OXIDE COPPER ORE FLOTATION USING CONDENSATION REACTION PRODUCT AS FLOTATION REAGENT

In a flotation separation process wherein oxide copper ores in subdivided form are concentrated by slurrying raw ores containing oxide copper ores in an aqueous solution of a flotation reagent followed by generating gas bubbles in the slurry to float the oxide copper ores and recovering the concentrated oxide copper ores from the surface of the slurry, the improvement wherein which comprises employing as the flotation reagent a condensation reaction product derived from

A. a substituted phenol of the formula

\[ \text{OR'} \]

wherein R' is H or a \((CH\text{\textsubscript{2}}CH\text{\textsubscript{2}}O\text{\textsubscript{x}})_2\text{H}\) radical where \(x\) is an integer of 1 to 3,

B. an alkylene polyamine of the formula

\[ \text{H(NH-9 CH}\text{\textsubscript{2}}\text{CH}_2\text{NH}_2} \]

wherein \(y\) is an integer of 2 to 6, and

C. formaldehyde.

6 Claims, No Drawings
OXIDE COPPER ORE FLOTATION USING
CONDENSATION REACTION PRODUCT AS
FLOTATION REAGENT

This invention relates to the novel use of certain compounds as flotation reagents in producing oxide copper ore concentrates by flotation separation and, in particular, to producing oxide copper ore concentrates by flotation separation of ores containing copper in oxidized form such as malachite, azurite, cuprite, tenorite and chrysocolla.

Therefore, flotation separation techniques for concentrating copper ores have been applied to sulfide copper ores due to the availability of suitable flotation reagents, or collectors as they are sometimes called, for these ores such as the xanthates. Generally, in the typical flotation technique the raw ore containing gangue rock is first pulverized to a finely divided form and slurried with water to form a pulp. The pulp is then charged to a flotation cell along with the flotation reagent and usually a frother (e.g., a hydroxy compound) and a regulating agent to control the pH. With agitation of the slurry the particles containing sulfide copper ore are floated to the surface through the action of the flotation reagent, become suspended in the froth and are then continuously removed from the surface of the slurry. The undesired particles of gangue remain behind in the slurry and are discarded in the tailings from the cell.

While the above-described flotation techniques have been in general use in concentrating sulfide copper ores, they have not been utilized to any extent with oxide copper ores. This has been primarily due to the lack of suitable flotation reagents for the direct flotation of the oxide copper ores since these ores are not as readily floated as the sulfide ores. It has been reported in the literature that mercaptobenzothiazole and salts of fatty acids have sometimes been found effective for direct flotation of the oxide ores but, in general, the oxide ores are first subjected to sulfidization to convert them to the sulfide ores and then concentrated by the usual flotation techniques and reagents applicable to sulfide ores. This approach obviously has drawbacks and there is considerable interest in the mining industry in developing direct flotation techniques for oxide copper ores.

In accordance with this invention, it has unexpectedly been found that certain compounds are highly effective as flotation reagents for concentrating oxide copper ores by flotation separation without the necessity of first subjecting such oxide ores to a sulfidization treatment. These compounds may be described as the condensation reaction products of a substituted phenol, an alkylene polyamine and formaldehyde, and are generally known in the art as shown by U.S. Pat. No. 2,353,491; U.S. Pat. No. 2,459,112; U.S. Pat. No. 3,036,003; U.S. Pat. No. 3,214,376; U.S. Pat. No. 3,278,637 and U.S. Pat. No. 3,539,633.

In particular, the condensation reaction products contemplated by the invention are those obtained by reacting

1. a substituted phenol of the formula

\[
\text{HON-\text{CH}_2\text{CH}_3}_{y}N\text{H}_2
\]

wherein \( y \) is an integer of 2 to 6, and

2. an alkylene polyamine of the formula

\[
R'<\text{H}_2\text{C}_x=\text{NCH}_2\text{H}_{y-1}\text{OCH}_2\text{CH}_3
\]

wherein \( R' \) is an alkyl group having 8 to 12 carbon atoms and \( R'' \) is \( \text{H} \) or \( \text{—(CH}_2\text{CH}_3)}_x\text{H} \) radical where \( x \) is an integer of 1 to 3,

3. formaldehyde.

Examples of the substituted phenols include octyl phenol, nonyl phenol, decyl phenol, dodecyl phenol, isooctyl phenol, ethoxylated nonyl phenol wherein an average of 2–3 ethoxy units are present per molecule, ethoxylated dodecyl phenol wherein an average of 2–3 ethoxy units are present per molecule, ethoxylated octyl phenol wherein an average of one ethoxy unit is present per molecule, and the like. The preferred substituted phenols are those wherein \( R' \) is hydrogen.

The alkylene polyamines include such amines as diethylenetriamine, tetraethylenepentamine, hexyethylene heptamine, triethylenetetramine and the like.

The third reactant, formaldehyde, need not be used per se to produce the compounds employed in the invention. Suitable formaldehyde yielding sources such as aqueous and alcoholic solutions of formaldehyde, parafomaldehyde and trioxymethylene may be used as well. The term formaldehyde is used herein to include these latter materials.

While the above-mentioned patents disclose various methods for carrying out the condensation reaction, a typical reaction procedure involves charging the substituted phenol and alkylene amine to a reactor along with a solvent therefor, e.g., methanol, followed by addition of the formaldehyde and heating to elevated temperatures in the range of 75° to 95°C. The reaction mixture is maintained at these temperatures for a suitable period of time, e.g. from one to several hours, until completion. Thereafter, the reaction mixture is heated to higher temperatures while sparging with \( \text{N}_2 \) to remove water and the solvent from the reaction product.

In general, suitable condensation reaction products are obtained by reacting 0.5 to 5 mols of each of the alkylene polyamine and formaldehyde per mol of substituted phenol, preferably 0.5 to 3 mols per mol of substituted phenol.

A solvent is commonly used in the reaction as an aid in solubilizing the reactants although it is not an absolute requirement for the reaction. While methanol was mentioned above, other solvents may also be used such as methanol, ethanol, isopropanol, benzene, toluene, xylene, mineral oil and the like.

The above-described condensation reaction products have been found useful in flotation separation techniques to concentrate oxide copper ores and, particularly, for concentrating low grade ores. These low grade ores may contain as little as one-half percent copper or less, expressed as \( \text{CuO} \), in association with gangue rock. As previously indicated, flotation separation generally involves subdividing the raw ore, most desirably to an extent wherein each particle is composed as nearly as possible of either the valuable or worthless material only. The subdivided ore is slurried in water, or the water may be added during the subdividing, so as to form a pulp which will normally contain about 10 to 75 percent solids. The flotation reagent is then added to the pulp and gas bubbles are either gen-
erated or introduced in the pulp whereby the solid particles containing the copper ore adhere to the gas bubbles and rise to the surface of the pulp for easy removal as a concentrated copper ore composition. These techniques are well-known in the art and a more complete and detailed discussion may be found in Flotation by A. M. Gaudin, Second Edition, 1957, published by McGraw-Hill. It is also desirable to employ a frothing agent and a pH regulating agent in these techniques as explained in that text. A partial list of some common frothers and regulating agents is presented at page 154 of An Introduction to the Theory of Flotation by Klassen and Mokrousov, Second Edition, 1963, published by Butterworth and Co. Ltd. (London).

In general, the condensation reaction products may be used as the flotation reagent in the flotation separation process in any amount which is suitable to provide the desired flotation of the oxide copper ore. Of course, for economic reasons the amount employed should be the minimum required to achieve the desired results. Generally, amounts in the range of about 0.01 to about 5 pounds per ton of ore may be used with a range of about 0.05 to about 2 pounds per ton of ore being preferred.

The amount of flotation reagent and the degree of flotation achieved will be dependent, in part, on the pH of the flotation slurry. Thus, in optimizing the separation process it is recommended that a series of simple experiments be run using a conventional Hallimond cell, first determining the optimum pH range with a constant flotation reagent concentration and then determining the optimum flotation reagent concentration at a constant optimum pH. These experiments can be conducted as described in the examples to follow.

The following examples will further illustrate the invention:

EXAMPLE 1
Preparation of Flotation Reagent:
A 500 ml creased flask equipped with a stirrer, thermometer and reflux condenser was charged with 0.3 mol (66.5 g) nonyl phenol and 0.6 mol (114.4 g) tetraethylene pentamine along with 100 ml methanol as inert solvent. The charge was heated to 70°-80°C and 0.6 mol (49.5 g) formaldehyde as a 37 percent aqueous solution was added dropwise. After addition of the formaldehyde the reaction mixture was stirred at temperatures in the range of 80°-90°C for about 3 hours. The resulting reaction product mixture was thereafter stripped to a 150°C bottoms temperature and sparged with nitrogen for about 15 to 20 minutes at 150°C. The recovered condensation reaction product was then used as the flotation reagent in the following flotation separation tests.

Flotation Separation Tests:
The above-prepared condensation reaction product was evaluated as a flotation reagent in a series of tests involving various pH values using a conventional modified Hallimond tube flotation cell. In each test a flotation slurry was first prepared and then transferred to the cell. The flotation slurry was prepared by desliming a 1 g sample of -48+150 (Tyler) mesh chrysocolla (CuSiO₃·2H₂O) with distilled water and then charging the deslimed mineral to a beaker along with 100 ml aqueous solution of the condensation reaction product having a concentration of 1X10⁻⁴ mol/liter. The pH of the flotation slurry was then adjusted to the desired value using HCl for pH values of 3-4, Na₂CO₃ for pH values of 5-9 and KOH for pH values of 10-11. The slurry was stirred for a few minutes and then charged to the modified Hallimond cell. Then a total of about 100 cc of air was bubbled through the slurry over a period of 3 minutes during which time the particles of chrysocolla were floated and recovered through the upper side arm of the cell. At the end of the 3-minute period the test was terminated and the recovered chrysocolla which was floated was dried and weighed. The remaining chrysocolla which was not floated was also recovered, dried and weighed. Based on these two determinations the percent recovery (floated chrysocolla) was calculated. The results of the tests are set forth in the following table:

<table>
<thead>
<tr>
<th>Test</th>
<th>pH</th>
<th>% Recovery</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>3</td>
<td>31.6</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>62.8</td>
</tr>
<tr>
<td>C</td>
<td>5</td>
<td>72.8</td>
</tr>
<tr>
<td>D</td>
<td>6</td>
<td>87.7</td>
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<td>100.0</td>
</tr>
<tr>
<td>I</td>
<td>11</td>
<td>100.0</td>
</tr>
</tbody>
</table>

EXAMPLE 2
Flotation recovery may be obtained using a condensation reaction product derived from dodecyl phenol, triethylene tetramine and formaldehyde as the flotation reagent and malachite (CuCO₃·Cu(OH)₂) as the oxide copper ore.

EXAMPLE 3
A condensation reaction product derived from ethoxylated octyl phenol (2-3 ethoxy units per molecule), pentaethylene hexamine and formaldehyde may be used as the flotation reagent in floating tenorite (CuO) or cuprite (Cu₂O).

EXAMPLE 4
A condensation reaction product was prepared according to the procedure described in Example 1 using 0.25 mol nonyl phenol, 0.5 mol diethylenetriamine and 0.5 mol formaldehyde. The reaction product was evaluated for flotation reagent capability at 1X10⁻⁴ mol/liter concentration on chrysocolla as described in Example 1. There resulted a 40 percent recovery for pH values in the range of 3 to 12.

EXAMPLE 5
Aurite (2CuCO₃·Cu(OH)₂) may be floated using a flotation reagent comprising the condensation reaction product derived from octyl phenol, hexaethylene heptamine and formaldehyde.

Thus having described the invention in detail, it will be understood by those skilled in the art that certain variations and modifications may be made without departing from the spirit and scope of the invention as described herein and in the appended claims.

I claim:
1. In a flotation separation process wherein oxide copper ores in subdivided form are concentrated by slurring raw ores containing oxide copper ores in an aqueous solution of a flotation reagent followed by generation of gas bubbles in the slurry to float the oxide copper ores and recovering the concentrated oxide copper ores from the surface of the slurry, the improvement therein which comprises employing as the flotation reagent a condensation reaction product obtained by reacting

A. a substituted phenol of the formula

\[
\text{O R'}
\]

wherein \( R \) is an alkyl group having 8 to 12 carbon atoms and \( R' \) is \( \text{H} \) or \( \text{O}-(\text{CH}_2\text{CH}_2\text{O})_x\text{H} \) radical where \( x \) is an integer of 1 to 3,

B. an alkylene polyamine of the formula

\[
\text{H}(\text{HN-CH}_2\text{CH}_2)_y\text{NH}_2
\]

wherein \( y \) is an integer of 2 to 6, and

C. formaldehyde,

wherein the mol ratio of (A) to (B) to (C) is 1:0.5–5:0.5–5.

2. A process according to claim 1 wherein \( R' \) is hydrogen.

3. A process according to claim 1 wherein the substituted phenol is nonyl phenol and the alkylene polyamine is tetraethylene pentamine.

4. A process according to claim 1 wherein the flotation reagent is employed in amounts in the range of about 0.01 to about 5 pounds per ton of ore.

5. A process according to claim 1 wherein the substituted phenol is nonyl phenol and the alkylene polyamine is diethylene triamine.

6. A process according to claim 1 wherein the oxide copper ore is chrysocolla.

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