United States Patent [19]

McGuire et al.

[11] **3,845,862**

[45] **Nov. 5, 1974**

[54] **CONCENTRATION OF OXIDE COPPER ORES BY FLOTATION SEPARATION**

[75] Inventors: **Stephen E. McGuire; Carl D. Kennedy; John C. Stauter,** all of Ponca City, Okla.

[73] Assignee: **Continental Oil company,** Ponca City, Okla.

[22] Filed: **Jan. 4, 1973**

[21] Appl. No.: **321,087**

[52] **U.S. Cl.** **209/166**

[51] **Int. Cl.** **B03d 1/02**

[58] **Field of Search** 209/166, 167

[56] **References Cited**

UNITED STATES PATENTS

2,087,565	7/1937	Bulle	209/166 X
2,129,264	9/1938	Downing	209/166 X
2,132,902	10/1938	Lenher	209/166
2,190,133	2/1940	Epstein	209/166 X
2,214,352	9/1940	Schueller	209/166 X
2,242,224	5/1941	Bley	209/166 X
2,267,496	12/1941	Ellis	209/166
2,337,118	12/1943	Lontz	209/166
3,438,494	4/1969	Fuerstenau	209/166

FOREIGN PATENTS OR APPLICATIONS

203,943	11/1956	Australia	209/166
410,956	5/1934	Great Britain	209/166

Primary Examiner—Robert Halper

Attorney, Agent, or Firm—Ronald J. Carlson; Joseph C. Kotarski, Jr.

[57] **ABSTRACT**

Oxide copper ores in subdivided form may be concentrated in a flotation separation process by slurrying said ores in an aqueous solution of a flotation reagent followed by generating gas bubbles in the slurry to float the oxide copper and recovering the concentrated oxide copper from the surface of the slurry, wherein the flotation reagent is a quaternary hydrocarbyl ammonium or phosphonium halide salt.

8 Claims, No Drawings

CONCENTRATION OF OXIDE COPPER ORES BY FLOTATION SEPARATION

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 copper concentrates by flotation separation of ores containing copper in oxidized form such as malachite, azurite, cuprite, tenorite and chrysocolla.

Heretofore, 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 along with the copper ore 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 of 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 gangue remains behind in the slurry and is descarded 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. 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. 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 a certain class of compounds are effective as flotation reagents concentrating oxide copper ores by flotation separation without the necessity of first subjecting such oxide ores to a sulfidization treatment. This class of compounds include quaternary hydrocarbyl ammonium or phosphonium halide salts and may be described by the general formula

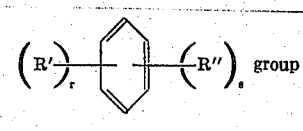
$$(R)_4Y^+X^-$$

wherein

Y is a nitrogen or phosphorus atom;

X is a bromine, chlorine, or iodine atom; and

each R is, independently, an alkyl radical or a



group

wherein

R is an integer of 1 or 2;

R′ is hydrogen or an alkyl radical;

s is 0 or 1; and

R″ is an alkylene radical,

provided that total number of carbon atoms of $(R_4)Y^+X^-$ is in the range of 10 to 45.

In the above general formula, when R or R′ are alkyl radicals they may be branched or straight chain having one to 30 carbon atoms and R″ may have one to 15 carbon atoms, provided that the total number of carbon atoms for the compounds is in the range of 10 to 45.

It is also essential that these compounds be water soluble, that is, water soluble to the extent of the minimum concentration that such reagents would be employed.

The above-described class of compounds are generally known in the art, commonly referred to as quaternary ammonium and phosphonium halide salts, and are readily synthesized by known techniques. Examples of the above compounds are disclosed in British No. 632,346 and British No. 1,227,144. Further illustrative examples include tridodecyl propyl ammonium chloride; benzyl dimethyl propyl ammonium bromide; tributyl stearyl phosphonium bromide; tetrabutyl phosphonium chloride; dibenzyl didodecyl ammonium bromide; tributyl ethyl phosphonium iodine; tributyl hexadecyl phosphonium iodide; dioctadecyl dimethyl ammonium chloride; trioctyl ethyl ammonium chloride; tribenzyl decyl phosphonium iodide; hexadecyl trihexyl ammonium chloride; and the like.

The above-described compounds have been found useful in flotation separation techniques to concentrate oxide copper ores and, particularly, for concentrating low grade ores containing considerable gangue. These low grade ores may contain as little as one-half percent copper or less, expressed as CuO. 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 by weight. The flotation reagent is then added to the pulp and gas bubles are either generated or introduced in the pulp whereby the solid particles containing the oxide copper ore adhere to the gas bubles and rise to the surface of the pulp for easy removal as a concentrated oxide copper ore. 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 compounds 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 will usually be employed with a range of

about 0.05 to about 2 pounds per ton of ore being normally 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 a particular 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

Di(C_{12}-C_{16} alkyl) dimethyl ammonium chloride (ALIQUAT 221) 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 ($CuSiO_3 \cdot 2H_2O$) with distilled water and then charging the deslimed mineral to a beaker along with 100 ml aqueous solution of the reagent having a concentration of 1×10^{-4} mol/liter. The pH of the flotation slurry was then adjusted to the desired value using HCl for pH values of 3–4, $NaCO_3$ for pH values of 5–9 and KOH for pH values of 10–12. The slurry was stirred for a few minutes for preconditioning 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 three-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 I

pH	% Recovery	pH	% Recovery
3	24.5	8	97.4
3	35.2	9	98.8
4	53.2	10	100.0
5	81.4	11	100.0
6	90.0	12	97.7
7	100.0		

EXAMPLE 2

Several flotation separation tests were run as described in Example 1 using lauryl trimethyl ammonium chloride (ALIQUAT 4) as reagent at a concentration of 1×10^{-4} mol/liter. The results of the tests are shown in the following table.

TABLE II

pH	% Recovery	pH	% Recovery
3	23.8	11	31.4
4	27.5	12	68.4
5	33.5	12	70.3

TABLE II-Continued

pH	% Recovery	pH	% Recovery
6	30.2	11	35.2
7	34.6	10	41.0
8	26.5	9	32.1
9	47.4	8	12.7
10	33.4		

EXAMPLE 3

A series of flotation tests using tricapryl methyl ammonium chloride (ALIQUAT 336) as reagent at a concentration of 1×10^{-4} mol/liter were conducted as described in Example 1. The results are shown in TABLE III.

TABLE III

pH	% Recovery	pH	% Recovery
3	22.6	8	28.2
4	22.3	9	27.9
5	26.4	10	32.2
6	32.1	11	29.2
7	37.9	12	32.7

EXAMPLE 4

Another series of flotation tests were run as described in Example 1 using tridodecyl propyl ammonium bromide as reagent at a concentration of 2×10^{-4} mol/liter. The results of the tests are shown as follows:

TABLE IV

pH	% Recovery	pH	% Recovery
3	28.7	7	29.8
4	16.5	8	15.9
5	15.6	9	30.3
6	30.5	10	16.8

EXAMPLE 5

A further series of flotation tests were run as described in Example 1 using benzyl dimethyl propyl ammonium bromide as reagent at a concentration of 2×10^{-4} mol/liter. The results of the tests are shown as follows:

TABLE V

pH	% Recovery	pH	% Recovery
3	8.2	7	13.7
4	5.4	8	11.2
5	13.0	9	12.6
6	7.2	10	12.8

EXAMPLE 6

Tributyl stearyl phosphonium bromide was evaluated as a reagent in a manner as described in Example 1 at a concentration of 2×10^{-4} mol/liter. The results appear as follows:

TABLE VI

pH	% Recovery	pH	% Recovery
3	12.2	7	15.6
4	14.9	8	17.5
5	16.7	9	17.5
6	16.6	10	19.0

EXAMPLE 7

Tetrabutyl phosphonium chloride was also evaluated as a reagent in accordance with the procedure outlined in Example 1 using a concentration of 2×10^{-4} mol/-liter. The results were as follows:

TABLE VII

pH	% Recovery	pH	% Recovery
3	13.8	7	26.7
4	22.0	8	38.8
5	20.4	9	33.1
6	35.5	10	35.0

EXAMPLE 8

Tributyl ethyl phosphonium iodide was evaluated as a reagent in the manner outlined in Example 1 using a concentration of 2×10^{-4} mol/liter. The results were as follows:

TABLE VIII

pH	% Recovery	pH	% Recovery
3	15.1	7	16.8
4	15.6	8	15.7
5	17.9	9	16.3
6	12.1	10	17.3

EXAMPLE 9

Two related quaternary ammonium halide salts were considered for possible use as reagents but were found to be insoluble in water and therefore unsuitable. These salts were tridodecyl carboethoxyethyl ammonium bromide and tridodecyl carboxyethyl ammonium bromide.

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.

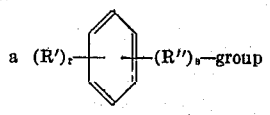
We claim:

1. In a flotation separation process wherein oxide copper ores in subdivided form are concentrated by slurrying said ores in an aqueous solution of a flotation reagent followed by generating gas bubbles in the slurry to float the oxide copper and recovering the concentrated oxide copper from the surface of the slurry, the improvement therein which comprises employing a quaternary salt as a flotation reagent, said quaternary salt being defined by

$$(R)_4\ Y^+\ X^-$$

wherein Y is a nitrogen or phosphorus atom; X is a bromine, chlorine, or iodine atom; and

each R is, independently, an alkyl radical having one to 30 carbon atoms; or

a  group

wherein "*r*" is an integer of 1 or 2; "*s*" is 0 or 1;

R′ is hydrogen or an alkyl radical having 1 to 30 carbon atoms; and

R″ is an alkylene radical having one to 15 carbon atoms; provided that the total number of carbon atoms of $(R)_4\ Y^+\ X^-$ is in the range of 10 to 45.

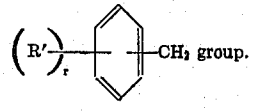
2. A process according to claim **1** wherein Y is nitrogen.

3. A process according to claim **1** wherein Y is phosphorus.

4. A process according to claim **1** wherein X is bromine or chlorine.

5. A process according to claim **1** wherein each R is an alkyl radical.

6. A process according to claim **1** wherein at least one R is a

 group.

7. A process according to claim **1** wherein one R is an unsubstituted benzyl radical and the remaining R groups are alkyl radicals.

8. A process according to claim **1** wherein about 0.01 to about 5 pounds of flotation reagent per ton of raw ore are employed.

* * * * *