FROTH FLOTATION OF ORES IN THE PRESENCE OF AN α,α-DIALKYLARYLMETHYL HYDROPEROXIDE

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No Drawing. Application June 30, 1948, Serial No. 36,268

1. 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 hereinafter employed in the flotation of minerals include pine oil, cresylic acid, cresolates, 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 or are as effective 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 unseetable as a consequence of their high cost.

Particularly it is desirable that a frother be characterized by a lack of collecting properties. If a substance possesses both frothing and collecting 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 discovered 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. Either mono- or di-hydroperoxides may be employed. The hydroperoxides of this invention are α,α-dialkyarylalkyl hydroperoxides.

The α,α-dialkyarylalkyl hydroperoxides used in accordance with this invention have the following structural formula:

\[
R_1 \quad X \quad R_4
\]

in which R₁ and R₂ represent alkyl groups, Ar represents a substituent selected from the group consisting of aryland alkaryl groups and X represents the hydroperoxy (–OOH) group. As illustrative of the alkyl-substituted aromatic organic compounds which may be oxidized, phenylcycme, cumene, and disopropylbenzene may be mentioned. These compounds lead to α,α-dimethylp-methylbenzyl, α,α-dimethyldimethylbenzyl, and α,α-dimethyl-p-isopropylbenzyl hydroperoxides, respectively. Also in the case of disopropylbenzene there may be obtained α,α,α,α-tetramethyl-p-xylene dihydroperoxide. These compounds also may be named as aryl(diaryl)methyl hydroperoxides; for example, α,α-dimethylbenzyl hydroperoxide may be designated α-phenyl(diaryl)methyl hydroperoxide. The aryl and alkaryl groups need not be derived from benzene, as is the case in the above-mentioned compounds, for compounds containing aromatic nuclei derived from naphthalene, anthracene, phenanthrene, and the like are also operable when dissolved in a suitable solvent during the oxidation.

The aryl group may be substituted with alkyl groups such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secondary butyl, tertiary butyl, and the like, to give alkaryl substituents, the same alkyl groups also being representative of R₁ and R₂ in the structural formula. R₁ and R₂ may be either the same or different. These organic hydroperoxides exhibit substantially no collecting properties and are attended by none of the other afore-mentioned disadvantages which characterize the frothers known to the prior art. These organic hydroperoxides may be used either alone or in conjunction with standard frothers hereinafter 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

One thousand twenty g. of lead ore was ground for 14 minutes in a ball mill with 1000 ml. of
water. This ore was composed of galena in a dojomite gangue and contained about 1.2% lead. The ground ore was screened through a 48-mesh screen and the feed transferred to a 1000-g flotation machine. The pulp was diluted to about 20% solids with water, and 0.15 lb. of sodium sulfide and 0.10 lb. of potassium isopropyl xanthate per ton of ore were added. Then the frothers listed below were added and a lead concentrate was removed for 10 minutes. The following results were obtained.

<table>
<thead>
<tr>
<th>Example</th>
<th>Frother</th>
<th>Found Per Ton</th>
<th>Per Cent Lead in Tailing</th>
<th>Per Cent Lead in Concentrate</th>
<th>Per Cent Lead Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>a-α-Dimethylbenzyl hydroperoxide</td>
<td>0.12</td>
<td>0.14</td>
<td>46.9</td>
<td>89.7</td>
</tr>
<tr>
<td>II</td>
<td>a-α-Dimethyl-β-isopropylbenzyl hydroperoxide</td>
<td>0.12</td>
<td>0.17</td>
<td>58.1</td>
<td>87.3</td>
</tr>
</tbody>
</table>

1 The a-α-dimethylbenzyl hydroperoxide was prepared by the air oxidation of cumene. In this instance, however, all but 6% of the a-α-dimethylbenzyl alcohol and acetophenone were removed.

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 metallic 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, superaerator, 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.

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 α,α-dialkylarylmethy hydroperoxides as frothing agents in flotation processes for the beneficiation of ores. Such hydroperoxides may be prepared by the oxidation of alkyl-substituted aromatic organic compounds having the structural formula

\[
\text{R}_1\text{R}_2\text{R}_3\text{H}_{\text{Cl}}\text{Ar}_1\text{Ar}_2
\]

in which \(\text{R}_1\) and \(\text{R}_2\) represent alkyl groups and \(\text{Ar}\) represents a substituent selected from the group consisting of aryl and alkaryl groups. The oxidation may be carried out in the liquid phase utilizing air or molecular oxygen as the oxidizing agents. A preferred method of preparing these hydroperoxides involves the liquid phase oxidation of the alkyl-substituted aromatic organic compounds having the above structural formula by passing an oxygen-containing gas through the compounds at a temperature between about 25°C and about 95°C in the presence of an aqueous alkali. The concentration of the aqueous alkali may be between about 1% and about 35% although it is preferable to use concentrations of about 2% to about 8%. Vigorous agitation is desirable during the oxidation reaction. The hydroperoxides of this invention can also be prepared by the auto-oxidation of the corresponding hydrocarbons at elevated temperature on irradiation with light of short wave length. This method is disclosed in detail by Hock and Lang, Ber., 77, 257-64 (1944). Although all of the organic hydroperoxides embraced by the structural formula previously mentioned are operable, \(\text{α,α-dimethyl-p-phenylbenzyl hydroperoxide, α,α-dimethylbenzyl hydroperoxide, α,α-dimethyl-p-p-isopropylbenzyl hydroperoxide, α,α,α,α'-tetramethyl-p-xylen dihydroperoxide, α-ethyl - α - methylbenzyl hydroperoxide, α,α-dimethyl-p-ethylbenzyl hydroperoxide and α,α-dimethylaphtylmethyl hydroperoxide are preferred.}

In carrying out this invention the flotation agents comprising an α,α-dialkylarylmethy 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 an alkyl-substituted aromatic organic compound having the structural formula shown previously. 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 α,α-dialkylarylmethy hydroperoxide is obtained in mixture with smaller or larger amounts of the original hydrocarbon, which is an α,α-dialkylarylmethane, and the mixture also may contain secondary reaction products such as the corresponding alcohols, which are α,α-dialkylarylmethyl alcohols. The oxidation of cumene, for example, leads to a reaction product containing α,α-dimethylbenzyl hydroperoxide, α,α-dimethylbenzyl alcohol, a small amount of acetophenone, and unchanged cumene. Such a reaction product may be used per se in forming the flotation agents of this invention. In cases 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 dis-
The organic hydroperoxides of this invention are efficiently 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, sulfurizing 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 compounds 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 nonmetallic ores and, as sulfurizing agents, as activating agents for metallic ores and, as sulfurizing agents, as metallic sulfides and polysulfides of the alkaline earth metals are employed. Dispersing agents commonly utilized are sodium silicate, sodium sulfide, citric acid, tannic acid, and laetic acid. Protective colloids, such as starch, 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 organic 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 organic 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 organic 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 organic 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 are:

1. In the method of beneficiating 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 1 lb./ton of the ore of a frother consisting of a substantially pure a,a-diarylethylhydroperoxide.

2. The process of claim 1 wherein the hydroperoxide is a,a-dimethylethylhydroperoxide.

3. The process of claim 1 wherein the hydroperoxide is a,a-dimethyl-p-methoxybenzylhydroperoxide.

4. The process of claim 1 wherein the hydroperoxide is a,a-dimethyl-p-isopropoxybenzylhydroperoxide.

5. In the method of beneficiating 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 the ore of a frother consisting of a substantially pure a,a-diarylethylhydroperoxide.

6. 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 the ore of a frother consisting of a substantially pure a,a-diarylethylhydroperoxide.

7. 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 the ore of a frother consisting of a substantially pure α,α-dialkylarylalkyl hydroperoxide.

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