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PROCESS OF CONCENTRATING ORES AND MINERALS BY FLOTATION

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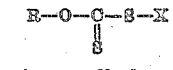
28 Claims. (Cl. 209—166)

This invention relates to the concentration of certain ores and minerals by flotation and comprises more particularly the concentration of such ores and minerals by means of a new class of organic flotation reagents.

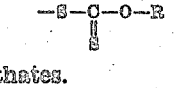
It has been shown by Sayre in U. S. Patent 1,512,139 that the heavy metal salts of xanthic acid are admirable flotation agents in a non-acid or alkaline pulp. Such xanthates are claimed to have a marked selective action on sulfide minerals, as distinguished from gangue minerals and cause the sulfide minerals to float readily with an attendant high recovery of metal values Both the heavy metal and alkali metal salts of xanthic acid while of unquestioned value as flotation agents are open to certain objections in respect to purity and stability.

One object of my invention is to provide a class of flotation agents which not only possess the good flotation properties resulting from the presence of the chemically reactive xanthic acid group, but which are chemically different from, and have properties equal to or better than those possessed by, the heavy metal salts of xanthic acid. Moreover I have found it possible to produce compounds of this type in a very pure state and, in some cases, in the form of liquids at ordinary temperatures.

I have discovered that various organic xanthates, as distinguished from metal xanthates, constitute excellent flotation agents and possess the desirable properties specified above. These new organic xanthate flotation agents have in general a molecular structure indicated by the following type formula:

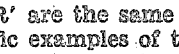


where R represents an alkyl group, and X stands for an organic radical such as (1) an alkyl group (which may or may not be the same as R), (2) an acyl group, or (3) another xanthic radical such, for example, as



1. Alkyl xanthates.

The members of this class have the general line formula



where R and R′ are the same or different alkyl groups. Specific examples of this class are:

Ethyl ester of ethyl-xanthic acid, $C_2H_5OCSS—C_2H_5$ n-Butyl ester of ethyl-xanthic acid, $C_2H_5OCSS—C_4H_9$ Ethylene ester of ethyl-xanthic acid, $(C_2H_5OCSS—)_2C_2H_4$

These compounds can be made by the action of the appropriate alkyl chloride or alkylene dichloride on sodium ethyl-xanthate (see Debus, Liebig's annalen, Vol. 75, P. 127 (1850)); or by the action of the appropriate alkyl bromide or alkylene dibromide (that is, ethyl bromide, n-butyl bromide, and ethylene dibromide) upon sodium ethyl-xanthate (Salomon, Journal für Praktische Chemie Second Series, Vol. 6, p. 445 (1872)). For production of the ethylene ester see also Welde, Journal für Praktische Chemie, Second Series, Vol. 15, page 55 (1877).

Flotation tests with ore obtained from the Phelps Dodge Corporation were run as follows:

500 grams of minus 28 mesh ore were ground for 20 minutes in a pebble mill with 500 c. c. of water, 0.6 grams of lime, and .025 grams of ethyl ethyl-xanthate. The lime and the ethyl ethyl-xanthate were used in the proportion of 2.4 pounds and 0.10 pounds respectively per ton of ore. The pulp from the pebble mill was diluted to about two liters, a drop of terpineol added, and the resulting pulp treated in a Janney laboratory flotation machine.

The flotation results were as follows:

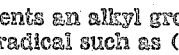
% copper in heads	1.48
% copper in rougher concentrate	8.71
% copper in rougher tailing	.23
% copper recovered in concentrate	93.6

Using ethylene ethyl-xanthate, the following results were obtained with ore from the Phelps Dodge Corporation by the same procedure as previously described.

% copper in heads	1.48
% copper in rougher concentrate	7.25
% copper in rougher tailing	.26
% copper recovered in concentrate	93.9

2. Acyl xanthates.

The acyl xanthates, constituting the second class of my new flotation agents, have the following general line formula:



where R represents an alkyl group, and $—C(:O)R^2$ an acyl radical, R^2 representing either a hydrogen radical or a substituted or unsubstituted hydrocarbon radical. Specific examples of this class are:

Benzoyl ethyl-xanthate, $C_2H_5OCS·S—CO·C_6H_5$;

Acetyl ethyl-xanthate, $C_2H_5OCS·S—CO·CH_3$;

Benzoyl propyl-xanthate, $C_3H_7OCS·S—CO·C_6H_5$;

Benzoyl n-butyl-xanthate, $C_4H_9OCS·S—CO·C_6H_5$;

Benzoyl amyl-xanthate, $C_5H_{11}OCS·S—CO·C_6H_5$.

The method of preparing these acyl xanthates may be illustrated by the following example:

280 grams of benzoyl chloride are dissolved in 500 c. c. of benzene, and 320 grams of potassium ethyl-xanthate in 1000 c. c. of ether are added. After allowing the mixture to stand with frequent agitation for several days, the precipitated po'as-

sium chloride is filtered off, and the filtrate evaporated first in a desiccator and then under vacuum by means of a hot water bath. By following this procedure there may be obtained 150 grams of benzoyl ethyl-xanthate having a purity between 83 and 84%, as shown by total sulfur analysis.

When tested as a flotation agent, benzoyl ethyl-xanthate gave the following results when tested in the manner previously described with ore from the Phelps Dodge Corporation:

% copper in heads	1.48
% copper in rougher concentrate	7.55
% copper in rougher tailing	.23
% copper recovered in concentrate	86.9

3. Xanthyl sulfides:

Important flotation agents of this class of compounds are the sulfocarbalkoxyl disulfides such as sulfocarbethoxyl disulfide (that is, ethyl-xanthyl disulfide), sulfocarbomethoxyl disulfide, etc., having the general line formula:

$$R—O—C(S)—S—S—C(S)—O—R'$$

where R and R' represent the same or different hydrocarbon radicals, especially alkyl radicals. This class includes also the corresponding xanthyl monosulfides (that is, xanthic acid anhydrides) such as ethyl-xanthyl monosulfide,

$$C_2H_5OCS\cdot S\cdot CS\cdot OC_2H_5.$$

As examples of other disulfides there may be mentioned,—

Propyl-xanthyl disulfide, $(C_3H_7O—C(S)S\cdot)_2$

n-Butyl-xanthyl-disulfide, $(C_4H_9O—C(S)S\cdot)_2$

Amyl-xanthyl disulfide, $(C_5H_{11}O—C(S)S\cdot)_2$

Flotation tests with ethyl-xanthyl disulfide, carried out in the manner previously described, with ore from the Phelps Dodge Corporation gave the following results:

% copper in heads	1.48
% copper in rougher concentrate	5.96
% copper in rougher tailings	.19
% of copper recovered in concentrate	89.9

Although my flotation agents are effective to a certain extent in an acid pulp, much better results are obtained by operating with a non-acid pulp, that is, one which has been rendered neutral or alkaline, preferably with lime. A frothing agent, as for example terpineol, is also, ordinarily, necessary, since my new flotation agents have little, if any, frothing power.

The xanthyl disulfides described above may be readily prepared by the action of a halogen or other suitable oxidizing agent upon a salt of xanthic acid such as sodium xanthate. A good method for preparing these disulfides, and specifically the n-butyl-xanthyl disulfide, is given by Adams in his U. S. Patent No. 1,491,021. According to that patent sodium hydroxide is mixed with carbon disulfide in approximately molecular proportions, while cooling, just enough water being added to permit the caustic soda to dissolve; the reaction mass is then chlorinated at about 40–50° C., the oil formed being removed. The product of this reaction is n-butyl-xanthyl disulfide.

Although my invention has been described with reference to certain specific examples, it will be understood that my invention is not limited to these examples, but may be modified in various respects without departing from the scope thereof, as set forth in the appended claims.

I claim:

1. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a flotation operation in the presence of an ethyl ester of ethyl xanthic acid.

2. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of an ester of an alkyl-xanthic acid.

3. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of a xanthyl disulfide.

4. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a flotation operation in the presence of an acyl derivative of an alkyl xanthate.

5. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of an ester of a xanthic acid.

6. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of an ester of an alkyl-xanthic acid.

7. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of a sulfocarboxyl sulfide.

8. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of a sulfocarbalkoxyl sulfide.

9. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of an ethyl-xanthyl disulfide.

10. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of an acyl alkyl-xanthate.

11. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of a substance whose molecular structure is that indicated by the following general formula:

$$R—O—C(:S)—S—X$$

where R is a hydrocarbon radical, and X is a radical containing at least one carbon atom.

12. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a non-acid pulp to a froth flotation operation in the presence of a substance whose molecular structure is that indicated by the following general formula:

$$R—O—C(:S)—S—X$$

where R is a hydrocarbon radical, and X is a radical containing at least one carbon atom.

13. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of an alkaline pulp to a froth flotation operation in the presence of a substance whose molecular structure is that indicated by the following general formula:

$$R—O—C(:S)—S—X$$

where R is an aliphatic radical, and X is a radical containing a carbon atom.

14. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of an alkaline pulp to a froth flotation operation in the presence of a substance whose molecular structure is that indicated by the following general formula:

$$R—O—C(:S)—S—X$$

where R is an aliphatic radical, and X is a radical containing both sulfur and carbon atoms.

15. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of an alkaline pulp to a froth flotation operation in the presence of an ester of a xanthic acid.

16. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of an alkaline pulp to a froth flotation operation in the presence of an acyl derivative of an alkyl-xanthic acid.

17. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of an alkaline pulp to a froth flotation operation in the presence of an acetyl alkyl-xanthate.

18. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of an alkaline pulp to a froth flotation operation in the presence of an ethyl alkyl-xanthate.

19. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of an alkaline pulp to a froth flotation operation in the presence of an alkyl-xanthyl disulfide.

20. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of an acyl alkyl xanthate in a non-alkaline medium.

21. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a non-acid pulp to a froth flotation operation in the presence of acetyl ethyl xanthate.

22. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a non-acid pulp to a froth flotation operation in the presence of an alkyl xanthyl disulphide.

23. The process of concentrating ores which consists in agitating a pulp of the ore with di-xanthogen under such conditions that a mineral-bearing froth is formed, and separating the froth.

24. The process of concentrating ores which consists in agitating a pulp of the ore with di-xanthogen in the presence of a mineral-frothing agent so as to produce a mineral-bearing froth, and separating the froth.

25. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of a xanthyl sulfide.

26. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of the product obtained by the reaction of a halogen upon an alkali metal xanthate.

27. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of the product obtained by the reaction of an alkyl halide upon an alkali metal alkyl xanthate.

28. In the process of concentrating ores and minerals by flotation, the step which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of the product obtained by the reaction of an acyl halide upon an alkali metal alkyl xanthate.

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