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ALLYL ESTERS OF ALKYL XANTHATES

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This invention relates to new sulfur-linked esters and to processes of using them in froth flotation. The esters may be considered as having the following type formula:

$$(RO)_n-\overset{S}{\overset{\|}{X}}-SCH_2-CH=CH_2$$

in which n is a positive integer not greater than 2, R is a saturated hydrocarbon radical having from 1–6 carbon atoms and X is selected from the group consisting of carbon and phosphorus. By way of nomenclature the compounds of the present invention may be considered as S-allyl xanthates or dithiophosphates.

Xanthates and dithiophosphates have long been standard collectors in the froth flotation of sulfide and precious metal ores. However, the universal applicability of these reagents has been seriously affected by the fact that in the case of certain ores, notably certain sulfide ores of copper which are floated in acid circuit, the efficiency of the ordinary xanthates and dithiophosphates has been low and excessive losses of valuable mineral in the flotation tailings have taken place. The reagents of the present invention show a remarkably enhanced recovery when they are used as collectors with certain ores in acid circuit flotation. This desirable property is obtained without any off-setting lack of efficiency with other ores. In other words, the reagents of the present invention can be used with the same success as ordinary xanthates and dithiophosphates with ores for which these latter are suitable collectors and, in addition, produce markedly improved results with certain difficultly floating ores, in some cases, making certain of the lower grades of these ores commercially available as a source of copper.

The uniformly good results obtained with the compounds of the present invention are surprising because very closely related compounds do not show the same properties, for example, S-allyl allyl xanthate shows very inferior results in the flotation of certain copper ores. It is not known why the improved results of the present invention are obtained when the allyl group is present in the molecule, linked to carbon or phosphorus through sulfur, and are completely destroyed if there is in the molecule another allyl group. Since we have no explanation for this eccentric behavior, the invention is not intended to be limited to any theory of action or flotation mechanism.

The compounds of the present invention find their greatest field of utility as collectors in froth flotation. This, however, is not their only use as some of them are effective as insecticides and rubber chemicals. From the standpoint of the compounds as new chemical compounds, therefore, it is not intended to limit the invention to any particular use thereof. However, in a more specific aspect, froth flotation processes utilizing the new compounds as collectors are included within the scope of the invention.

The invention will be described in greater detail in conjunction with the following specific examples, the parts being by weight unless otherwise specified.

EXAMPLE 1

Allyl methylxanthate

Thirty-one parts of potassium hydroxide were wet with

7 parts of water and mixed with 18 parts of methyl alcohol and 50 parts by volume of acetone. 38 parts of carbon disulfide were added gradually at a temperature below 40° C. After reaction was complete, 38.2 parts of allyl chloride were added gradually at a temperature below 45° C. Reaction was completed by refluxing for a few minutes. The mixture was treated with 500 parts of water and an oil layer was recovered which was washed with 250 parts of water. The crude red oil, 66 parts, was dried with sodium sulfate and distilled. 42 parts of light yellow liquid were recovered between 75–97° C. at 15 mm. pressure.

EXAMPLE 2

Allyl n-propylxanthate

Sixty-six parts of sodium hydroxide were dissolved in 30 parts of water and added to 400 parts of n-propyl alcohol. 125 parts of carbon disulfide were added gradually with stirring at a temperature below 13° C. The resulting solution was allowed to warm to room temperature. 109 parts of allyl chloride were added gradually at a temperature below 42° C. Near the end of the addition cooling was discontinued and the temperature was allowed to rise spontaneously to 57° C. The sodium chloride was filtered off and washed with n-propyl alcohol. 85 parts were obtained. The filtered solution was diluted with 500 parts of water and the oil thus obtained was washed with 250 parts of water. The product was shaken with 5 parts of sodium sulfate, filtered and warmed on the water bath under reduced pressure to remove volatile contaminants. 216 parts of light yellow liquid remained.

EXAMPLE 3

Allyl ethylxanthate

Fifty-five parts of sodium ethylxanthate (flotation reagent grade) were mixed with 90 parts by volume of acetone and filtered from insoluble material. 24 parts of allyl chloride were added rapidly with stirring. The temperature rose steadily to 65° C. where refluxing occurred for a few minutes. After cooling to room temperature the mixture was filtered from sodium chloride. Eighteen parts were obtained. The filtered solution was diluted with 200 parts of water, and the oil layer thus obtained was washed with 200 parts of water. The product was dried by warming on the water bath under reduced pressure. 40 parts of pale yellow liquid remained.

EXAMPLE 4

Allyl sec-butylxanthate

253 parts of reagent grade sodium sec-butylxanthate were dissolved in 500 parts of water. 101 parts of allyl chloride were added to the well stirred solution in three portions at 15 minute intervals. A little cooling was needed to keep the temperature below 45° C. to avoid loss of allyl chloride. The mixture was finally warmed to 48° C. for 2 hours to assure complete reaction. The aqueous layer was discarded and the oily layer was washed with 250 parts of water. The product was treated with 5 parts of sodium sulfate, decanted cleanly and warmed on the water bath under reduced pressure to remove volatile contaminants. 234 parts of golden yellow oil were obtained.

EXAMPLE 5

Allyl isopropylxanthate

3,440 parts of reagent grade sodium isopropylxanthate were suspended with good agitation in 4,000 parts of water. 1,575 parts of allyl chloride were added gradually at a temperature below 45° C. The mixture was stirred and warmed to 60° C. to assure complete reaction. The aqueous layer was discarded and the oily layer was

warmed on the water bath under reduced pressure to remove moisture and volatile materials. 3,330 parts of a light yellow oil were obtained.

EXAMPLE 6

Allyl esters of a variety of xanthates were produced according to the procedures of Examples 1 to 5 inclusive with the results given in the accompanying table:

Allyl esters of alkyl xanthates

Sodium Alkyl Xanthate		Weight, grams	
Type	Grams	Allyl Chloride	Product
Butyl	244	101	222
Isobutyl	240	101	226
sec-Amyl	62	15	38
"Pentasol"	62	15	37
Methylamyl	54	19	38
Cyclohexyl	55	19	45

EXAMPLE 7

Ally diisopropyl- and disec. butyldithiophosphate

Fifteen and one-half parts of allyl chloride were added to a solution containing 52 parts of sodium diisopropyldithiophosphate in 210 parts by volume of methyl ethyl ketone. The mixture was stirred and heated at 71° C. for 1½ hours to assure complete reaction. After cooling to room temperature, 200 parts of water were added to dissolve the sodium chloride. Treatment of the organic layer with 600 parts of water removed most of the solvent. The product was freed of moisture and volatile materials by warming on a water bath under reduced pressure. 50 parts of dark amber-colored liquid remained.

Similarly, 43.7 parts of allyl disec. butyldithiophosphate were obtained by reacting 14 parts of allyl chloride and a solution containing 54 parts of disec. butyldithiophosphate in 210 parts by volume of methyl ethyl ketone.

EXAMPLE 8

Allyl diethyldithiophosphate

84 parts of allyl chloride were added to a solution containing 251 parts of sodium diethyldithiophosphate in 1,000 parts of water. The mixture was stirred and heated at 48–52° C. for four and one-half hours. The aqueous layer was discarded and the organic layer was treated with 5 parts of sodium sulfate to remove moisture and heated on a water bath under reduced pressure to remove volatile contaminants. 198 parts of light amber-colored liquid were obtained.

EXAMPLE 9

A South American copper ore, assaying about 2.1% Cu, was ground to about minus 65 mesh in the presence of 0.2 lb./ton of various 3-carbon atom esters of 3-carbon atom alkyl xanthates as promoters. The ore pulp was diluted to about 22% solids and 5.4 lb./ton sulfuric acid and 0.22 lb./ton cresylic acid frother added. The ore was floated for 9 minutes to remove a concentrate of the copper-bearing minerals. The results of the flotation tests with the above-mentioned esters are summarized in the following table:

Test No.	Concentrate, Percent Copper		Tailing, Percent Copper Assay	Promoter
	Assay	Distribution		
1	18.61	83.01	0.38	Allyl Isopropylxanthate.
2	15.42	41.73	1.27	Allyl Allylxanthate.
3	19.05	77.61	0.50	Propyl Isopropylxanthate.
4	20.06	75.68	0.55	Isopropyl Isopropylxanthate.

EXAMPLE 10

A second South American sulfide copper ore, assaying 2.0% Cu, was treated as described in Example 9, using 0.2 lb./ton of various allyl esters of alkyl xanthates. Sulfuric acid and cresylic acid frother in the respective amounts of 6.8 lb./ton and 0.29 lb./ton were used. A control test with sodium ethylxanthate was conducted also. The following table lists the various allyl esters used as promoters together with the metallurgical results:

Test No.	Concentrate, Percent Copper		Tailing, Percent Copper Assay	Promoter Used
	Assay	Distribution		
1	18.76	83.58	0.36	Allyl Methylxanthate.
2	18.44	81.02	0.42	Allyl Ethylxanthate.
3	17.14	85.38	0.32	Allyl Propylxanthate.
4	16.47	86.20	0.31	Allyl Isopropylxanthate.
5	16.13	87.17	0.28	Allyl Butylxanthate.
6	15.80	87.28	0.28	Allyl Isobutylxanthate.
7	18.08	87.41	0.29	Allyl Sec. butylxanthate.
8	20.45	80.21	0.45	Allyl Sec. amylxanthate.
9	18.77	79.73	0.48	Allyl Pentasolxanthate.
10	18.45	40.03	0.96	Sodium Ethylxanthate.

EXAMPLE 11

The allyl esters of xanthates are effective promoters in the flotation step of the leach-precipitation-flotation process which is frequently used on copper ores containing oxidized copper minerals or combinations of oxide and sulfide copper minerals. An ore from the northwestern part of the United States, containing both sulfide and oxide copper minerals and assaying about 1.6% total copper, was ground and leached with sulfuric acid. The copper was precipitated by means of sponge iron and any unused iron was removed by magnetic separation methods. The sulfide copper minerals and precipitated copper were floated with 0.04 lb./ton pine oil and 0.2 lb./ton of the allyl esters of various alkylxanthates. The results of several flotation tests are as follows:

Test No.	Concentrate, Percent Copper		Tailing, Percent Copper Assay	Promoter Used
	Assay	Distribution		
1	7.79	82.50	0.11	Allyl Ethylxanthate.
2	7.17	78.29	0.13	Allyl Methylxanthate.
3	6.44	80.88	0.13	Allyl Propylxanthate.

EXAMPLE 12

A zinc ore (about 2.65% Zn) from the southeastern part of the United States was floated with various allyl esters. The ore was ground to minus 65 mesh and diluted to 22% solids. The pulp was agitated in a Fagergren flotation machine with 0.5 lb./ton copper sulfate for 5 minutes and then 0.1 lb./ton pine oil and 0.1 lb./ton allyl ester of various xanthates added to float off a zinc concentrate. Test results follow:

Test No.	Concentrate, Percent Zinc		Tailing, Percent Zinc Assay	Promoter Used
	Assay	Distribution		
1	46.61	95.69	0.12	Allyl Isopropylxanthate.
2	46.83	95.71	0.12	Allyl Ethylxanthate.
3	45.97	95.84	0.12	Allyl Propylxanthate.
4	47.13	95.78	0.12	Allyl Sec. butylxanthate.

EXAMPLE 13

The allyl esters of diethyl, diisopropyl, and di-sec. butyl dithiophosphate described in Examples 7 and 8 were used as promoters on the zinc ore described in the preceding

example and the same testing procedure was followed. The allyl esters were used in amounts of 0.1 lb./ton. The test results are summarized in the following table:

Test No.	Concentrate, Percent Zinc		Tailing, Percent Zinc Assay	Promoter Used
	Assay	Distribution		
1	39.06	95.70	0.12	Allyl Diethyldithiophosphate.
2	43.52	94.88	0.13	Allyl Diisopropyldithiophosphate.
3	40.83	95.97	0.11	Allyl Disec. butyldithiophosphate.

EXAMPLE 14

The allyl esters of diethyl, diisopropyl and disec. butyldithiophosphoric acid were used as promoters with the ore of Example 9 and the same testing procedure was employed. The results are summarized in the following table:

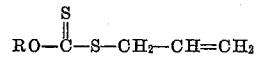
Test No.	Concentrate, Percent Copper		Tailing, Percent Copper Assay	Promoter Used
	Assay	Distribution		
1	18.19	87.10	0.30	Allyl Diethyldithiophosphate.
2	19.44	80.81	0.44	Allyl Diisopropyldithiophosphate.
3	19.66	80.92	0.43	Allyl Disec. butyldithiophosphate.

EXAMPLE 15

A pyritic gold ore assaying about 0.19 oz. Au./ton was ground and floated with 0.18 lb./ton allyl ethylxanthate and 0.12 lb./ton pine oil frother. A concentrate was produced, assaying 1.44 oz. Au./ton and containing 94.2% of the total gold. The flotation tailing assayed 0.013 oz. Au./ton.

We claim:

1. A process of froth flotation which comprises subjecting an ore pulp selected from the group consisting of sulfide and precious metal ores to froth flotation in the presence of a collector of the formula



in which R is a saturated hydrocarbon radical having from 1 to 6 carbon atoms.

2. A process according to claim 1 in which the ore is a copper sulfide ore and the froth flotation is effected in an acid circuit.

3. A process according to claim 1 in which the collector is O-ethyl-S-allyl xanthate.

4. A process according to claim 1 in which the collector is O-propyl-S-allyl xanthate.

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