ABSTRACT OF THE DISCLOSURE

Alkali metal salts of dithiocarbamates and di-dithiocarbamates are disclosed as collectors in froth flotation separation of sulfide minerals from metallic sulfide ores, particularly oxidized metallic sulfide ores.

This invention relates to a process for froth flotation separation of metallic sulfide ores, and more particularly to the use of dithiocarbamate compounds as flotation collectors for metallic sulfide mineralization, especially of oxidized sulfide ores.

In treating crude ores and mineral products to separate the valuable minerals, such as copper, lead and zinc, from the crude material, the process of froth flotation depends for its efficacy on the ability of the collector to wet selectively some mineral particles while other desirable constituents remain unwetted and adhere to air bubbles which float to the surface of the mixture and are removed as a concentrate in the froth. Coating finely ground mineral particles is accomplished by agitating a mixture of ore, water, and a suitable chemical collector such as sodium ethylxanthate in a conditioner for a short time during which the chemical attaches to the surface of the mineral particles to form a new surface which is more water repellent than the original surface and which is therefore air avid. Minerals that naturally tend to resist wetting may be treated so that their surfaces will be wetted and they will sink in the water and thereby not be floated with the concentrates containing desired mineral particles.

An object of the invention is to provide a process in which dithiocarbamate compounds are employed as flotation collectors in the separation of metallic sulfide ores, and particularly oxidized ores. A further object is to provide a process in which dithiocarbamate compounds are used in the recovery of copper sulfide, zinc sulfide, and complex sulfide ores.

Yet another object is to provide as collectors in our process for flotation separation of metallic sulfide ores, alkali metal and amine salts of dithiocarbamates prepared from N-aliphatic substituted poly alkylene diamines in which the aliphatic hydrocarbon has from 8 to 22 carbon atoms or mixtures thereof.

Other specific objects and advantages will appear as the specification proceeds.

In the synthesis of the compounds useful in our process, an excess of CS₂ is dissolved in an NaOH alcohol solution of a primary or secondary aliphatic amine, or a N-substituted polyalkylene diamine. The reaction can then be evaporated to give the sodium salt. If desired, the amine salt can be prepared by omitting the NaOH. In the case of dithiocarbamates of diamines, either a monodithiocarbamate can be prepared, or if both amino nitrogens are substituted with CS₂, a di-dithiocarbamate will result. Other methods known to those skilled in the art may be employed.

Preferred dithiocarbamate salts useful in the process of this invention have the formula:

R\(^-\)N\(^-\)-(CH₂)\(_x\)-N\(^-\)-(CH₂)\(_y\)-S-M

wherein R is an aliphatic hydrocarbon radical containing from 6 to 22 carbon atoms, R' is selected from the group consisting of hydrogen and

[Structural formula]

radical, x is an integer from 2 to 4, and M represents an alkali metal radical.

Examples of long chain aliphatic hydrocarbon radicals having from 6 to 22 carbon atoms coming within the definition of R described hereinabove include octyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, octadecadienyl, octadecatrienyl, docosy, eicosy, and mixtures of the foregoing carbon radicals as contained in naturally occurring glycerides such as coconut oil, tallow, soybean oil, and the like. These long chain aliphatic hydrocarbon radicals may either be straight or branched chain. Collectors containing diamines particularly useful in the practice of this invention are those with the trade name Duomelon by Armour and Company, having the letter "C" for the symbol "Coco" indicating that the long chain aliphatic hydrocarbon radicals in the compound are mixtures derived from coconut oil, the letter S for the symbol "soya" indicating mixtures derived from soybean oil, and the letter T for the symbol "tallow" indicating mixtures derived from tallow.

Alkali metal radicals coming within the definition of M described hereinabove include the monovalent metals lithium, sodium, potassium, rubidium and cesium. However, in the practice of this invention we prefer to employ sodium as the alkali metal radical contained in the collectors of our process. Short chain hydrocarbon radicals coming within the definition of (CH₂)\(_x\) wherein x is an integer from 2 to 4 as described hereinabove include ethylene, propylene and butylene; however, in the practice of our invention, we prefer to employ propylene in our collectors.

In the practice of the process of this invention, suitable mineral containing sulfide ores may be comminuted to a suitable size for flotation by any of the methods known such as crushing and then grinding in a ball mill at 50% solids in a water suspension (pulp). The ground ore may be directly charged to a flotation cell and the pulp diluted to about 16% solids. The water suspension of finely-divided metallic sulfide ores is then conditioned after adding our alkali metal salt of dithiocarbamate collector. Rates of collector addition to the cell may vary directly proportional to the amount of ore present. Our
rate of collector addition may be from 0.005 to 0.5 i/t (pounds per ton), although we prefer a rate of from 0.03 to 0.10 i/t. The pH of the pulp may be adjusted to the alkaline range, and we prefer a pH of from 10.5 to 13. The dithiocarbamates desirable in our invention may be synthesized at various concentrations with isopropanol or other suitable alcohols as solvents in order to facilitate their addition to the cell as a liquid, although the stock solution may be added in solid form. A frother such as pine oil is added to the cell and the total mixture in the flotation cell may be conditioned about one minute before the introduction of air. Flotation may be conducted for from 3 minutes to about 15 minutes.

In a preferred embodiment of our process for the flotation separation of a sample of oxidized copper sulfide ore, the sample is ground to flotation size in a ball mill at about 50% solids in a water suspension with CuO and the ground ore is charged directly to a flotation cell where the pulp is diluted to about 16% solids by the addition of water. A fifty percent solution of the sodium salt of Duomeen C mono-dithiocarbamate is added as collector at the rate of about 0.1 i/t. (about 0.05 i/t isopropanol being present therein) and increments of about 0.04 i/t. of pine oil are added at the beginning time and again after 4 minutes of froth time. Conditioning time is about one minute before introduction of air and froth is removed for nine minutes. The pH is maintained at 12.0 to 12.3. The copper is floated and only one rougher concentrate containing floated copper mineral particles is collected, although further concentrates may be collected.

In the following specific examples, flotation collectors were tested, the collectors being identified by reference numbers as set out in the following list:

RF No.:  
1. Sodium salt of Duomeen S mono-dithiocarbamate.  
2. Sodium salt of N-tallow (B-cyanooethyl) dithiocarbamate.  
4. Sodium salt of Duomeen C di-dithiocarbamate.  
5. Sodium salt of Duomeen T di-dithiocarbamate.  
7. Sodium salt of Duomeen T mono-dithiocarbamate.

The procedures are outlined in the following specific examples in testing the above-referenced compounds as flotation collectors, with typical results as shown:

EXAMPLE I

In each test a 500 gram sample of fresh copper sulfide ore analyzing 4.5% Cu was ground to flotation size in a laboratory ball mill at 50% solids with 13 grams CaO. The ground ore was charged directly to a Fagergren laboratory flotation cell without desliming, where the pulp was diluted to about 16% solids. Collector addition rates in each test are shown in the results. Conditioning time was one minute before introduction of air. Pine oil was added at 0.04 i/t. at the beginning of each test and again after four minutes of froth time. The pH was maintained at 12.0–12.3. Froth was removed for nine minutes. Only one rougher concentrate was collected in each test.

<table>
<thead>
<tr>
<th>Collector</th>
<th>RF No.</th>
<th>Rate of added</th>
<th>Isopropanol</th>
<th>Pine oil</th>
<th>Collector rate</th>
<th>Percent recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.005</td>
<td>0.08</td>
<td>0.05</td>
<td>18.32</td>
<td>2.47</td>
<td>48.40</td>
</tr>
<tr>
<td>2</td>
<td>0.08</td>
<td>0.066</td>
<td>0.08</td>
<td>17.22</td>
<td>1.02</td>
<td>50.32</td>
</tr>
<tr>
<td>3</td>
<td>0.08</td>
<td>0.065</td>
<td>0.08</td>
<td>18.04</td>
<td>2.83</td>
<td>52.78</td>
</tr>
<tr>
<td>4</td>
<td>0.08</td>
<td>0.065</td>
<td>0.08</td>
<td>18.11</td>
<td>1.15</td>
<td>59.40</td>
</tr>
</tbody>
</table>

EXAMPLE II

Test procedure and conditions are the same as for Example I, except that increments of 0.04 i/t. of pine oil were added. The same ore as used in Example I was used except that it had been subjected to atmospheric oxidation in storage for up to two years. No artificial sulfidization was used in the referenced tests.

<table>
<thead>
<tr>
<th>Collector</th>
<th>RF No.</th>
<th>Rate of added</th>
<th>Isopropanol</th>
<th>Pine oil</th>
<th>Collector rate</th>
<th>Percent recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.005</td>
<td>0.05</td>
<td>0.05</td>
<td>18.67</td>
<td>1.12</td>
<td>76.29</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>0.029</td>
<td>0.05</td>
<td>18.14</td>
<td>1.16</td>
<td>77.91</td>
</tr>
<tr>
<td>3</td>
<td>0.05</td>
<td>0.033</td>
<td>0.05</td>
<td>20.50</td>
<td>0.72</td>
<td>82.52</td>
</tr>
<tr>
<td>4</td>
<td>0.05</td>
<td>0.034</td>
<td>0.05</td>
<td>15.65</td>
<td>2.08</td>
<td>76.73</td>
</tr>
</tbody>
</table>

EXAMPLE III

Ore for this test was obtained from the pulp stream of an operating flotation mill prior to the addition of collector for zinc sulfide flotation. Copper sulfate for zinc activation had been added in the mill, but all other reagents were added in the laboratory. Test procedure is as follows:

The pulp was charged to a laboratory flotation cell and the pH of the pulp was adjusted to 11.0 with CaO. The collector and an appropriate creosote frother were added, followed by 10 minutes flotation time. Results are shown in the following table.

<table>
<thead>
<tr>
<th>Collector</th>
<th>RF No.</th>
<th>Weight percent</th>
<th>Analyzes, percent</th>
<th>Cu tails</th>
<th>Percent recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>18.4</td>
<td>81.8</td>
<td>4.1</td>
<td>0.30</td>
</tr>
<tr>
<td>2</td>
<td>0.03</td>
<td>15.8</td>
<td>82.4</td>
<td>4.4</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Sodium ethyl xanthate.

EXAMPLE IV

A 500 gram sample of a complex sulfide ore analyzing 1.6% Cu and 22% Fe was ground to flotation size in a laboratory rod mill at 50% solids. Sufficient lime was used in the grind to obtain a subsequent flotation pH of 11.6–11.8. Sodium-(3-coco amino) propyl dithiocarbamate was added at 0.05 i/t. and Dowfroth 250 was added as frother at 0.08 i/t. The pulp was conditioned 1 minute before flotation. Flotation was conducted for 10 minutes. One rougher concentrate was obtained. A standard test was conducted under identical conditions except potassium amyl xanthate was used at 0.10 i/t.

<table>
<thead>
<tr>
<th>Collector</th>
<th>RF No.</th>
<th>Weight percent</th>
<th>Analyzes, percent</th>
<th>Cu tails</th>
<th>Percent recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.01</td>
<td>16.19</td>
<td>8.81</td>
<td>0.01</td>
<td>76.9</td>
</tr>
<tr>
<td>2</td>
<td>0.03</td>
<td>9.21</td>
<td>0.09</td>
<td>0.81</td>
<td>12.9</td>
</tr>
</tbody>
</table>

It is clear from the foregoing examples that the referenced compound or collector is unusually and surprisingly effective on oxidized ore. Example I testing the thiocarbamates on fresh copper sulfide ore did not show the grade and recovery as did Example II testing the same ore subjected to atmospheric oxidation. Further, in Example III, the collector obtained slightly higher zinc grade and 18.5% higher zinc recovery at only one-third of the collector addition rate of sodium ethyl xanthate used as a standard collector.

While in the foregoing specification, we have set forth specific steps and collector compounds in considerable detail for the purpose of illustrating embodiments of the invention, it will be understood that such embodiments may be varied by those skilled in the art without departing from the spirit of our invention.

We claim:

1. In a process for the separation of metallic sulfide
minerals from metallic sulfide ores by froth flotation, wherein said minerals are floated, the step of conditioning a water suspension of finely-divided metallic sulfide ores with an alkali metal salt of dithiocarbamate having the formula:

\[
R' - N - (CH_2)_x - N - C - S - M
\]

wherein \( R \) is an aliphatic hydrocarbon radical containing from 6 to 22 carbon atoms, \( R' \) is selected from the group consisting of hydrogen and

\[
\text{radical, } x \text{ is an integer from 2 to 4, and } M \text{ represents an alkali metal radical.}
\]

2. The process of claim 1 in which the ores are oxidized metallic sulfide ores.

3. The process of claim 1 in which the ores are zinc sulfide ores.

4. The process of claim 1 in which \( R \) is coco and \( R' \) is hydrogen.

5. The process of claim 4 in which \( M \) is sodium and \( x \) is 3.

6. The process of claim 1 in which \( R \) is soya and \( R' \) is hydrogen.

7. The process of claim 1 in which \( R \) is tallow and \( R' \) is hydrogen.

8. The process of claim 1 in which \( R \) is coco and \( R' \) is hydrogen.

9. The process of claim 1 in which \( R \) is soya and \( R' \) is hydrogen.

10. The process of claim 1 in which \( R \) is tallow and \( R' \) is hydrogen.

11. The process of claim 1 in which \( R \) is dodecyl.

References Cited

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3,298,520 1/1967 Bikales --------- 209—166

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