure may be reversed with the value mineral concentrated in the tailing and the gangue removed in the froth, as illustrated by Example VII.

Bulk flotation involves the flotation from the ore of a single rough concentrate containing a

group of valuable minerals of the ore. Divisional flotation involves a more refined separation of minerals of similar flotation properties from each other, giving a product or number of products each of which contains, in so far as possible, one mineral or only minerals whose presence together is commercially desirable.

The frothing agents of this invention are, of course, operable in both bulk and divisional flotation procedures involving any mineral or ore. Furthermore, these frothing agents are equally advantageous when employed in any of the various types of machines adapted to the processes involved.

The objects of this invention are accomplished by using secondary cyclic hydroperoxides as frothing agents in flotation processes for the beneficiation of ores. Such hydroperoxides may be prepared by the oxidation of cyclic compounds having between 6 and 15 carbon atoms and preferably between 8 and 13 carbon atoms. The oxidation may be carried out with air or commercial oxygen either in the presence of a catalyst such as cobalt, manganese, lead or iron naphthenate or in the presence of ultraviolet light. Alternatively, the oxidation may be effected with or without any of the foregoing catalysts but in a liquid phase system in the presence of an initiator such as, for example, an organic peroxide or hydroperoxide capable of producing free radicals. Exemplary of such an initiator is α,α -dimethylbenzyl hydroperoxide. A preferred method of preparing these hydroperoxides involves the liquid phase oxidation of the cyclic hydrocarbons by passing an oxygen-containing gas through the hydrocarbons in the liquid phase at a temperature between about 25° C. and about 50° C. in the presence of an initiator such as α,α -dimethylbenzyl hydroperoxide. Vigorous agitation is desirable during the oxidation reaction. Although all of the secondary cyclic hydroperoxides previously mentioned are operable, the hydroperoxides of α -tetrahydronaphthalene, cyclohexene, decahydronaphthalene, dipentene, carvomenthene, 2-menthene, and β -pinene are preferred.

In carrying out this invention the flotation agents comprising a secondary cyclic hydroperoxide may be prepared using several different modifications of the hydroperoxide material. The hydroperoxide may be used, for example, either in the form of the pure hydroperoxide, or in the form of a crude reaction mixture containing the hydroperoxide and obtained by the oxidation with air or oxygen of a cyclic compound such as, for example, a cyclic terpene. When the hydroperoxide is obtained by such an oxidation, the oxidation usually is interrupted before all of the hydrocarbon has reacted in order to avoid or limit side reactions. In this manner the secondary cyclic hydroperoxide is obtained in mixture with smaller or larger amounts of the original hydrocarbon, and the mixture also may contain secondary reaction products such as the corresponding alcohols. Such a reaction product may be used *per se* in forming the flotation agents of this invention. In case it is desirable, however, to obtain the hydroperoxide in a more concentrated form, the hydroperoxide may be separated from the other constituents of the crude reaction mixture. The hydroperoxides may be separated from the reaction mixtures by, for example, fractional distillation at very low pressures, of the order of 0.01 to 1.0 mm./sq. cm., the hydroperoxides having higher boiling points than the related hydrocarbon, alcohol and ketone. In

some instances the hydroperoxides also may be separated from the oxidation reaction mixtures by crystallization, which may be facilitated by first distilling off at least part of the hydrocarbon. Steam distillation usually is sufficient to remove the hydrocarbon.

The secondary cyclic hydroperoxides of this invention may be utilized in amounts of from about 0.005 lb. to about 1 lb./ton of ore but are preferably employed in amounts of from about 0.01 lb. to about 0.5 lb./ton of ore. In most instances, it is advantageous to employ other flotation agents in addition to the frothers to achieve the most effective separation of the minerals from the ore. These additional froth flotation reagents include collectors and modifying agents.

Collecting agents are chemical compounds which cause the collection of the desired material into the froth. The compounds most commonly employed with metallic sulfide and oxidized metallic ores are the xanthates, dithiophosphates, and diphenyl thiourea. Potassium or sodium ethyl, butyl, and amyl xanthates or mixtures of these are also widely used. The collectors known as "dithiophosphates" are prepared by the reaction of phosphorus pentasulfide with alcohols or phenols. The most utilized of such compounds are the phosphocresylic acids which contain various percentages of cresylic acid added in excess during the manufacturing process. Sodium salts of these phosphocresylic acids are also valuable collectors. Likewise, useful collecting agents may be prepared from phosphorus pentasulfide and ethyl, amyl, or butyl alcohols.

In the flotation of nonmetallic ores, fatty acids, fatty acid soaps, and derivatives thereof are most commonly employed as collectors. Typical fatty acids utilized are oleic, stearic, and palmitic. Likewise, soaps comprising the alkali metal salts of these acids are excellent collectors. Sulfonated fatty acids and fatty acid soaps are also widely employed in the art as collecting agents and have the advantage of being more selective in their action. As shown in Example VII dehydrogenated rosin amine acetate also is a very effective collecting agent for the siliceous minerals in nonmetallic ores. Other comparably effective collectors for ore are those amines derived from a rosin or a modified rosin, such as hydrogenated rosin, polymerized rosin, heat-treated rosin, isomerized rosin, or the like, and the water-soluble salts of these amines. The amines may be prepared either from the rosin materials or from the pure acids contained therein, such as abietic acid, dehydroabietic acid, dihydroabietic acid, tetrahydroabietic acid and the like. The amine derived from dehydroabietic acid, for example, is dehydroabietylamine.

The secondary cyclic hydroperoxides of this invention may be efficaciously and advantageously utilized with any of the various collecting agents hereinbefore mentioned. Furthermore, these hydroperoxides are also operable with other collecting agents known to the art.

Modifying agents are of various types and include pH and pulp control agents, depressing agents, activating agents, sulfidizing agents, dispersing agents, and inhibitors.

The most commonly employed pH and pulp control agents are lime and soda ash for alkaline circuits and sulfuric acid for acid circuits.

Depressing agents include lime, sodium and potassium cyanide, sodium sulfate, sodium sulfite, sodium sulfide, sulfur dioxide, and potassium and sodium dichromate. These com-

pounds are employed both independently and in various combinations.

Copper sulfate, sodium sulfide, and sulfuric acids are used as activating agents for metallic ores. Soluble basic salts of copper, lead, and iron are so utilized in the soap flotation of non-metallic ores and, as sulfidizing agents, sodium sulfide, hydrogen sulfide, and the various other sulfides and polysulfides of the alkali and alkaline earth metals are employed. Dispersing agents commonly utilized are sodium silicate, sodium sulfide, citric acid, tannic acid, and lactic acid. Protective colloids, such as starch, glue, gum arabic, casein gelatin, and the like, are excellent inhibitors.

One skilled in the art of ore beneficiating by froth flotation will be cognizant of the proper collecting and modifying agents to employ to obtain the optimum results from the flotation of a particular ore. The secondary cyclic hydroperoxides of this invention may be utilized in conjunction with any of the modifying and collecting agents hereinbefore mentioned, either alone or in combination. It is to be understood, however, that the secondary cyclic hydroperoxides are also operable with any of the various other flotation reagents known to the art.

The frothing agents of this invention may be used generally in the dressing of ores. Sulfide ores, nonsulfide ores, both simple and complex, and nonmetallic ores may be advantageously so treated. Thus, lead, zinc, copper, iron, molybdenum, nickel, and precious metal sulfide and nonsulfide ores may be economically concentrated by froth flotation in the presence of the terpene hydroperoxides of this invention. Likewise, mineral ores, such as coal ores, are most efficaciously beneficiated in the presence of the froth flotation reagents disclosed.

The flotation agents herein disclosed are generally operable for the conditioning of ores or the treating of minerals. However, the conditions most desirable for frothing operations are dependent, in addition to the froth flotation agent, on the size of the ore being treated, the temperature at which the treatment is carried out, the per cent solids in the pulp, and the pH of the flotation mixture. In each case, one skilled in the art will be able to adjust the various conditions to achieve the optimum advantages from the flotation agents employed.

The physical properties of the froth produced by these secondary cyclic hydroperoxides are excellent. The froths are composed of fine bubbles which adequately support the weight of the floated mineral, thus facilitating its removal. Furthermore, the froths do not demonstrate undue stiffness or brittleness but collapse rapidly and completely after the concentrate has been removed. In addition, the froths produced by the hydroperoxides are clean with respect to the fine, slimy gangue which has a tendency to float and contaminate the metallic concentrate.

What we claim and desire to protect by Letters Patent is:

1. In the method of beneficiating ores by froth flotation, a step which comprises aerating a pulp of the ore containing a collector and a secondary cyclic hydroperoxide having the struc-

tural formula $>CH-OOH$ where C is a carbon atom in a carbon ring.

2. The process of claim 1 wherein the hydroperoxide is α -tetrahydronaphthalene hydroperoxide.

3. The process of claim 1 wherein the hydroperoxide is a terpene hydroperoxide.

4. The process of claim 1 wherein the hydroperoxide is a menthadiene hydroperoxide.

5. The process of claim 1 wherein the hydroperoxide is a menthene hydroperoxide.

6. The process of claim 1 wherein the hydroperoxide is dipentene hydroperoxide.

7. The process of claim 1 wherein the hydroperoxide is carvomenthene hydroperoxide.

8. In the method of beneficiating ores by froth flotation, the step which comprises aerating a pulp of the ore which contains a collector and about 0.005 lb./ton to about 1 lb./ton of the ore of a secondary cyclic hydroperoxide having the structural formula $>CH-OOH$ where C is a carbon atom in a carbon ring.

9. In the method of beneficiating ores by froth flotation, the step which comprises aerating a pulp of the ore which contains a collector and about 0.01 lb./ton to about 0.5 lb./ton of the ore of a secondary cyclic hydroperoxide having the structural formula $>CH-OOH$ where C is a carbon atom in a carbon ring.

10. In the method of beneficiating metaliferous ores by froth flotation, the step which comprises aerating a pulp of the ore containing a collector and from about 0.01 lb./ton to about 0.5 lb./ton of a secondary cyclic hydroperoxide having the structural formula $>CH-OOH$ where C is a carbon atom in a carbon ring.

11. In the method of beneficiating coal ores by froth flotation, the step which comprises aerating a pulp of the ore containing a collector and from about 0.01 lb./ton to about 0.5 lb./ton of a secondary cyclic hydroperoxide having the structural formula $>CH-OOH$ where C is a carbon atom in a carbon ring.

12. In the method of beneficiating ores by froth flotation, a step which comprises aerating a pulp of the ore containing a collector and a secondary cyclic alcohol and a secondary cyclic hydroperoxide having the structural formula $>CH-OOH$ where C is a carbon atom in a carbon ring.

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