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FROTH FLOTATION OF MINERALS

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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 aryl and 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 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 that by the treatment of a suitable metal xanthate with a suitable aryl or aralkyl derivative, esters of alkyl and aralkyl xanthic acids can be obtained which contain an aryl nucleus in their composition and 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_6C_{11}—, $C_6H_5CH_2$—, $C_6H_5C_2H_4$—, etc.); and R′ is an aryl or aralkyl radical (such as, C_6H_5—, $CH_3C_6H_4$—, $(CH_3)_2C_6H_3$—, $C_6H_5CH_2$—, $C_6H_5C_2H_4$— $(C_6H_5)_3C$—, etc.). It has furthermore been found that said esters having the probable formula:

ROCSSR′

wherein R is an alkyl or aralkyl radical, and R′ is an aryl or aralkyl radical, are highly selective and 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 a hydrocarbon radical which contains a phenyl radical in its composition, and especially when R′ is a hydrocarbon radical of the benzene series, specifically a phenyl 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 diazo salt of an aromatic compound, or with a halide of an aryl-aliphatic compound, preferably in a suitable solvent or diluent; such as, water, alcohol, 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 the 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 employed in the flotation process will vary, depending upon the character and composition of the ores, 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.

Aryl esters of xanthic acids

Example 1: Phenyl ester of methyl xanthic acids.—9.3 parts of aniline is diazotized in the usual manner with sodium nitrite and hydrochloric acid, and the solutions are treated with sodium carbonate solution until faintly acid to Congo red paper. 14.7 parts of potassium methyl xanthate are dissolved in about 100 parts of water at about 80° C. The diazotized aniline solution is slowly run into the warm agitated xanthate solution, nitrogen being given off in the reaction. Care is taken to prevent the reaction from foaming over due to the too rapid evolution of nitrogen. Upon completion of the addition of the diazo solution, the reaction mixture is agitated for an additional hour and then allowed to stratify by standing for about an hour. The oil which separates is removed from the aqueous layer, is filtered with suction, is washed, first with dilute caustic alkali, then with dilute acid, and then with water until the wash water reacts neutral to Congo red paper, and is dried over anhydrous sodium sulfate. The phenyl ester of methyl xanthic acid thus obtained has the probable formula $CH_3OCSSC_6H_5$, and is a dark red-brown oil, very slightly soluble in water, and readily soluble in ether. If desired, the ester can be further purified by distillation with steam, extraction of the distillate with ether, and evaporation of the ether from the extract.

Example 2: Tolyl ester of isopropyl xanthic acid.—60 parts of isopropyl alcohol, 40 parts of sodium hydroxide and 76 parts of carbon bisulfide are mixed with agitation while maintaining the temperature between about 20° to 28° C. 38 parts of the resulting crude sodium isopropyl xanthate is dissolved in about 300 parts of water, and the excess alkali is neutralized with hydrochloric acid until neutral to Clayton yellow paper. 21.4 parts of o-toluidine are diazotized with sodium nitrite and hydrochloric acid in the usual manner, the solution is treated with sodium carbonate solution until faintly acid to Congo red paper, and the resulting o-diazo-toluene chloride solution is gradually added to the aqueous isopropyl xanthate solution heated to a temperature of about 70° C. The temperature rises to about 90° to 95° C. Upon treating the resulting reaction mixture in the manner described in Example 1, the o-tolyl ester of isopropyl xanthic acid having the probable formula

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHOCSSC_6H_4CH_3$$

is obtained as a red-brown oil, soluble in ether and benzol, and very slightly soluble in water.

If, in the above examples, there are substituted for the alkali-metal xanthates therein employed corresponding molecular proportions of other suitable salts of alkyl or aralkyl xanthic acids (e. g., sodium methyl xanthate, alkali-metal salts 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 benzyl xanthic acid, of phenyl ethyl xanthic acid, of cyclo-hexyl xanthic acid, etc.) and/or there are substituted for the salts of diazotized aniline and o-toluidine therein employed corresponding molecular proportions of other salts of diazotized aryl amines (e. g., the chlorides or sulfates of diazotized p-toluidine, of diazotized xylidine, of diazotized cumidine. of diazotized benzidine, of diazotized anisidines, of diazotized alpha- or beta-naphthylamines, of diazotized beta-amino anthraquinone, and the like) corresponding aryl esters of alkyl or aralkyl xanthic acids may be obtained. These esters are all included in the probable, general 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 aryl radical.

Instead of a diazotized arylamine, an aralkyl halide (e. g., benzyl chloride or bromide, phenyl ethyl chloride or bromide, triphenyl methyl chloride or bromide, etc.) may be reacted with a metal salt of an alkyl or aralkyl xanthic acid, as illustrated in the following example, whereby aralkyl esters of alkyl or aralkyl xanthic acids may be obtained having the probable, general 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.

Aralkyl esters of xanthic acids

Example 3: Benzyl ester of ethyl xanthic acid.—12.6 parts of benzyl chloride are mixed with 16.1 parts of potassium ethyl xanthate and 80 parts of ethyl alcohol (denatured), and the mixture is 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 ethyl xanthic acid thus obtained is a practically colorless liquid having a faint odor. It does not solidify at 0° C., boils at a temperature of about 172.5° C. (corr.) under 15 millimeters pressure, is soluble in alcohol to the extent of about 1 part in 6 parts of alcohol at 21° C., is very slightly soluble in water, and readily soluble in ether and benzol. It has the probable formula, $C_2H_5OCSSCH_2C_6H_5$.

Flotation of minerals

Example 4.—500 parts of a copper sulfide ore (from the Chino mine of the Nevada Consolidated Copper Co., Hurley, N. M.) assaying 1.26 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 0.054 parts of phenyl ester of ethyl xanthic acid,

$$C_2H_5OCSSC_6H_5,$$

(equivalent to about one-fifth pound 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. 27.5 parts of a cleaner concentrate assaying 19.18 per cent copper were obtained. A recovery of about 84 per cent of the copper was therefore obtained in the cleaner concentrate. The tailings assayed 0.145 per cent copper. The equivalent of about 18.3 tons of ore was required to give about 1 ton of concentrate.

Example 5.—500 parts of copper sulfide ore (from the Chino mine of the Nevada Consolidated Copper Co.) assaying 1.33 per cent copper were treated as described in Example 4, with the difference that 1.0 part of hydrated lime (equivalent to about 4 pounds per ton of dry ore) and about 0.05 part of phenyl ester of methyl xanthic acid, $CH_3OCSSC_6H_5$, produced as described in Example 1, (equivalent to about 0.2 pounds per ton of dry ore) were employed. 10.6 parts of a concentrate assaying 42.90 per cent copper were obtained. The tailings assayed 0.25 per cent copper. This illustrates the high selective action of the esters of the present invention with respect to copper sulfide minerals.

In a similar manner other aryl and aralkyl esters of alkyl and 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. The diazo-aromatic salts employed may be prepared in any suitable manner, preferably by the diazotization of the corresponding primary aromatic amine.

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 aryl or 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}—, or an aralkyl radical; and R′ is a hydrocarbon radical which contains a phenyl radical in its composition.

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 aryl or aralkyl radical.

4. 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 aryl radical.

5. 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 a hydrocarbon radical of the benzene series.

6. 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 a phenyl radical.

7. A composition of matter comprising an ester of an alkyl 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}—, or C_6H_{11}—; and R'' is an aryl radical.

8. A composition of matter comprising an ester of an alkyl 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}—, or C_6H_{11}—; and R'' is a hydrocarbon radical of the benzene series.

9. A composition of matter comprising an ester of an alkyl 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}—, or C_6H_{11}—; and R'' is a phenyl radical.

10. A composition of matter comprising an ester of an alkyl xanthic acid having the probable formula

$ROCSSC_6H_5$

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}—, or C_6H_{11}—.

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 an aryl or aralkyl radical.

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 ester of a xanthic acid having the probable formula

ROCSSR'

wherein R is an alkyl or aralkyl radical, and R' is an aryl or aralkyl radical which contains a hydrocarbon radical of the benzene series in its composition.

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 ester of a xanthic acid having the probable formula

ROCSSR'

wherein R is an alkyl or aralkyl radical, and R' is a 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 an ester of a xanthic acid having the probable formula

ROCSSR''

wherein R is an alkyl or aralkyl group and R'' is an aryl radical.

15. 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 group and R'' is a phenyl radical.

16. 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 an alkyl xanthic acid having the probable formula

ROCSSR'

wherein R is an alkyl group and R' is an aryl or aralkyl radical.

17. 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 an alkyl xanthic acid having the probable formula

ROCSSR'

wherein R is an alkyl group and R' is a hydrocarbon radical which contains a phenyl radical in its composition.

18. 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 an alkyl xanthic acid having the probable formula

$$ROCSSR''$$

wherein R is an alkyl group and R'' is a phenyl radical.

19. 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 an alkyl xanthic acid having the probable formula

$$ROCSSC_6H_5$$

wherein R is an alkyl group.

20. 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 aryl or aralkyl radical.

21. 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 group and R'' is a phenyl radical.

22. 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 an alkyl xanthic acid having the probable formula

$$ROCSSR'$$

wherein R is an alkyl group and R' is an aryl or aralkyl radical.

23. 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 an alkyl xanthic acid having the probable formula

$$ROCSSC_6H_5$$

wherein R is an alkyl group.

In testimony whereof I affix my signature.

ROBERT L. PERKINS.