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FLOTATION REAGENT COMPOSITION

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This invention relates to a new composition for use as a promoter or collector in the froth flotation of ores, and which contains various esters of mono and dithiophosphoric acids.

Diesters of dithiophosphoric acid have achieved an enormous success as flotation promoters and collectors for sulfide and precious metal ores. In fact, this class of flotation agent has for nearly thirty years been one of the main classes of flotation reagents. In the beginning, phenol esters were extensively used, such as dicresyl dithiophosphoric acid. These compounds are liquids which can be shipped in drums and which present no problem in feeding in the actual flotation operations, in spite of the fact that amounts of collector used are often very small fractions of a pound per ton. The liquids can be accurately measured and fed uniformly to the flotation operations. A little later, it was found that for certain purposes, aliphatic esters of dithiophosphoric acid, such as the diethyl, diisopropyl, disecondarybutyl, diamyl esters and the like, were advantageous. These compounds, however, presented a serious problem because in the form of their free acids they are corrosive, presenting an economically insoluble transportation problem. This problem was solved by producing dry salts, such as the sodium and potassium salts of the dialkyl dithiophosphoric acid which could be readily shipped and, being soluble in water, could be fed as solutions.

In spite of the great utility of the dithiophosphoric esters and their salts in a wide variety of flotation operations, their effectiveness in certain specialized fields was not all that could be desired. Thus, in froth flotations which are effected in strongly acid circuit, as is the case with a number of copper sulfide ores, for example of the type mined in large quantities in Chile, the ordinary dithiophosphates were found unsuitable where maximum results were desired. Another mineral product which is beneficiated by flotation in an acid circuit is the product obtained by the well-known leach-precipitation procedure as applied to oxide and oxide-sulfide copper ores. These special fields, although only part of the general field of flotation of sulfide and precious metal ores, nevertheless represent a very large tonnage, as some of the ores, particularly copper sulfide ores which are mined in large tonnage in Chile and elsewhere, require flotation in acid circuit for best results.

Over the years, numerous attempts have been made to produce reagents which are particularly suitable for use in acid circuits, for the lack of effectiveness in such circuits is not limited to the dithiophosphates, being shared to a considerable extent by the other large class of flotation agents, namely the xanthates. Certain special reagents were prepared, for example, by condensing xanthates or dithiophosphates through their ionizable sulfur atom to form more complex compounds. Ethyl xanthogen ethyl formate is an example of such a condensation product. Some of these compounds have achieved a marked commercial success in the field of acid circuit flotation and also for certain specialized purposes

where the pH is not so low. However, these compounds have left much to be desired, not the least of the undesirable characteristics being their relatively high price. As a result in many cases compromises have been necessary, using much cheaper dithiophosphates or xanthates, rather than the more expensive special reagents, in spite of the fact that the results were not quite as good from the metallurgical standpoint.

According to the present invention a somewhat different and relatively cheap thiophosphoric ester reagent is used. These reagents, which are new mixtures, are readily produced by the partial hydrolysis of dialkyl dithiophosphoric acid in an aqueous alcoholic medium. The products obtained are not single chemical compounds. They are mixtures of unhydrolyzed dialkyl dithiophosphoric acid, dialkyl monothiophosphoric acid and comparatively smaller and varying amounts of the neutral O,O,O-trialkyl monothiophosphate and O,O,S-trialkyl dithiophosphate. Depending on the length of time during which the hydrolysis is effected and the temperature, the relative amounts of the three components will vary. However, for useful reagents, the mono and dithiophosphoric acids are present in roughly comparable amounts. Typical proportions for a good reagent are from 60:40 to 40:60. While useful reagents can be prepared in which the proportions are outside the above preferred range, the products are somewhat less desirable and, of course, where either component is present with very little of the other, the properties do not differ sufficiently from the pure product to be of any added use.

It is possible to use the mixtures of the two thiophosphoric acids and the neutral triester as such, but it requires corrosion-resistant feeding equipment. Of course, shipment over any distance of the highly corrosive mixture is economically undesirable because of the excessive cost of corrosion-resistant containers. In the case of the equally corrosive dialkyl dithiophosphoric acids, the corrosion problem has been met by neutralizing the acids, for example with sodium carbonate. When such a procedure is applied to the mixture of acids and neutral ester of the present invention, products are obtained which vary from fairly dry solids to highly pasty materials. The difference in physical properties is primarily due to the varying amounts of the neutral triester present, as it is an oily material.

When products are produced which are relatively low in triester and are, therefore, comparatively dry, ordinary shipping procedures may be used. In the case of products of higher triester content, which may be very sticky taffy-like pastes, they may be used if produced at the flotation site. However, they present a difficult shipping and handling problem. This problem may be solved by preparing a solution of the mixture in a cheap phenol, such as commercial cresylic acid. This may be effected very easily by dissolving the mixed acids and triester in the cresylic acid and then neutralizing. The reverse procedure is, of course, possible, but is less desirable.

The solution in cresylic acid is stable, can be shipped in cheap containers and, when fed, is actually superior to the mixed reagent because it possesses the additional frothing characteristics of the cresylic acid which are nearly ideal for effective froth flotation in acid circuit. The product, therefore, can be used both as a frother and a collector without adding additional frother or additional collector. In other words, a single product is capable of performing functions that formerly required two different products.

The sodium salts of the acids have been referred to above because these are normally the cheapest salts. As far as flotation effectiveness is concerned, the potassium or ammonium salts are equally useful and are included

in the scope of the invention, although their normally added cost is rarely justified.

While it is an important advantage of the cresylic acid or other phenol solutions of the reagent which constitutes a preferred embodiment of the present invention that under favorable circumstances the product can be used as the only flotation agent, the invention is not limited to use in this manner and, if desired, additional reagents such as additional frother may be added in the flotation operation itself. There is considerable advantage in marketing a uniform product, which means one with a uniform amount of cresylic acid, and where for certain special purposes a somewhat different ratio is desirable or where the addition of small amounts of the different type of frother prove to be desirable, it is a simple matter to change the composition by the addition of other reagents and still retain the desirability of having a stable liquid which can be fed very accurately.

The preferred embodiment of the invention is not limited to an exact proportion of cresylic acid to the mixed thiophosphoric esters. There is, of course, a lower limit which is determined by the solubility of the salts in the cresylic acid. This varies a little with the composition and with the particular salt and in general will range from 25 to 35% of the total weight of the liquid product. It is desirable to use somewhat more cresylic acid because this assures a liquid of maximum stability under widely differing climatic conditions, whereas when the minimum amount of cresylic acid is used, under certain circumstances, partial precipitation may take place. The upper limit is determined practically by the amount of frother which can be used. If there is too much cresylic acid, over-frothing and other undesirable conditions may occur. In general, the upper limit will approximate 75 to 80% of the weight of the solution. As in the case of the lower limit, it is advantageous to market a product which is not at the extreme limit, as then there is no danger of over-frothing and it is easier to add additional frother if this should become necessary. Therefore, while the two limits given above represent the operating range of cresylic acid content, the two extremes are less satisfactory, and so it is preferred to market compositions which are somewhat removed from the extremes.

It is an advantage of the present invention that the reagent mixture does not require high purity. It is a crude product and normally undergoes no purification as by-products present have been found ordinarily not to be harmful to flotation. In the same manner the cresylic acid solution is also crude and the purity of the cresylic acid or other phenolic product is more or less immaterial. Ordinarily commercial cresylic acid, such as is obtained as a by-product from the manufacture of metallurgical coke or from petroleum sources, is satisfactory, even though it may contain smaller amounts of non-phenolic liquid constituents.

The method of producing the mixed flotation collector of the present invention by partial hydrolysis of dialkyl dithiophosphoric acids is not the only method by which the mixture can be prepared. It does, however, present considerable economical advantages. The invention, of course, is not limited to the process by which the mixed collector is prepared.

The invention will be described in greater detail in connection with typical specific examples. It should be understood that the method of making the product of the present invention is a representative one, and that small variations which are typical in manufacturing operations where close control is not necessary will vary the exact composition of the ingredients from batch to batch. As has been pointed out above, it is an advantage of the invention that the proportions are not critical.

It is another advantage of the present invention that the froth flotation technique itself is not altered materially by the use of the present invention. The general

operating procedure which is typical with the flotation of a particular sulfide or precious metal ore, especially one in acid circuit, may be employed with the new reagent with excellent results. As in all flotation operations, the exact amount of collector used varies from ore to ore and even sometimes with different portions of the same ore body. In each case, in accordance with the conventional procedure, the amount of collector used will be adjusted for optimum results. The examples, therefore, are not intended to limit the invention to the use of a precise amount of collector, but represent typical operating conditions for the particular ores, the flotation of which is described.

Example 1

Diethyldithiophosphoric acid (206.7 parts by weight) of about 90% purity was dissolved in an equal weight of anhydrous ethyl alcohol. Water (18 parts by weight) was added and the mixture refluxed for 2 hours at 78–80° C. Alcohol was then distilled off under vacuum and the residual liquid hydrolyzed product was obtained for use as a flotation agent.

Example 2

A second lot of diethyldithiophosphoric acid was treated with water as in Example 1. Before removing the alcohol, a representative sample of the reaction mixture was removed and titrated with alkali. Sodium carbonate equivalent to the acidity of the hydrolysis product plus about 5% excess was added and the alcohol then removed, leaving a brittle solid on cooling which was ground to a granular grayish powder. This product was readily soluble in water and was suitable for use as a flotation reagent.

Example 3

The potassium salt of the hydrolysis product was obtained by the same procedure outlined in Example 2 except that potassium carbonate was used in the neutralization instead of sodium carbonate.

Example 4

Following the hydrolysis as described in Example 1, the alcoholic solution was neutralized with gaseous ammonia. The resulting ammonium salt in alcohol could be fed readily to the flotation cell and was an effective promoter for sulfide minerals.

Example 5

An alcoholic solution of diethyldithiophosphoric acid was prepared by reacting 8 moles of anhydrous ethyl alcohol with 1 mole of phosphorus pentasulfide below 60° C. One mole of water was added and the mixture heated for 12 hours, during which time the temperature was gradually raised to 95° C. The resulting acidic solution is suitable for direct use as a flotation promoter. If desired, the residual alcohol may be removed to give a concentrated product for flotation use.

Example 6

A second lot of the hydrolyzed product was prepared as in Example 5. Following removal of the alcohol, an equal weight of anhydrous sodium carbonate was added and the water formed in the neutralization was removed by heating under vacuum at 60° C. The final product was an oil-containing paste. This product may be fed to flotation as a water solution.

Example 7

The hydrolyzed product of Example 5 was prepared and was stripped of unreacted alcohol. Fifty parts of this product were neutralized with 10.5 parts sodium hydroxide added as a 50% solution in water. Cresylic acid, 44 parts, was added and the mixture heated at 80° C. at 25 mm. to remove water. The final product, a

cresylic acid solution of the sodium salt of the hydrolysis product, is stable and may be fed directly to flotation.

Example 8

The hydrolyzed product of Example 5 was prepared and stripped of residual alcohol. To 50 parts of this product were added 44 parts of cresylic acid and the resulting solution neutralized by passing in gaseous ammonia. The cresylic acid solution of the ammonium salt was used directly as a flotation agent.

Example 9

The hydrolysis product of diisopropyldithiophosphoric acid was prepared as in Example 1 by treating 2308 parts of this acid (91.8% grade) with 1840 parts of ethanol which contained 187 parts of water. The mixture was refluxed four hours at 78–80° C. and was then neutralized with 5% excess sodium carbonate as described in Example 2. The residual alcohol was removed to yield a granular, grayish solid which was soluble in water.

Example 10

Disecondarybutyldithiophosphoric acid (2000 parts), anhydrous ethyl alcohol (1600 parts) and water (145 parts) were refluxed for 2 hours at 78–80° C. and treated as described in Example 9. The final neutralized product was a paste which dissolved in water to give solutions suitable for use as flotation promoters.

Example 11

A South American copper sulfide ore (2.01–2.24% Cu) was ground at 60% solids to −65 mesh in the presence 0.1 lb./ton of the promoters obtained in Examples 1 to 10 above, was diluted to 22% solids, conditioned in a Fagergren flotation machine for 1 minute with 5.4 lb./ton sulfuric acid and then for 1 minute longer with 0.20 lb./ton cresylic acid as frother, and floated for 8 minutes. A copper concentrate was removed. The following table summarizes the metallurgical results obtained in this series of tests. For purposes of comparison, included in the table are the results of tests under the same conditions with comparable amounts of ethyl xanthogen ethyl formate, the promoter in regular use on this ore, and also with diethyldithiophosphoric acid, the starting material from which most of the above promoters were made.

Promoter Tested	Concentrate, Percent Copper Assay	Tailing, Percent Copper Assay
Ethyl xanthogen ethyl formate	11.78	0.35
Diethyldithiophosphoric Acid	11.61	0.47
Example 1	11.56	0.31
Example 2	11.75	0.31
Example 3	11.67	0.31
Example 4	11.53	0.30
Example 5 [a]	11.65	0.28
Example 6	11.10	0.31
Example 7 [b]	12.00	0.32
Example 8 [b]	12.05	0.30
Example 9	11.93	0.30
Example 10	11.72	0.31

[a] After concentration by removal of alcohol.
[b] 0.1 lb./ton cresylic acid added as frother in this test.

Example 12

The promoters herein described are useful in the leach-precipitation-flotation process used in the treatment of oxidized or mixed sulfide-oxidized ores such as those of copper. In a series of tests, the slime portions of a copper ore from the western United States, which contained 1.45–1.49% Cu as mixed sulfide and oxide copper-bearing minerals, were leached with 10 lb./ton sulfuric acid for 30 minutes at about 35% solids and treated with 100 lb./ton sponge iron to precipitate dissolved copper. The pulp was transferred to a Fagergren flotation machine and floated at about 20% solids with 0.20–0.30 lb./ton of the promoters described in Examples 2 and 7 and 0.2 lb./ton pine oil to remove both sulfide and precipitated copper as a flotation concentrate. Following this flotation operation, residual sponge iron with some adhering copper was removed by magnetic separation methods. (In usual operations this fraction would be returned along with fresh sponge iron as precipitant in the next treatment cycle.) The flotation concentrates, tailings and the magnetic portions were assayed for copper. The following table summarizes these tests.

	Wt. Percent	Percent Copper		Test 1
		Assay	Distribution	
Calculated Head	100.00	1.49	100.0	0.20 lb./ton Promoter from Example 2.
Copper Concentrate	17.59	6.82	80.5	
Magnetics	11.07	2.19	16.1	
Tailings	71.34	0.07	3.4	
				Test 2
Calculated Head	100.00	1.46	100.0	0.20 lb./ton Promoter from Example 7.
Copper Concentrate	16.02	7.33	80.1	
Magnetics	9.76	2.29	15.1	
Tailings	74.22	0.09	4.8	

Example 13

A copper ore from the western United States, containing 1.15% Cu mainly as sulfide copper minerals and also some oxidized copper minerals, was ground to −65 mesh in the presence of 15.0 lb./ton lime and was floated in a Fagergren flotation machine at 22% solids with 0.07 lb./ton of a polypropylene glycol frother and with 0.1 lb./ton of the promoters from Examples 6 and 7. The results of these tests were as follows.

	Wt. Percent	Percent Copper		Test 1
		Assay	Distribution	
Heads	100.0	1.15	100.00	0.1 lb./ton Promoter of Example 6.
Concentrate	15.5	6.84	92.17	
Tailing	84.5	0.11	7.83	
				Test 2
Heads	100.0	1.15	100.00	0.1 lb./ton Promoter of Example 7.
Concentrate	16.1	6.65	93.0	
Tailing	83.9	0.10	7.0	

Example 14

A zinc ore (2.7% Zn) from the southeastern United States was ground to −65 mesh and conditioned at 22% solids in a Fagergren flotation machine with 0.5 lb./ton copper sulfate and 0.15 lb./ton of the promoters described in Examples 6 and 7. The following metallurgical results were obtained.

	Wt. Percent	Percent Zinc		Test 1
		Assay	Distribution	
Concentrate	6.30	40.64	96.24	0.15 lb./ton Promoter of Example 6.
Tailing	93.70	0.11	3.76	
Heads	100.00	2.66	100.00	
				Test 2
Concentrate	6.51	39.93	97.01	0.15 lb./ton Promoter of Example 7.
Tailing	93.49	0.09	2.99	
Heads	100.00	2.68	100.00	

Example 15

A Missouri lead ore (5.3% Pb) was ground to about −65 mesh in particle size and floated at about 22% solids in a Fagergren flotation machine to recover a lead concentrate. Two flotation tests were conducted, em-

ploying as promoters the products described in Examples 6 and 7. These promoters were used in amounts of 0.09 lb./ton and as frother 0.20 lb./ton of creosote oil and 0.05 lb./ton of mixed amyl alcohols. The metallurgy obtained was as follows

Concentrate			Tailing, Percent Pb Assay	
Wt. Percent	Percent Pb			
	Assay	Distribution		
8.36	62.24	98.48	0.09	0.09 lb./ton Promoter of Example 6.
8.42	61.79	98.11	0.10	0.09 lb./ton Promoter of Example 7.

We claim:

1. A collector for froth flotation containing as its principal and essential ingredients a major portion comprising a mixture in comparable amounts of monovalent water-soluble salts of dialkyl monothiophosphoric acid and dialkyl dithiophosphoric acid together with a substantial but relatively minor proportion comprising the corresponding O,O,S-trialkyl dithiophosphate and O,O,O-trialkyl monothiophosphate, the alkyl radicals being identical lower-alkyl radicals.

2. A collector according to claim 1 in which the relative proportions of the salts of dialkyl monothiophosphoric acid and dialkyl dithiophosphoric acid are from 60:40 to 40:60.

3. A collector according to claim 1 in which the dialkyl thiophosphoric acids are diethyl thiophosphoric acids.

4. A collector according to claim 3 in which the salts are in solution in cresylic acid.

5. A collector according to claim 3 in which the dialkyl thiophosphoric acids are diisopropylthiophosphoric acids.

6. A collector according to claim 5 in which the salts are in solution in cresylic acid.

7. A collector according to claim 3 in which the dialkyl thiophosphoric acids are disecondarybutyldithiophosphoric acids.

8. A collector according to claim 7 in which the salts are in solution in cresylic acid.

9. A process of froth flotation which comprises subjecting an ore of the sulfide type to froth flotation in the presence of sufficient of the product of claim 1 to act as a collector, whereby a flotation concentrate is produced relatively rich in metal values and a tailing relatively poor in metal values and separately recovering concentrate and tailing.

10. A process of froth flotation according to claim 9 in which the flotation is effected in acid circuit.

11. A froth flotation process according to claim 10 in which the ore is a copper sulfide ore.

12. A process of froth flotation which comprises subjecting the product of a leach precipitation of a copper ore to froth flotation in the presence of sufficient of the product of claim 1 to act as a collector, whereby a flotation concentrate is produced relatively rich in metal values and a tailing relatively poor in metal values and separately recovering concentrate and tailing.

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