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FLOTATION PROCESS WITH CYANOETHYL ALKYLXANTHATE ESTERS

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4 Claims. (Cl. 209—166)

ABSTRACT OF THE DISCLOSURE

A new class of cyanoethyl alkyl xanthates having the formula

$$RO-\overset{\overset{S}{\|}}{C}-SCH_2CH_2CN$$

where R is an alkyl radical of from 3 to 8 carbon atoms are useful as flotation promoters in the froth flotation of metal-bearing ores, such as copper ores, to recover the mineral values thereof.

This application is a division of my copending application Ser. No. 241,144 now Patent Number 3,226,416, filed Nov. 30, 1962.

This invention generally relates to xanthate esters. More specifically, it relates to the provision of a new class of cyanoethyl alkylxanthates of the following formula:

$$RO-\overset{\overset{S}{\|}}{C}-SCH_2CH_2CN \qquad I$$

wherein R is an alkyl radical of from three to eight carbons. Furthermore, it relates to the use of these xanthates as promoters in the flotation of base metal ores.

Alkylxanthates as a general class, are known compounds, and some have been employed as promoters in ore flotation. Many members of this class, however, are not satisfactory for this purpose. It is, therefore, surprising that the compounds of Formula I are extremely effective in the recovery of metals, such as copper, from sulfide ores containing them. The surprise is heightened upon the discovery that even the chemically more similar prior art xanthates are relatively ineffective in this field of utility.

Compounds of Formula I, in the most preferred embodiment of this invention, are prepared by the reaction of an alkali metal (e.g., sodium or potassium) alkylxanthate wherein the alkyl radical has from three to eight carbons (e.g., n-propyl, isopropyl, n-butyl, sec. butyl, isobutyl, amyl, hexyl and octyl) with β-halopropionitrile (e.g., β-chlorpropionitrile). The reaction may be conducted in an aqueous medium or in an organic solvent (preferably a water-miscible one) such as acetone or tetrahydrofuran. Approximately molar proportions of each reactant may be used. The reaction proceeds at ambient temperature, yielding the desired product as an oil and an alkali metal halide (e.g., sodium chloride). The product may be isolated and purified by conventional methods.

In an alternative precedure, compounds of Formula I may be obtained by reaction of an alkali metal alkylxanthate with acrylonitrile in an aqueous medium. This reaction proceeds in accordance with the following equation:

$$R-O\overset{\overset{S}{\|}}{C}-SM + CH_2{=}CHCN \xrightarrow{H_2O} RO\overset{\overset{S}{\|}}{C}SCH_2CH_2CN + MOH$$

wherein M is an alkali metal. The reaction mixture becomes highly alkaline as the reaction approaches completion, and various hydrolytic side-reactions occur as a result of this. It has be discovered that these interfering

side-reactions can be held to a minimum and almost eliminated entirely if the pH is maintained at about 7–10 by neutralizing the alkali as fast as it is formed using an acid such as hydrochloric acid or any other strong acid, either organic or inorganic.

The compounds of this invention can be employed as flotation promoters in a conventional way. Thus, general flotation practice is to grind an ore in water to liberate its mineral values from gangue and to aerate the resulting ore pulp in the presence of a forthing agent and one or more promoters. The function of the forthing agent is to create a forth column at the surface of the ore pulp, which acts as a medium of separation to remove the mineral values from the body of the pulp. The promoter serves to promote the flotation of the mineral values by the froth, or serves as a collector for these values. In certain flotation operations, chemicals known as modifiers may be added which serve to accelerate flotation, to inhibit the flotation of unwanted minerals in the froth, to control the pH of the pulp, etc. The mineral-laden froth is removed from the flotation machine and the resulting concentrate of the desired minerals may be further upgraded, as required, by reflotation.

The xanthate esters, herein described, are excellent promoters for metallic ores where values occur in the form of free metals such as copper and gold; and for ores whose values occur as, or associated with, sulfide, oxide and oxidized minerals. Examples of the latter include copper, lead, zinc, gold, silver, iron, mercury, arsenic, antimony and molybdenum ores.

The xanthate ester promoters, herein described, are readily applied in the flotation techniques and equipment in regular use and function well in both pneumatic and mechanical types of flotation cells. These promoters may be used with flotation frothers such as pine oils, creosols, alcohols, polyglycols and alkoxyalkanes; with froth modifiers such as hydrocarbons, oils, creosotes; and with various flotation modifiers such as activaters, depressants, dispersants and pH regulators. They may also be used in combination with other promoters such as other xanthates, dithiophosphates, mercaptobenzothiazole derivatives, dithiocarbamates, xanthate esters and improve the efficiency of such promoters in many applications.

The xanthate esters of this invention are especially effective for floating copper ores in flotation circuits of low pH, but also are highly effective in low concentrations of alkali, as well as at high pH commonly used in floating copper ores.

It is a notable advantage of the compounds of Formula I that they are quite effective as flotation promoters at basic pH values approximating neutrality. Thus, in cases where the natural pH of the ore is 7 or higher, flotation may be effected even without the addition of lime. This is in direct contrast to most flotation promoters which are not generally satisfactory at a pH below about 9.

The following examples are presented to further illustrate the present invention.

Example 1.—2-cyanoethyl isopropylxanthate

To 79.0 g. of sodium isopropylxanthate in 250 ml. of water there was added 44.7 g. of β-chloropropionitrile. The mixture was stirred at room temperature overnight. The aqueous layer was separated from the insoluble oil and extracted with chloroform. The extract was mixed with the oil and then treated with activated carbon. Upon filtration and removal of volatiles at 80° C./1 mm. for 2 hours, there remained a light yellow oil, weighing 74.6 g.

Example 2.—2-cyanoethyl sec-butylxanthate

The procedure of Example 1 was repeated except that 86 g. of sodium sec-butylxanthate was used. The yield was 68.0 g. of a light-yellow oil.

Example 3.—2-cyanoethyl amylxanthate

The procedure of Example 1 was repeated except that 81.0 g. of potassium amylxanthate and 35.8 g. of β-chloropropionitrile were used. The product was a light yellow oil weighing 60.6 g. which distilled at 125–126° C./0.35–0.45 mm.

Example 4.—2-cyanoethyl hexylxanthate

The procedure of Example 1 is repeated using equimolal quantities of sodium hexylxanthate and acrylonitrile, thereby yielding 2-cyanoethyl hexylxanthate as an oil.

Example 5.—2-cyanoethyl isopropylxanthate

The procedure of Example 1 was repeated except that 28.6 g. of acrylonitrile was substituted for β-chloropropionitrile. The yield was only 25.9 g. and the product was of lesser purity than in Example 1.

Example 6.—2-cyanoethyl isopropylxanthate

The procedure of Example 5 was repeated except that acrylonitrile was added over a period of one hour while CO_2 gas was introduced into the reaction mixture concurrently. The yield was 70%.

Example 7

The procedure of Example 5 was repeated except that an equivalent amount of concentrated hydrochloric acid was added instead of CO_2 to keep the pH at 8.0–9.5. The yield was 74%.

Example 8.—2-cyanoethyl secondary butylxanthate

The procedure of Example 5 is repeated using 202 grams of sodium secondary butylxanthate (90%) in 150 ml. of water to which 58.3 grams of acrylonitrile and 100 grams of hydrochloric acid diluted with water to 200 ml., were added over a period of about five hours. The product is obtained.

Example 9.—2-cyanoethyl amylxanthate

The procedure of Example 5 is followed over a period of about 4 hours at 40–45° C., using 202 grams of potassium amylxanthate (81%) in 150 ml. of water, 58.3 grams of acrylonitrile, and 100 grams of hydrochloric acid diluted with water to 200 ml. A yield of about 81% is obtained.

Example 10.—2-cyanoethyl hexylxanthate

The procedure of Example 5 is followed with molal quantities of sodium hexylxanthate and acrylonitrile and 200 ml. of the diluted hydrochloric acid as used in the last example. A yield of about 80% of 2-cyanoethyl hexylxanthate is obtained.

Example 11.—2-cyanoethyl octylxanthate

To 4.8 g. of potassium n-octylxanthate in 30 ml. of acetone there is added 2.2 g. of β-chloropropionitrile. The mixture is refluxed for 150 minutes and filtered to remove potassium chloride. The filtrate is then heated to 90° C. at a pressure of 0.5 mm. to remove any volatiles. The residue is a light-yellow oil, weighing 4.6 g.

Example 12

Products of the preceeding examples are employed as promoters in the following manner:

A copper ore (0.8% Cu) from the Western United States is ground for 6 minutes at 60% solids with 0.03 lb. of promotor per ton of ore, is conditioned for 3 minutes at 22% solids with 0.025 lb. fuel oil and 0.09 lb. cresylic acid per ton of ore and floated for 6 minutes at pH of 7.7. The pulp tailing is filtered off, dried and analyzed for residual copper with the following results.

TABLE I

Promoter:	Percent Cu in tailing
2-cyanoethyl amylxanthate	0.15
2-cyanoethyl sec-butylxanthate	0.16
2-cyanoethyl isopropylxanthate	0.18
2-cyanoethyl-octylxanthate	0.18

Example 13

A second copper ore (0.68% Cu) from the Western United States was ground 6 minutes at 60% solids with 1.5 lb. lime/ton (pH=7.8) and 0.05 lb. promoter/ton, conditioned 5 minutes at 22% solids with 0.1 lb. polypropylene glycol per ton as frother, and floated for 4 minutes. Comparing the results thus obtained with tests in which allyl amylxanthate and 2-cyanoethyl ethylxanthate were employed, the following results are obtained.

TABLE II

Promoter:	Percent Cu in tailing
Allyl amylxanthate	0.16
2-cyanoethyl isopropylxanthate	0.09
2-cyanoethyl sec-butylxanthate	0.10
2-cyanoethyl amylxanthate	0.11
2-cyanoethyl ethylxanthate	0.21

As will be seen from Table II, the 2-cyanoethyl alkyl xanthates typical of the present invention, i.e., 2-cyanoethyl isopropyl-, 2-cyanoethyl secondary butyl- and 2-cyanoethyl amyl xanthates, provide markedly improved copper recovery over allyl amyl xanthate and 2-cyanoethyl ethyl xanthate.

I claim:

1. The process of beneficiating metal sulfide ores which comprises grinding said ores and subjecting the ground ore to froth flotation in the presence of a compound of the formula:

$$RO-\overset{\overset{S}{\|}}{C}-SCH_2CH_2CN$$

wherein R is an alkyl radical having three to eight carbon atoms, and to obtain a relatively high concentration of metal sulfide in the froth.

2. The process of claim **1** wherein R is isopropyl.

3. The process of claim **1** wherein R is amyl.

4. The process of claim **1** wherein the ore is a copper-containing ore.

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