Patented June 2, 1936 2,043,192

UNITED STATES PATENT OFFICE

2,043,192

FLOTATION REAGENT

Ludwig J. Christmann, Jersey City, and David W. Jayne, Jr., Elizabeth, N. J., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application May 9, 1934, Serial No. 724,760

24 Claims. (Cl. 209—166)

This invention is directed to a composition for and a method of froth flotation of ores.

More particularly the present invention relates to a new combination of flotation promoters, whereby increased effectiveness is obtained in the froth flotation operation.

It has been well known for a number of years that thiocarbanilid is an effective promoter in the froth flotation of various ores, as for example, lead sulphide ores. However, this substance is but very slightly soluble in the flotation circuit, so that it has been impossible to utilize the full effectiveness of this compound in the flotation operation. This deficiency has been long recognized and it has been proposed to dissolve the thiocarbanilid in orthotoluidine, whereby a 20% solution thereof is formed. The orthotoluidine is a very weak promoter and detracts from the effectiveness of the mixture. Furthermore, the solution is not stable at ordinary temperatures and it becomes necessary to heat the same in order to prevent the thiocarbanilid from precipitating. Because of this, this mixture has not been used extensively.

The defect of this solution has been recognized and it has been proposed to add thereto cresylic acid, so that a 20% solution of the thiocarbanilid was contained in a mixture of one part of orthotoluidine and three parts of the cresylic acid. Even this solution has the disadvantage that at ordinary temperatures the thiocarbanilid is precipitated after about 24 hours, and in order to maintain the same in solution it is necessary to heat the solution. This, of course, is in most cases impractical.

The present invention is intended to obviate the defects heretofore encountered in the attempts to utilize thiocarbanilid as a flotation promoter. The invention is based essentially on the discovery that certain flotation promoters have a fair degree of solvent capacity for thiocarbanilid. These promoters are the class of the so-called organic di-thiophosphoric acid compounds. Quite a number of such compounds are known and used as promoters in the flotation of ores. Generally these compounds are di-alkyl or di-aryl substituted di-thiophosphoric acids or their alkali metal salts, and the ammonium salts.

We have found that, although the di-thiophosphates are excellent promoters, the effectiveness thereof is very materially increased by the addition thereto in solution of even a relatively small amount of thiocarbanilid. Such effectiveness is not merely the sum of the effectiveness of each of the compounds constituting the mixture, when used by itself, but the composition is superior to either of the ingredients thereof as a flotation promoter.

While various di-thiophosphates may be utilized in conjunction with the thiocarbanilid in the present invention we have found that excellent results are obtained in the use of certain aryl di-thiophosphates, as for example, the diphenyl or the di-cresyl di-thiophosphoric acid. They may be formed by reacting 15 parts by weight of phosphorous pentasulphide with 85 parts of cresylic acid whereby a reaction takes place with the formation of the di-cresyl di-thiophosphoric acid.

In some cases we may treat the cresylic acid with larger amounts of phosphorous pentasulphide as for example, 25 parts by weight, which results in the formation of a larger proportion of the di-cresyl di-thiophosphoric acid. These compounds are capable of dissolving up to about 6% of thiocarbanilid and we prefer to utilize such a proportion. The thiocarbanilid enters readily into the solution by stirring, although it is preferable to warm the di-thiophosphoric acid to facilitate the solution thereof. The solution is stable under all atmospheric temperature conditions.

In practical operation with the use of this composition we ground a lead ore of the St. Joseph Lead Company to minus 20 mesh in the presence of an amount of water equal to 50% of the weight of the ore. The pulp was then transferred to a flotation machine and was diluted to 22% solids. The promoter was added and a suitable amount of pine oil as a frother was introduced into the flotation circuit. A froth flotation operation was conducted, as is well known.

In order to show the superiority of the present composition a comparison was made with ethyl xanthate and further with the di-thiophosphates without the addition of thiocarbanilid. The following table indicates the results obtained.

Test No.	Assays per cent Pb			Distribution per cent Pb		Lbs./ton		Reagent used
	Heads	Conc.	Tails	Conc.	Tails	Pine oil	Promoter	
1	3.20	47.85	0.163	95.22	4.78	0.054	0.05	Ethyl xanthate.
2	3.14	55.05	0.171	94.86	5.14	0.027	0.062	A—F 15.
3	3.36	48.80	0.164	95.43	4.57	0.027	0.062	A—F 15+6% thiocarbanilid.
4	3.12	54.68	0.127	96.08	3.72	0.027	0.062	A—F 25.
5	3.14	52.18	0.093	97.23	2.77	0.027	0.062	A—F 25+6% thiocarbanilid.

In the table the notation A—F 15 indicates the compound formed by the reaction of cresylic acid with 15% P_2S_5. The notation A—F 25 indicates the compound formed by the reaction of cresylic acid with 25% of P_2S_5.

Whereas the ethyl xanthate showed a recovery of 95.22% of the lead mineral the thiocarbanilid mixtures showed a recovery of 95.43% and 97.23%.

The results obtained with the thiocarbanilid mixtures were superior to the results obtained with the di-thiophosphate alone. Test numbers 2 and 3 are comparative and from these it will be seen that the recovery of lead mineral with the thiocarbanilid mixture was 95.43% as compared to 94.86% without the thiocarbanilid. In a similar manner test numbers 4 and 5 are comparative and the results are shown to be very materially in favor of the thiocarbanilid mixture, which resulted in a recovery of 97.23% as compared with 96.08% without the thiocarbanilid.

While in the above description a single example has been given showing the application of the invention to a specific ore, the invention is not limited to such ores, as this reagent is also superior in its results on other base and on precious metal ores. The thiocarbanilid may be used in conjunction with other di-thiophosphoric acid compounds, as for example, a solution may be made of the thiocarbanilid with the ammonium salt of di-amyl di-thiophosphoric acid. In this case because the material does not remain liquid at ordinary temperatures it is usually preferable to add to the solution some ethyl alcohol or the like which renders the composition entirely fluid at ordinary temperatures. Similarly a mixture may be made of the compound formed by the reaction of 75 parts by weight of cresylic acid with 25 parts of P_2S_5 and containing 6% of thiocarbanilid, with about 10% of ethyl alcohol. The mixture may be cooled and anhydrous ammonia introduced until the solution is saturated therewith. This results in the formation of the ammonium salt of the di-cresyl di-thiophosphoric acid.

From the above it will be apparent that there are numerous possible combinations within the scope of the present invention. Therefore, this invention is to be broadly construed and not to be limited except by the terms of the claims appended hereto.

What we claim is:

1. A composition of matter comprising a major proportion of an organic dithiophosphoric acid compound and a minor proportion of thiocarbanilid the organic dithiophosphoric acid compound being present in an amount at least several times that of the thiocarbanilid.

2. A composition of matter comprising a major proportion of an aryl dithiophosphoric acid compound and a minor proportion of thiocarbanilid the organic dithiophosphoric acid compound being present in an amount at least several times that of the thiocarbanilid.

3. A composition of matter comprising a major proportion of dicresyl dithiophosphoric acid and a minor proportion of thiocarbanilid the organic dithiophosphoric acid compound being present in an amount at least several times that of the thiocarbanilid.

4. A composiiton of matter comprising an organic dithiophosphoric acid compound and approximately 6% of thiocarbanilid.

5. A composition of matter comprising an aryl dithiophosphoric acid compound and approximately 6% of thiocarbanilid.

6. A composition of matter comprising dicresyl dithiophosphoric acid and approximately 6% of thiocarbanilid.

7. A composition of matter comprising a major proportion of an organic dithiophosphoric acid compound, a minor proportion of thiocarbanilid, and an alcohol.

8. A composition of matter comprising a major proportion of an alkali metal salt of an organic dithiophosphoric acid, a minor proportion of thiocarbanilid, and an alcohol.

9. A composition of matter comprising a major proportion of the ammonium salt of an organic dithiophosphoric acid, a minor proportion of thiocarbanilid, and an alcohol.

10. A composition of matter comprising a major proportion of an alkali metal salt of an organic dithiophosphoric acid and a minor proportion of thiocarbanilid the organic dithiophosphoric acid compound being present in an amount at least several times that of the thiocarbanilid.

11. A composition of matter comprising a major proportion of the ammonium salt of an organic dithiophosphoric acid and a minor proportion of thiocarbanilid the organic dithiophosphoric acid compound being present in an amount at least several times that of the thiocarbanilid.

12. A method of flotation which comprises providing a pulp of ore and water, adding thereto a flotation promoter including a mixture of a major proportion of an organic dithiophosphoric acid compound and a minor proportion of thiocarbanilid the organic dithiophosphoric acid compound being present in an amount at least several times that of the thiocarbanilid, and subjecting the pulp to a froth flotation operation.

13. A method of flotation which comprises providing a pulp of ore and water, adding thereto a flotation promoter including a mixture of a major proportion of an aryl dithiophosphoric acid compound, and a minor proportion of thiocarbanilid the organic dithiophosphoric acid compound being present in an amount at least several times that of the thiocarbanilid, and subjecting the pulp to a froth flotation operation.

14. A method of flotation which comprises providing a pulp of ore and water, adding thereto a flotation promoter including a mixture of a major proportion of dicresyl dithiophosphoric acid and a minor proportion of thiocarbanilid the organic dithiophosphoric acid compound being present in an amount at least several times that of the thiocarbanilid, and subjecting the pulp to a froth flotation operation.

15. A method of flotation which comprises providing a pulp of ore and water, adding thereto a flotation promoter including a mixture of an organic dithiophosphoric acid compound and approximately 6% of thiocarbanilid, and subjecting the pulp to a froth flotation operation.

16. A method of flotation which comprises providing a pulp of ore and water, adding thereto a flotation promoter including a mixture of an aryl dithiophosphoric acid compound and approximately 6% of thiocarbanilid, and subjecting the pulp to a froth flotation operation.

17. A method of flotation which comprises providing a pulp of ore and water, adding thereto a flotation promoter including a mixture of dicresyl dithiophosphoric acid and approximately

6% of thiocarbanilid, and subjecting the pulp to a froth flotation operation.

18. A method of flotation which comprises providing a pulp of ore and water, adding thereto a flotation promoter including a mixture of a major proportion of an alkali metal salt of an organic dithiophosphoric acid compound and a minor proportion of thiocarbanilid the organic dithiophosphoric acid compound being present in an amount at least several times that of the thiocarbanilid, and subjecting the pulp to a froth flotation operation.

19. A method of flotation which comprises providing a pulp of ore and water, adding thereto a flotation promoter including a mixture of a major proportion of an organic dithiophosphoric acid compound, a minor proportion of thiocarbanilid, and an alcohol, and subjecting the pulp to a froth flotation operation.

20. A method of flotation which comprises providing a pulp of ore and water, adding thereto a flotation promoter including a mixture of a major proportion of the ammonium salt of an organic dithiophosphoric acid compound, a minor proportion of thiocarbanilid, and an alcohol, and subjecting the pulp to a froth flotation operation.

21. A composition of matter comprising a solution of approximately 6% of thiocarbanilid in an aryl dithiophosphoric acid compound.

22. A composition of matter comprising a solution of approximately 6% of thiocarbanilid in dicresyldithiophosphoric acid.

23. A method of flotation which comprises providing a pulp of ore and water, adding thereto a flotation promoter containing a solution of approximately 6% of thiocarbanilid in an aryl dithiophosphoric acid compound and subjecting the pulp to a froth flotation operation.

24. A method of flotation which comprises providing a pulp of ore and water, adding thereto a flotation promoter containing a solution of approximately 6% of thiocarbanilid in dicresyldithiophosphoric acid and subjecting the pulp to a froth flotation operation.

LUDWIG J. CHRISTMANN.
DAVID W. JAYNE, JR.