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FLOTATION REAGENT AND PROCESS OF FROTH FLOTATION

No Drawing. Application filed April 22, 1929. Serial No. 357,339.

This invention relates to esters of xanthic acids and to the separation of minerals and the concentration of ores with the aid of said esters. It relates particularly to aralkyl esters of alkyl and aralkyl xanthic acids, and to the utilization of said esters as modifying or collecting agents in the froth flotation of minerals and ores.

One of the objects of the invention is the provision of efficient mineral collecting agents in the froth flotation of minerals and ores. Another object of the invention is the preparation of new organic compounds which are aralkyl esters of alkyl or aralkyl xanthic acids. These and other objects of the invention will be apparent from a consideration of the following disclosure which is given for the purpose of illustrating the invention.

Metal xanthates (metal salts of alkyl xanthic acids) have been prepared, as is well known, by reacting an alcohol with carbon bisulfide and a suitable metal hydroxide, and it has been heretofore proposed to employ such xanthates as modifying or collecting agents in the froth flotation of minerals.

It has been found, according to the present invention, that by the treatment of a suitable metal xanthate with a suitable aralkyl derivative, esters of alkyl and aralkyl xanthic acids can be obtained which correspond with the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical (such as, CH_3, C_2H_5—, C_3H_7—, C_4H_9—, C_5H_{11}—, C_6H_{13}—, C_7H_{15}—, C_8H_{17}—, C_9H_{19}—, C_6H_{11}—, $C_6H_5CH_2$—, $C_6H_5C_2H_4$—, etc.) and R′ is an aralkyl radical (such as, $C_6H_5CH_2$—, $C_6H_5C_2H_4$—, $(C_6H_5)_3C$—, etc.). It has furthermore been found, according to the present invention, that said esters having the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is an aralkyl radical, are efficient modifying or collecting agents when employed in the separation of minerals and concentration of ores by froth flotation; particularly when R′ in the above formula is an aralkyl hydrocarbon radical or a straight chain aralkyl hydrocarbon radical, specifically a straight chain aralkyl hydrocarbon radical which contains a phenyl radical, and especially when R′ is a benzyl radical.

In preparing the esters of the present invention according to a preferred method of procedure, an alkali-metal salt of an alkyl or aralkyl xanthic acid is reacted with a halide of an aryl-aliphatic compound, preferably in a suitable solvent or diluent; such as, alcohol, benzol, water, and the like. The bodies thus obtained are the crude esters of the present invention. They are generally oils substantially insoluble in water and soluble in ether and benzene. If desired, the crude esters can be purified by a suitable treatment.

In utilizing the said esters in the froth flotation of minerals and the concentration of ores, the mineral or ore is subjected to froth flotation in the presence of one or more of said esters, which may be either crude or purified, and which may be incorporated with the ore or mineral pulp in any suitable manner and at any suitable time that will produce satisfactory flotation. Thus, they may be added to the ore while it is being reduced to a pulp, or they may be added to the pulp either before or after its introduction into the flotation machine; they may, if necessary, be used in conjunction with a suitable or well known frothing agent, such as, pine oil, tar acids, terpineol, etc.; they may be used with lime, copper sulfate, sodium silicate, caustic soda, soda ash, an alkali-metal cyanide, or other conditioning agent; they may be employed in a neutral, alkaline or acid circuit, although a non-acid circuit is preferred; they may be employed in admixture with each other or with other suitable flotation reagents, such as, the organic sulfides, polysulfides, other xanthates, etc.; and they may be added as such or in the form of a solution or suspension in a suitable solvent or suspension medium, such as, water, a suitable frothing agent, another suitable flotation agent, etc.

The amount of ester to be employed in the flotation process will vary, depending upon

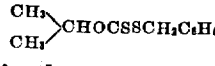
the character and composition of the ore, the particular ester employed, the method of treatment, and the like. In general, one-fifth to one-half pound of ester per ton of dry ore will be sufficient for satisfactory operation.

For a better understanding of the invention, reference should be had to the following specific examples wherein are described and illustrated representative products and methods for producing and employing said products in accordance with the invention; but it is to be understood that the invention is not limited thereto. The parts are by weight.

Aralkyl esters of xanthic acids.

Example 1: Benzyl ester of methyl xanthic acid.—12.6 parts of benzyl chloride is mixed with 14.6 parts of potassium methyl xanthate and 80 parts of ethyl alcohol (denatured) and the mixture are continuously agitated at room temperature for several hours. The resulting mixture is added to about 1,000 parts of water, the water layer is drawn off, and the oil is again washed with about 500 parts of water. The mixture is filtered and the filtrate is allowed to stratify. The oily layer is separated from the aqueous layer, dried over anhydrous sodium sulfate, then over calcium chloride, and then vacuum distilled. The benzyl ester of methyl xanthic acid thus obtained has the probable formula $CH_3OCSSCH_2C_6H_5$, and is a practically colorless liquid having a faint odor. It does not solidify at 0° C., boils at a temperature of about 173° C. (corr.) under 20 millimeters pressure, is soluble in an excess of ethyl alcohol, is very slightly soluble in water, and is readily soluble in ether and benzol.

Example 2: Benzyl ester of isopropyl xanthic acid.—37.8 parts of benzyl chloride (boiling point 178°—179° C.), 60 parts of sodium isopropyl zanthate, and 250 parts ethyl alcohol are mixed and allowed to stand overnight. The resulting benzyl ester of isopropyl xanthic acid having the probable formula



is recovered in the manner above described.

If, in the above example, there are substituted for the alkali-metal xanthates therein employed corresponding molecular proportions of other suitable salts or alkali or aralkyl xanthic acids, (e. g., potassium or sodium salts of ethyl xanthic acid, of normal propyl xanthic acid, of normal and iso-butyl xanthic acids, of normal and iso-amyl xanthic acids, of normal hexyl xanthic acid, of normal heptyl xanthic acid, of normal octyl xanthic acid, of normal nonyl xanthic acid, of cyclohexyl xanthic acid, of benzyl xanthic acid, of phenyl ethyl xanthic acid, and the like), and/or if there are substituted for the benzyl chloride therein employed equivalent molecular proportions of other aralkyl halides (e. g. benzyl bromide, phenyl ethyl chloride or bromide, triphenyl methyl chloride or bromide, etc.), other corresponding aralkyl esters of alkyl and aralkyl xanthic acids may be obtained which, together with the above esters, are included within the probable, general formula

$$ROCSSR'$$

wherein R is an alkyl or aralkyl, such as, CH_3—, C_2H_5—, C_3H_7—, C_4H_9—, C_5H_{11}—, C_6H_{13}—, C_7H_{15}—, C_8H_{17}—, C_9H_{19}—, C_6H_{11}—, $C_6H_5CH_2$—, $C_6H_5C_2H_4$—, etc., and R′ is an aralkyl radical, such as, $C_6H_5CH_2$—, $C_6H_5C_2H_4$—, $(C_6H_5)_3C$—, etc.

Flotation of minerals

Example 3.—500 parts of a copper sulfide ore (from the Chino Mine of the Nevada Consolidated Copper Co., Hurley, N. M.) assaying 1.24 per cent copper, were ground in a ball mill with 215 parts of water and about 0.7 parts hydrated lime (equivalent to about 3 pounds hydrated lime per ton of dry ore) until practically all of the mixture was sufficiently fine to pass a 40 mesh screen (about 1 hour). The ground pulp was diluted with sufficient water to give a mixture containing about 16 per cent solids, and about 0.108 parts of the benzyl ester of ethyl xanthic acid, $C_2H_5OCSSCH_2C_6H_5$, (equivalent to about 0.43 pounds per ton of dry ore) was added. The mixture was subjected to agitation in a Janney flotation apparatus for a few minutes, then a small amount, e. g. 0.02 to 0.03 parts, of pine oil was added, and agitation and flotation were carried out for about 15 minutes with addition of about 0.02 to 0.03 more parts of pine oil. The rougher concentrate thus obtained was refloated for about 5 minutes without any additional flotation agent but with the addition of another small amount of pine oil. 19.4 parts of a cleaner concentrate assaying 25.4 per cent copper were obtained. A recovery of about 80 per cent of the copper was therefore obtained in the cleaner concentrate. The tailings assayed 0.178 per cent copper. The equivalent of about 25.8 tons of ore was required to give about 1 ton of concentrate.

Example 4.—500 parts of copper sulfide ore (from the Chino Mine of the Nevada Consolidated Copper Co.) assaying 1.16 per cent copper were treated as described in Example 3, with the difference that no lime was added and about 0.1 part of the benzyl ester of isopropyl xanthic acid,

$$(CH_3)_2CHOCSSCH_2C_6H_5,$$

produced as described in Example 2 (equivalent to about 0.4 pounds per ton of dry ore) was employed. 19.3 parts of a concentrate

assaying 18.4 per cent copper were obtained. The tailings assayed 0.33 per cent copper.

In a similar manner other aralkyl esters of alkyl or aralkyl xanthic acids may be employed as collecting agents in the froth flotation of minerals and the concentration of ores.

It will be understood that the invention is not limited to the specific examples given above, but may be varied within wide limits without departing from the spirit and scope of the claims.

Thus, in preparing the esters, other suitable methods of preparation may be employed. Instead of the metal xanthates employed in the above examples, other suitable metal xanthates may be employed, and even the crude reaction mixture resulting from the reaction of an alcohol, carbon disulfide and an alkali-metal hydroxide may often be used.

This application contains subject-matter broadly claimed in my copending application Ser. No. 357,338 filed on even date herewith for froth flotation of minerals.

I claim:

1. A composition of matter comprising an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is CH_3—, C_3H_7—, C_4H_9—, C_5H_{11}—, C_6H_{13}—, C_7H_{15}—, C_8H_{17}—, C_9H_{19}—, C_6H_{11}—, or an aralkyl radical; and R′ is an aralkyl radical.

2. A composition of matter comprising an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is CH_3—, C_3H_7—, C_4H_9—, C_5H_{11}—, C_6H_{13}—, C_7H_{15}—, C_8H_{17}—, C_9H_{19}—, C_6H_{11}—, $C_6H_5CH_2$—, or $C_6H_5C_2H_4$—; and R′ is an aralkyl radical.

3. A composition of matter comprising an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is CH_3—, C_3H_7—, C_4H_9—, C_5H_{11}—, C_6H_{13}—, C_7H_{15}—, C_8H_{17}—, C_9H_{19}—, C_6H_{11}—, $C_6H_5CH_2$—, or $C_6H_5C_2H_4$—; and R′ is an aralkyl hydrocarbon radical.

4. A composition of matter comprising an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is a straight chain aralkyl hydrocarbon radical.

5. A composition of matter comprising an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is a straight chain aralkyl hydrocarbon radical which contains a phenyl radical in its composition.

6. A composition of matter comprising an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl radical, and R′ is a straight chain aralkyl hydrocarbon radical.

7. A composition of matter comprising a benzyl ester of an alkyl xanthic acid having the probable formula

$ROCSSCH_2C_6H_5$

wherein R is an alkyl radical.

8. In the separation of minerals by flotation, the step which comprises subjecting a mineral pulp to a froth flotation operation in the presence of an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is an aralkyl radical.

9. In the separation of minerals by flotation, the step which comprises subjecting a mineral pulp to a froth flotation operation in the presence of an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is an aralkyl hydrocarbon radical.

10. In the separation of minerals by flotation, the step which comprises subjecting a mineral pulp to a froth flotation operation in the presence of an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is a straight chain aralkyl hydrocarbon radical.

11. In the separation of minerals by flotation, the step which comprises subjecting a mineral pulp to a froth flotation operation in the presence of an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is a straight chain aralkyl hydrocarbon radical which contains a phenyl radical in its composition.

12. In the separation of minerals by flotation, the step which comprises subjecting a mineral pulp to a froth flotation operation in the presence of an aralkyl ester of an alkyl xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl radical, and R′ is an aralkyl radical.

13. In the separation of minerals by flotation, the step which comprises subjecting a mineral pulp to a froth flotation operation in the presence of an aralkyl ester of an alkyl xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl radical, and R′ is a straight chain aralkyl hydrocarbon radical which contains a phenyl radical in its composition.

14. In the separation of minerals by flotation, the step which comprises subjecting a mineral pulp to a froth flotation operation in the presence of a benzyl ester of an alkyl xanthic acid.

15. In the separation of minerals by flotation, the step which comprises subjecting a copper sulfide mineral pulp to a froth flotation operation in the presence of an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is an aralkyl radical.

16. In the separation of minerals by flotation, the step which comprises subjecting a copper sulfide mineral pulp to a froth flotation operation in the presence of an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is a straight chain aralkyl hydrocarbon radical.

17. In the separation of minerals by flotation, the step which comprises subjecting a copper sulfide mineral pulp to a froth flotation operation in the presence of a benzyl ester of an alkyl xanthic acid.

In testimony whereof I affix my signature.

ROBERT L. PERKINS.

13. In the separation of minerals by flotation, the step which comprises subjecting a mineral pulp to a froth flotation operation in the presence of an aralkyl ester of an alkyl xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl radical, and R′ is a straight chain aralkyl hydrocarbon radical which contains a phenyl radical in its composition.

14. In the separation of minerals by flotation, the step which comprises subjecting a mineral pulp to a froth flotation operation in the presence of a benzyl ester of an alkyl xanthic acid.

15. In the separation of minerals by flotation, the step which comprises subjecting a copper sulfide mineral pulp to a froth flotation operation in the presence of an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is an aralkyl radical.

16. In the separation of minerals by flotation, the step which comprises subjecting a copper sulfide mineral pulp to a froth flotation operation in the presence of an ester of a xanthic acid having the probable formula

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is a straight chain aralkyl hydrocarbon radical.

17. In the separation of minerals by flotation, the step which comprises subjecting a copper sulfide mineral pulp to a froth flotation operation in the presence of a benzyl ester of an alkyl xanthic acid.

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CERTIFICATE OF CORRECTION.

Patent No. 1,819,113. **Granted August 18, 1931, to**

ROBERT L. PERKINS.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, line 19, for the word "is" read are; same page, line 22, for the word "are" read is, line 56, for "or alkali" read of alkyl, and, line 78, before the comma and after the word "aralkyl" insert the word group; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 6th day of October, A. D. 1931.

M. J. Moore,
Acting Commissioner of Patents.

(Seal)

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