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CONCENTRATED AQUEOUS SOLUTIONS OF
THE AMMONIUM SALTS OF DISUBSTITUTED
DITHIOPHOSPHORIC ACIDSDavid W. Jayne, Jr., Old Greenwich, Conn., as-
signor to American Cyanamid Company, New
York, N. Y., a corporation of MaineNo Drawing. Application October 21, 1939,
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7 Claims. (Cl. 252-9)

The present invention relates to promoters for use in the froth flotation and mineral separation of sulfide ores and the like. More particularly it relates to concentrated aqueous solutions of the ammonium salts of disubstituted dithiophosphoric acids and methods of preparation.

The dialkyl and/or diaryl dithiophosphoric acids have been used on a large scale for the flotation of various sulfide and precious metal ores for which they have been found to be very effective promoters. While these dithiophosphoric acid derivatives are excellent promoters there are, however, certain undesirable factors which accompany their use. For example, they are only slightly soluble in water and certain of the dialkyl dithiophosphoric acids are very corrosive and therefore require special containers and precaution in transportation, storage, handling, etc. Also water has a tendency to cause rather rapid decomposition of the disubstituted dithiophosphoric acids to render them less efficient as promoters and hence somewhat limits their use, particularly where it is desired to feed the reagent in the form of aqueous solutions, which presents important advantages.

To overcome the objectionable features of the disubstituted dithiophosphoric acids it has been proposed to use various salts of these acids, among which are the ammonium salts. There are, however, some undesirable properties possessed by certain of the ammonium salts which have not been satisfactorily solved heretofore. The ammonium salts of these di-substituted dithiophosphoric acids are difficult to prepare in the anhydrous form and usually occur in the form of either solids, pastes, or rather stiff jellies which are relatively unstable. These ammonium salts in the form of solids or pastes are not only difficult to prepare, but are difficult to handle and to dissolve, disperse or dilute with water when it is desired to feed them into a flotation circuit in the form of a solution.

According to the present invention a method is provided for preparing concentrated, homogeneous, stable, non-corrosive, aqueous solutions of the ammonium salts of disubstituted dithiophosphoric acids suitable for use as promoters or collectors in the froth flotation or mineral separation of sulfide ores. I have found that the ammonium salts of the disubstituted dithiophos-

phoric acids can be prepared in a concentrated aqueous solution of uniform strength suitable for use as a flotation reagent, and that the stability of such solutions is insured by maintaining an excess of ammonia. The excess ammonia, while it prevents the presence of any free disubstituted dithiophosphoric acids which would be hydrolyzed in the presence of water, does not interfere with the use of such solutions as flotation reagents.

In the preferred method of carrying out this invention disubstituted dithiophosphoric acids, such as diaryl dithiophosphoric acids or dialkyl dithiophosphoric acids are added to aqua ammonia (i. e., ammonium hydroxide containing 28-30% NH_3) in quantities that will leave an excess of ammonium hydroxide after neutralizing the acid, to give a stable concentrated aqueous solution of the ammonium salt. The concentrated aqueous solution so produced may be dissolved in water to give more dilute solutions which can be readily fed to an ore flotation circuit when such products are used as ore flotation reagents as promoters or collectors.

In producing the concentrated solutions of the ammonium salt of the disubstituted dithiophosphoric acids, the acid should be added to the aqua ammonia with good agitation and at such a rate and with sufficient cooling to keep the temperature at about 40° C. The aqua ammonia used should have as high an ammonia content as is practical (i. e., 28-30% NH_3) in order that the product will contain a maximum and relatively uniform quantity of active ingredient. While the ammonium hydroxide solution employed preferably contains 28 to 30% NH_3 weaker solutions may be used and solutions containing only about 25% NH_3 have been found to produce satisfactory results. The disubstituted dithiophosphoric acids used need not be absolutely pure but may be used in the crude form having impurities present such as for example cresylic acid. Mixtures of the various disubstituted dithiophosphoric acids, either crude or in a pure form, may be used, for example, mixtures of dialkyl and diaryl dithiophosphoric acid.

In utilizing the stable concentrated solution in flotation operations the solution is usually diluted with water to the desired strength and fed into the flotation circuit. The solution may be used in connection with other promoters or collectors, 50

frothers or the like, for example, the addition of a small amount of thiocarbanilid in many instances produces improved flotation results. The invention will be further illustrated by the following examples which are included for purposes of illustration and the invention is not limited thereto.

Example 1

10 100 grams of 26° Bé. aqua ammonia were placed in a 3 neck flask surrounded by a cooling bath and fitted with a mechanical agitator, thermometer and dropping funnel. 500 grams of a crude mixture of approximately 80% diaryl dithiophosphoric acids (cresyl, xylenyl, etc.) and
15 20% of free "cresylic acid" were placed in the dropping funnel. The crude acid was added to the aqua ammonia, with agitation, at such a rate that the temperature of the batch was maintained
20 between 30 and 35° C. The product (aqueous ammonium salt of the crude diaryl dithiophosphoric acid) was a clear, dark amber, fluid, homogeneous, stable, non-corrosive liquid. It contained approximately 69% of the ammonium
25 salts of the diaryl dithiophosphoric acids present in the crude acid, 15% of cresylic acid and 16% of water (plus a slight excess of ammonia). The product readily dissolved in water to give a clear, dilute, alkaline solution.

Example 2

30 50 g. of 26° Bé. aqua ammonia were placed in a 3 neck flask fitted with a mechanical agitator, thermometer and dropping funnel and surrounded by a cooling bath. 200 g. of crude di-secondary amyl dithiophosphoric acid were placed
35 in the dropping funnel and the acid added to the aqua ammonia, with agitation, at such a rate that the temperature of the batch was maintained between 25 and 30° C. The product
40 (aqueous ammonium salt of di-secondary amyl dithiophosphoric acid) was a clear dark yellow-green, homogeneous liquid, containing about 18% water. The product readily dissolved in water
45 to give a somewhat cloudy, dilute, alkaline solution.

The term "alkyl" and "aryl" used in the claims

are limited to and include only such radicals when they are hydrocarbons.

What I claim is:

1. A composition of matter comprising a stable, concentrated, aqueous solution of the ammonium salts of at least one of the compounds included in the group consisting of dialkyl and diaryl dithiophosphoric acids, said solution containing an amount of ammonium hydroxide in excess of the amount required to neutralize the acid. 5
2. A stable, concentrated, aqueous solution of the ammonium salt of a dialkyl dithiophosphoric acid, said solution containing an amount of ammonium hydroxide in excess of the amount required to neutralize the acid. 10
3. A stable, concentrated, aqueous solution of the ammonium salt of a diaryl dithiophosphoric acid, said solution containing an amount of ammonium hydroxide in excess of the amount required to neutralize the acid. 15
4. A method of preparing stable, concentrated, aqueous solutions of the ammonium salts of dialkyl dithiophosphoric acids which comprises adding dialkyl dithiophosphoric acids to ammonium hydroxide containing about 28% NH₃ in quantities insufficient to neutralize the ammonia, thereby leaving a slight excess of ammonium hydroxide. 20
5. A method of preparing stable, concentrated, aqueous solutions of the ammonium salts of diaryl dithiophosphoric acids which comprise adding diaryl dithiophosphoric acids to ammonium hydroxide containing about 28% NH₃ in quantities insufficient to neutralize the ammonia, thereby leaving a slight excess of ammonium hydroxide. 25
6. A stable, concentrated, aqueous solution of the ammonium salt of dicresyl dithiophosphoric acid, said solution containing an amount of ammonium hydroxide in excess of the amount required to neutralize the acid. 30
7. A stable, concentrated, aqueous solution of the ammonium salt of di-secondary amyl dithiophosphoric acid, said solution containing an amount of ammonium hydroxide in excess of the amount required to neutralize the acid. 35

DAVID W. JAYNE, Jr.