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FLOTATION OF ORES

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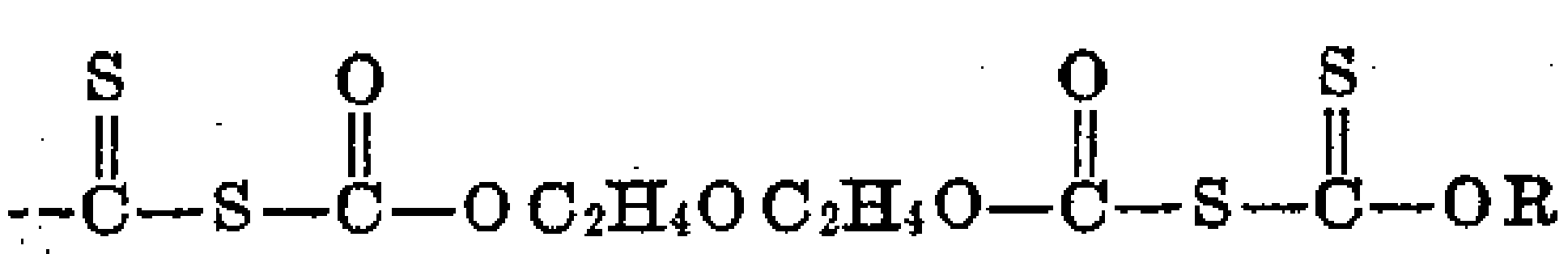
8 Claims. (Cl. 209—166)

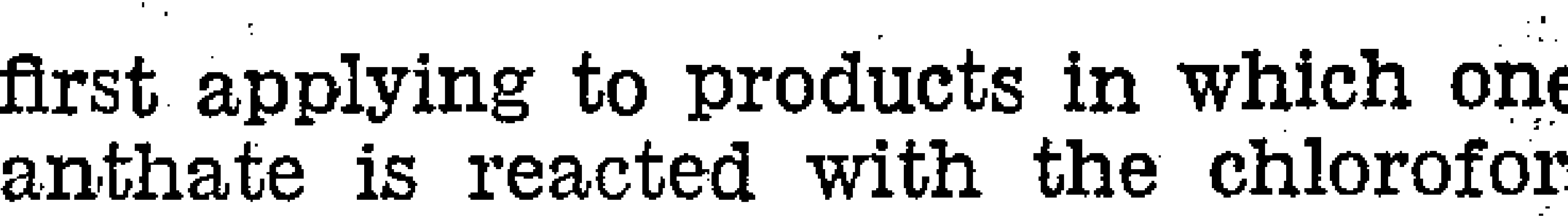
This invention relates to a new process for floating metal ores. Base metal and precious metal ores, particularly of the sulfide type, have been floated in the past in the main by three types of reagents. The first group is the xanthates, the second the dithiophosphates, and to a lesser extent thiocarbanilides and similar reagents have been used. While the standard flotation promoters for sulfide minerals give excellent results with the general run of ores, there is room for improvement, particularly with some ores containing both sulfide and oxide metal values. The present invention deals with processes of floating metal ores, particularly those containing some sulfides, with a new class of promoters. These promoters are reaction products of glycol chloroformates with one or two mols of xanthates. The reaction proceeds by a simple mixing of the reagents at room temperature. The compounds appear not to be completely pure chemical compounds in some cases and are probably mixtures. Furthermore, mixtures of two or more xanthates may be used in the reaction. Without limiting the invention to any precise chemical formula for the promoters, we believe it probable that at least a major constituent of the promoters have the following formulae:

(1)



$$RO-\overset{\overset{S}{\|}}{C}-S-\overset{\overset{O}{\|}}{C}-OC_2H_4OC_2H_4O-\overset{\overset{O}{\|}}{C}-Cl$$

(2)



$$RO-\overset{\overset{S}{\|}}{C}-S-\overset{\overset{O}{\|}}{C}-OC_2H_4OC_2H_4O-\overset{\overset{O}{\|}}{C}-S-\overset{\overset{S}{\|}}{C}-OR$$

the first applying to products in which one mol of xanthate is reacted with the chloroformate and the second where two mols are so reacted. In the formulae, one of the simplest glycols, diglycol, is used for illustrative purposes. The invention, however is not limited to the use of reaction products of chloroformates of this particular glycol with xanthates. On the contrary, chloroformates of other glycols may be used in the process.

We do not claim herein the new reagents as new chemical compounds as they form the subject matter of the co-pending application of Booth and Light, Serial No. 757,057 filed June 25, 1947 concurrently herewith.

The amount of reagent used with typical ores is of the same order of magnitude as is the case with xanthates, namely a few hundredths of a

pound per ton. Other flotation conditions are substantially the same as when xanthates or dithiophosphates are used. This is an advantage of the present invention as ordinary flotation circuits and conditions do not have to be changed in any material way. The novelty of the process of the present invention lies in the use of a new class of promoters.

While it is not essential that the ore be conditioned with the promoter before flotation, we find that with many ores this procedure is desirable. Here again the use of the new promoters does not materially change good flotation practice.

Although, as has been stated above, we believe that the promoters of the present invention are not always pure chemical compounds but often constitute mixtures, it is definitely proven that the improved results which are obtainable with many ores by following the procedure of the present invention are not due to unreacted chloroformate, as this appears to have extremely poor collecting power.

In the following specific examples, comparative tests with standard reagents are given. It should be noted that the flotation art, particularly with ores containing sulfides, has reached so high a state of development that improvements are limited to some extent. The present invention does improve to a substantial extent the recoveries obtainable. Particularly with low grade ores, the amount of mineral available is small and high recovery becomes essential in order to keep the process within economic limits. The improvement which is obtainable in recovery when the process of the present invention is used is, therefore, an important economic factor and permits a substantial lowering in cost with many ores.

Example 1

A copper ore from the southwestern United States containing various sulfide and oxide copper minerals and assaying about 0.90% Cu, was ground with lime and promoter at 60% solids, diluted to 22% solids, and conditioned with 0.072 lb./ton pine oil. Flotation followed for 6 minutes in a Fagergren type flotation machine. A series of tests using 0.01–0.025 lb./ton reaction products of 1 mol of xanthate and 1 mol of diglycol chloroformate were conducted. Also for purpose of comparison, tests were conducted with certain of the starting ingredients of these reaction products, viz., diglycol chloroformate, sodium ethyl xanthate, and potassium amyl xanthate. Metallurgical results follow:

Collector Used		Concentrate, percent Cu		Tailing Assay percent Cu
Reaction Product	Lbs./ton	Assay	Distribution	
1 mol Sodium Ethyl Xanthate 1 mol Diglycol Chloroformate	0.01	15.59	79.30	0.19
1 mol Sodium Ethyl Xanthate 1 mol Diglycol Chloroformate	0.025	14.44	81.07	0.18
1 mol Sodium Isopropyl Xanthate 1 mol Diglycol Chloroformate	0.025	14.39	83.04	0.16
1 mol Sodium Sec. Butyl Xanthate 1 mol Diglycol Chloroformate	0.025	15.07	80.40	0.19
1 mol Potassium Amyl Xanthate 1 mol Diglycol Chloroformate	0.025	13.77	82.56	0.17
Diglycol Chloroformate (alone)	0.1	----------	----------	0.51
Sodium Ethyl Xanthate (alone)	0.025	----------	----------	0.23
Potassium Amyl Xanthate (alone)	0.025	----------	----------	0.22

It will be noted that glycol chloroformate even in much larger amounts is not a useful collector even in comparison with the xanthates themselves. These latter gave results which were not as good as is obtainable with the process of the present invention, but of course of an entirely different order of magnitude than the chloroformate itself which cannot properly be considered as a practical promoter.

Example 2

A copper ore from the southwestern United States, generally similar to that used on Example 1, was ground with lime and floated with 0.025 lb./ton of the reaction products of 2 mols sodium isopropyl xanthate or sodium secondary butyl xanthate with 1 mol diglycol chloroformate and 0.07 lb./ton pine oil as frother. A comparative test was run with 0.025 lb./ton of a technical grade disecondary butyldithiophosphate, the standard reagent on this ore. Metallurgical results follow:

Collector Used—Reaction Product	Concentrate, Percent Cu		Tailing Assay, Percent Cu
	Assay	Distribution	
2 mol Sodium isopropyl xanthate 1 mol Diglycol chloroformate	14.77	77.51	0.21
2 mol Potassium Amyl Xanthate 1 mol Diglycol chloroformate	14.92	79.50	0.20
Disec. butyldithiophosphate (alone)	16.96	75.04	0.25

It will be noted that a substantial reduction in the copper content of the tailings was obtained with the above-listed reaction products as compared to the standard dithiophosphate reagent used on this ore.

Example 3

A South American copper ore containing about 2.3% Cu as both sulfide and oxidized copper minerals was ground at 60% solids, diluted to 22% solids, conditioned for 2 minutes with 5.0 lb./ton sulfuric acid and then 1 minute with 0.21 lb./ton cresylic acid, and floated for 8 minutes in a Fagergren type floating machine. The collectors were added to the grind in these tests. Metallurgical results follow:

Collector Used		Concentrate		Tailing Assay, Percent Cu
Reaction Product	lb./ton	Assay, Percent Cu	Distribution, Percent Cu	
2 mol Sodium Ethyl Xanthate 1 mol Diglycol Chloroformate	0.1	18.91	89.09	0.28
(1 mol Sodium Ethyl Xanthate) (1 mol Potassium Amyl Xanthate) 1 mol Diglycol Chloroformate	0.1	18.91	89.32	0.28

Example 4

A zinc ore from the southeastern United States was ground and conditioned with 0.5 lb./ton copper sulfate, 0.015 lb./ton of the reaction product of 1 mol of sodium ethyl xanthate and 1 mol of diglycol chloroformate, and 0.14 lb./ton pine oil. Flotation followed for 4 minutes with an additional 0.04 lb./ton pine oil added after 2 minutes. From a feed to flotation, assaying 3.07% Zn, 92% of the total zinc was recovered in a concentrate assaying 54.88% Zn. The flotation tailings assayed 0.26% Zn.

Example 5

A Tri-State lead ore containing mainly galena but also some oxidized lead minerals was ground and conditioned with 0.02 lb./ton of the reaction product of 1 mol of sodium ethyl xanthate and 1 mol of diglycol chloroformate and 0.18 lb./ton creosote oil. The ground pulp was diluted to 22% solids, conditioned for 0.5 minutes with mixed amyl alcohols as frother, and floated 4 minutes. From a feed to flotation assaying 2.76% Pb, 81.60% of the total lead was recovered in a concentrate assaying 53.73% Pb. The assay of the tailing was 0.53% Pb.

Example 6

Because of their high stability reagents of this type are suited especially to flotation in acid circuits, particularly the high acid concentrations used in the recovery of copper by the leaching-precipitation-flotation process. Metallic copper is readily floated by these promoters either in the presence or absence of sulfide minerals as is common in leach-precipitation practice.

A southwestern copper ore containing 1.29% total copper (0.82% sulfide copper and 0.47% non-sulfide copper) was ground and leached with sulfuric acid at a pH of 1.5. The pH was adjusted to about 2.8 by addition of lime and the dissolved copper precipitated by means of iron. The excess precipitant was screened from the ore pulp which together with the precipitated copper was passed to a Fagergren flotation machine, brought to a pH of about 5 by addition of lime, conditioned with 0.033 lb./ton pine oil and 0.05 lb./ton of the reaction product of 2 mol ethyl xanthate and 1 mol diglycol chloroformate and floated 10 minutes to produce a combined concentrate of copper sulfides and metallic copper. The tailings from the flotation operation assayed 0.06% total copper and 0.03% non-sulfide copper. About 95% of the copper was recovered.

Example 7

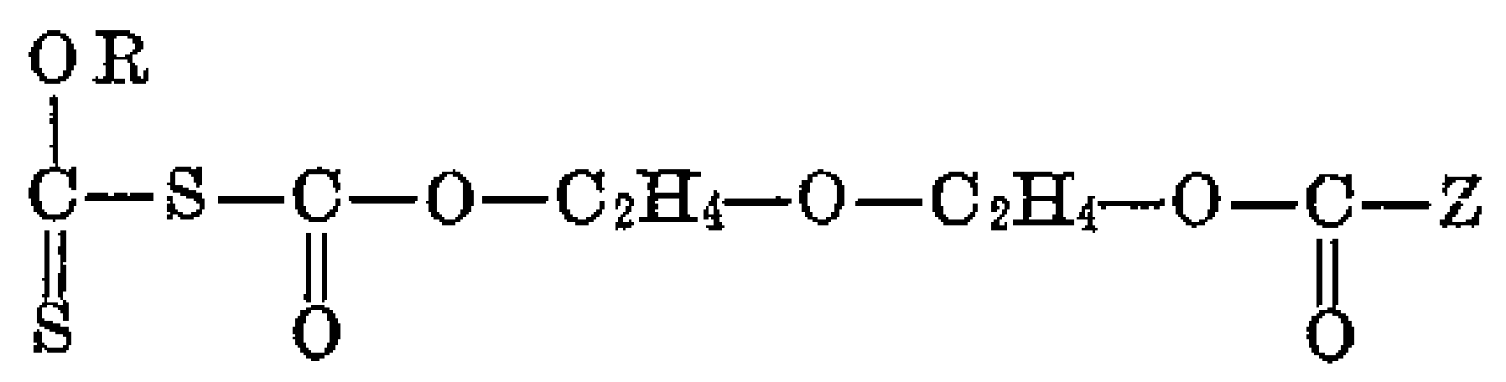
A copper ore (about 0.95% Cu) from the southwestern United States, containing chalcopyrite, bornite, pyrite, pyrrhotite, iron oxides, quartz, carbonates and silicates was ground with the collector and lime, conditioned at flotation density with 0.07 lb./ton pine oil, and floated for 6 minutes. Reaction products of various glycol chloroformates (1 mol) xanthates (2 mols) were used as collectors. Metallurgical results follow:

Xanthate (2 mols)	Chloroformate of—	lb./ton used	Concentrate		Tailing, Percent Cu Assay
			Percent Cu Assay	Distr.	
Sodium Ethyl	Ethylene Glycol	0.019	17.20	82.26	0.18
Sodium Isopropyl	do	0.018	14.66	83.31	0.17
Potassium Amyl	do	0.019	17.20	84.48	0.15
Sodium Isopropyl	Dipropylene Glycol	0.018	15.66	82.41	0.17
Do	Trimethylene Glycol	0.019	16.43	83.16	0.17
Sodium Ethyl	Octadecanediol	0.027	18.63	77.19	0.23
Do	Triethylene Glycol	0.021	16.32	81.39	0.18
Do	2 Methyl,2-4 Pentanediol	0.013	18.96	76.70	0.22
Do	2 Butyne,2-4 diol	0.020	20.51	-------	0.20
Sodium Ethyl (1 mol) Potassium Amyl (1 mol)	Diglycol	0.019	16.45	82.52	0.17
Sodium Ethyl (1 mol) Sodium Sec. Butyl (1 mol)	do	0.018	15.79	82.63	0.17

The reaction products have been found to be highly efficient promoters for gold-bearing pyrites and give high recoveries of gold in such floats.

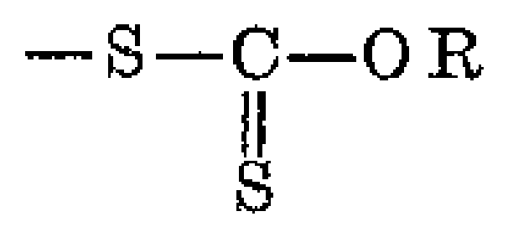
We claim:

1. A method of beneficiating metallic ores which comprises subjecting the ore to froth flotation in the presence of a promoter having as an essential promoting constituent a compound of the formula:



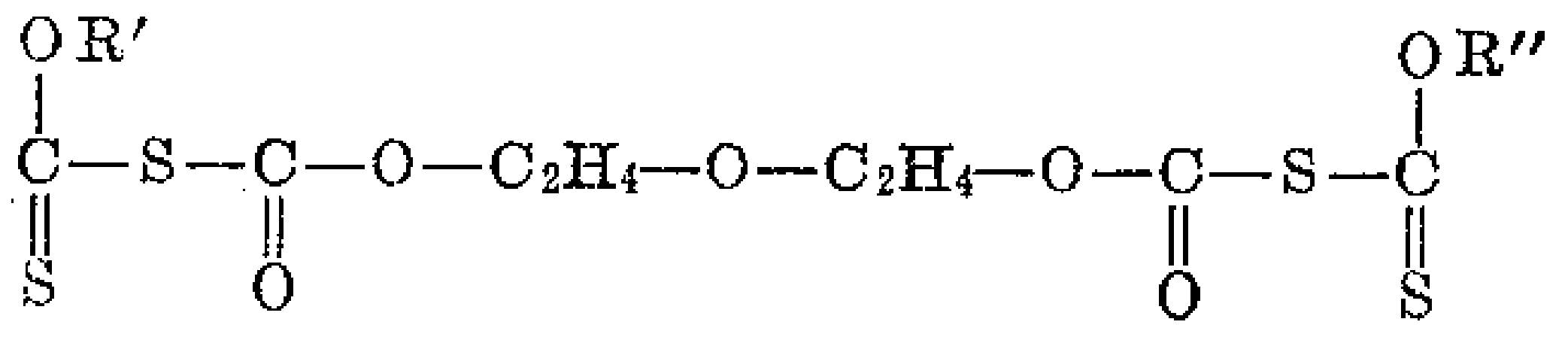
$$\mathrm{RO{-}C({=}S){-}S{-}C({=}O){-}O{-}C_2H_4{-}O{-}C_2H_4{-}O{-}C({=}O){-}Z}$$

in which R is an alkyl radical and Z is a radical selected from the group consisting of —Cl and



$$\mathrm{{-}S{-}C({=}S){-}OR}$$

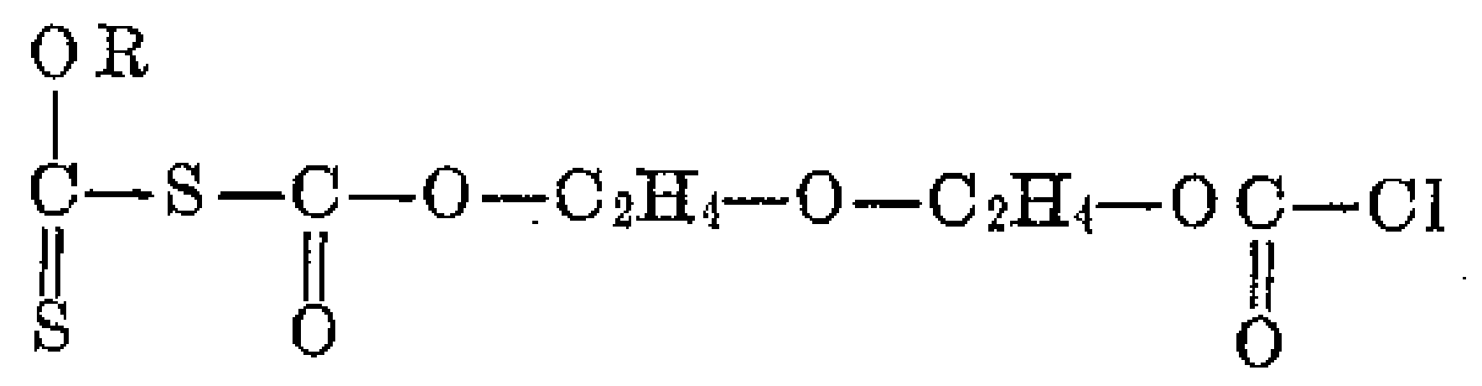
2. The method of concentrating sulphide ore which comprises subjecting the ore in the form of a pulp to a froth flotation operation in the presence of a compound having the structural formula:



$$\mathrm{R'O{-}C({=}S){-}S{-}C({=}O){-}O{-}C_2H_4{-}O{-}C_2H_4{-}O{-}C({=}O){-}S{-}C({=}S){-}OR''}$$

in which R' and R'' are alkyl radicals.

3. A method of beneficiating metallic ores which comprises subjecting the ore to froth flotation in the presence of a promoter having as an essential promoting constituent a compound of the formula:



$$\mathrm{RO{-}C({=}S){-}S{-}C({=}O){-}O{-}C_2H_4{-}O{-}C_2H_4{-}O\,C({=}O){-}Cl}$$

in which R is an alkyl radical.

4. A method according to claim 2 in which the ore is a copper ore containing sulfides of copper.

5. A method according to claim 3 in which the ore is a copper ore containing sulfides of copper.

6. A method according to claim 2 in which the ore is a zinc ore.

7. A method according to claim 3 in which the ore is a zinc ore.

8. A method according to claim 2 in which the ore is a lead ore.

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