United States Patent Office

3,034,985
Patented May 15, 1962

3,034,985

AMINE FLOTATION REAGENT PREPARATION

Edmund A. Schoeld, Carlsbad, N. Mex., assignor to Potash Company of America, Carlsbad, N. Mex., a corporation of Colorado

No Drawing. Filed Sept. 8, 1961, Ser. No. 136,740
20 Claims. (Cl. 252—61)

This invention relates to improvements in the flotation art, and more particularly it relates to a process for preparing amine salt flotation reagents, and this application is a continuation-in-part of my copending application Serial No. 707,863, filed January 9, 1958, now abandoned, for Amine Flotation Reagent Preparation.

Aliphatic amines have been used as a collector reagent for many different types of materials, and one important use of aliphatic amines has been in the flotation separation of sylvite from sylvinite ores. The aliphatic amines are generally utilized as a liquid preparation, which is added to an ore pulp with conditioning or mixing prior to the flotation treatment. In some cases considerable difficulty has been experienced in the preparation of the fluid reagent composition, and in a number of cases the liquid amine reagent composition has proved to be ineffectual to promote flotation separations.

The commonly used aliphatic amines themselves are practically insoluble in water, and in order to prepare a liquid composition it has been the general practice to utilize the soluble salts of the amines with certain acids. For this purpose, the acetate salts of the aliphatic amines are widely used because of their more favorable solubility. The commercially available aliphatic amine reagents, which are in the form of their amine acetate salts, are dissolved in water at the flotation site.

For a general flotation reagent, acetate salts of relatively high molecular weight aliphatic amines are used, and particularly the octadecyl, hexadecyl and oleyl amines and mixtures of these amines have been widely used. The actual hydrocarbon content of the commercial amine salts depends on the source which the amines are manufactured. The aliphatic amines which have found general use are those prepared from such materials such as tallow, lard, soybean oil, whale oil, coconut oil and other common oils and fats. Some of the products may be hydrogenated to reduce unsaturation and thus produce materials of higher melting points.

Commercially available aliphatic amine acetates are purchased as such, and are placed in hot water to melt and dissolve the same at the site of use. This preparation of these reagent compositions has resulted in variable flotation results, and in fact some batches of the reagent have been found to be ineffectual for flotation. Where flotation problems are the result of the amine reagent itself, it is very difficult to trace the trouble. This is especially true when different portions of a batch or a barrel of the aliphatic amine acetate gives different flotation results. Due to the difficulty of tracing the trouble caused by a poor amine reagent, often the reagent is used up before the cause of the poor flotation results can be recognized as being in the particular reagent batch.

The method of preparation of the amine acetate, which is accomplished by adding acetic acid to the amine, in many instances causes chemical changes in the compounds reducing their effectiveness as collector reagents. On adding acetic acid to the amine, the composition is heated by the exothermic reaction. Often hot spots occur in the batch due to inadequate mixing and the amine in the local hot zone is converted into a substance that actually injures flotation. Also, when the amine acetate is maintained at an elevated temperature, even when the temperature is not high enough to cause instantaneous

injury, for a substantial period of time, the amine acetate may also undergo a deleterious conversion. In preparing the reagent solution, it has been the practice to immerse the amine acetate in its shipping barrel, the standard container for shipping the amine acetate, in hot water to melt the amine and allow it to escape from the barrel. If the amine acetate is heated without melting and escaping into the water and it is maintained in that stage for a substantial length of time, the deleterious conversion occurs.

It has been found that once an aqueous solution has been made of the amine acetate, no further conversion occurs, since the conversion consists generally of a dehydration. Thus once an aqueous solution of relatively low content of amine acetate is achieved, the amine acetate reagent is relatively free from further conversion.

Included among the objects and advantages of the present invention is to provide a process for preparing an amine solution without converting part or all of the amine salt to a material that is ineffectual or injurious to a flotation separation. The process of the invention provides a means for producing an amine salt solution simply and economically, and provides means for producing either a true solution of the amine salt or an emulsion of the amine in an amine salt solution. The process, further, provides a means for producing uniformly standard amine salt flotation reagent liquids which may be stored for considerable periods of time without deteriorating.

In general, the process of the invention comprising melting a minor amount of an aliphatic amine in a major portion of water, and after the amine is completely melted, an amount of acid is added to the resultant fluid to convert at least a portion of the amine into a water soluble salt. Such acids as acetic, nitric, hydrochloric, formic, hydrobromic, etc. produce salts of sufficient solubility as to form effective reagent solutions or emulsions. In one form of the invention, a stoichiometric amount of acid is added to the amine and water liquor to convert substantially all of the aliphatic amine. In another modification, a lesser amount of acid is introduced into the amine liquor to convert less than the total amount of the amine to thereby produce an emulsion of the amine in an amine salt solution. Solutions of amine salts are very effective reagents in concentrations of 2% and the emulsions of the partially neutralized amines have been found to be highly effective reagents as 2–5% emulsions.

In carrying out the objects and advantages of the invention, the following examples illustrate a preparation of several reagent compositions:

EXAMPLE I

A 2% by weight aqueous solution of an aliphatic amine acetate flotation reagent solution may be obtained as follows:

About 200 pounds of tallow amine (this corresponds to approximately the formula $C_{18}H_{37}NH_2$) are added to about 9756 pounds of water. The water and added amine are heated sufficiently to completely melt the amine. After the amine is completely liquefied, the mixture is thoroughly mixed and during the mixing 44 pounds of concentrated acetic acid are added. After the reaction of the acetic acid with the amine is complete, the solution becomes clear, and after cooling may be stored for use.

EXAMPLE II

By using the directions of Example I, and by using a hydrogenated tallow amine, a very viscous liquor is produced on heating the same quantity of water and hydrogenated tallow amine. The viscous solution is very difficult to handle. By adding 13 pounds of acetic acid, the mixture becomes a creamy emulsion and on cooling it remains liquefied and readily handled. In this case the amine is only partially neutralized (about 34%), so an emulsion of the hydrogenated tallow amine is produced in a hydrogenated tallow amine acetate solution.

Under normal conditions, hydrogenated tallow amine acetate has such a low solubility that in prior practices it was found necessary to maintain the mixture hot to insure satisfactory feeding as a flotation reagent. However, by using the procedure of the present invention which includes melting the amine in water and then adding the acetic acid, the quantity of the acetic acid may be adjusted so as to secure a readily handled emulsion. Such an emulsion, also retains its easy handling characteristics when cooled.

Partial neutralization, as set forth in Example II, provides substantial advantages in that it produces greater concentrations of the reagent as an emulsion rather than as a true solution. As provided in the example, by neutralizing about 30% based on an equivalent of the amine, very stable emulsions are produced. The emulsions of tallow amine may be made in concentrations as much as about 5% or slightly above, at ambient or room temperature, while true solutions are essentially limited to around 2% or less, depending upon the particular salt. Thus, where higher concentrations of the reagent are desired in a flotation process, less than stoichiometric neutralization is desirable so as to produce an emulsion. It has been found that at about 30% neutralization of an equivalent of the amine produces a very stable emulsion at generally higher concentrations of reagent in the aqueous mixture. After preparing the reagent aqueous compositions, the reagents were used in actual flotation tests to determine the characteristics of the reagent.

The partially neutralized compositions are, in effect, colloidal solutions. These reagents as partially neutralized colloidal solutions are very easy to handle at room temperature. They are, also, very effective as flotation reagents in the lower to the higher concentrations.

The salts and colloidal solutions of other acids were prepared by following either the procedure of Example I for 100% neutralization, or by the procedure of Example II to produce the 30% neutralization which forms the emulsions or colloidal solutions.

EXAMPLE III

Following the procedure of Example II, about 200 pounds of hydrogenated tallow amine was treated with about 70.5 pounds of 37.5% hydrochloric acid, which gave a 100% neutralization of the tallow amine, which is based on a molecular combined weight of 275. This neutralization was performed by adding the acid to the amine, which had been melted in about 9756 pounds of water. A 30% neutralization is produced by reacting about 21.2 pounds of 37.5% hydrochloric acid with the 200 pounds of amine previously melted in an equivalent amount of water. Both reagents showed very good activity as flotation reagents. In addition, the solutions handled easily and stored very well.

In the following of the procedure above, solutions and compositions of the amine with other acids were prepared, and the results tabulated in the following table:

Acid Required to Neutralize 200 Lbs. of Amine (Mol. Comb. Wt. of 275) to 100% and 30% Levels

Acid	Percent Acid in Conc. Soln.	Lb./gal.	100% Neut.		30% Neut.	
			Lb.	Gal.	Lb.	Gal.
Nitric	70	11.8	65.5	5.55	15.5	1.63
Formic	85	10.15	39.3	3.88	11.75	1.15
Hydrobromic	48	12.37	122.0	9.85	36.5	2.95
Orthophosphoric	86	15.28	55.0	3.6	16.5	1.1
Sulphuric	96	15.32	37.0	2.4	11.0	.75

Of the salts set forth in the table above, the nitrate, formate and bromide amine salts produced good emulsions which performed very well in flotation tests. The amine phosphate produced from orthophosphoric acid is based on 1½ hydrogens entering the neutralization step, but the amine phosphate is of limited solubility and are not desirable for normal flotation procedures. Similarly, the amine sulfate is of low solubility and its usefulness as a flotation reagent is quite limited.

The solubility of the resulting amine salt seems to be the determining factor for choice of the precursor acid for the neutralization. Acids which produce amine salts of essentially no water solubility do not form useful emulsions and obviously do not form true aqueous solutions. The stability of the emulsion of the amine also is a factor, since an unstable emulsion would not produce the desired flotation results.

The acetic acid and hydrochloric acid produce excellent salts for flotation reagents both as true solutions and preferably as emulsions. The nitric, formic and hydrobromic acids also produce good solutions or emulsions since the amine salt of each has good solubility.

While the invention has been specifically illustrated by certain examples, it is applicable to the full range of aliphatic amines normally used in flotation. Also, while other acids may be utilized to form other acid salts of the amine in solution, the acetate, hydrochloride are the preferred acids since these compositions have generally favorable solubility characteristics. Since the amine reagents are normally used in low percentage solutions or emulsions (on the order of one-half to five percent), it is preferable to maintain the volume of water sufficiently high to initially produce the low percent solutions without adding more water. It has been found satisfactory, however, to prepare concentrated solutions and then add water to such a concentrated solution prior to the use of the solution as a flotation reagent. The concentrated amine produced by either composition methods are easily stored and are not subject to deterioration.

While the invention has been illustrated by reference to specific illustrations, there is no intent to limit the spirit or scope of the invention to the precise details so set forth except insofar as defined in the following claims.

I claim:

1. In a process for preparing a liquefied amine collector reagent for flotation separations, the steps of melting a minor quantity of a normally solid, high molecular weight aliphatic amine composition in a major quantity of water, and then introducing into the resultant liquor a sufficient amount of an acid to react with not more than a stoichiometric amount of the amine present in the liquor, and forming therewith a water soluble salt of the amine whereby to form a stabilized aqueous amine composition containing at least about 1% by weight of the amine composition.

2. In a process for preparing a liquefied amine collector reagent for flotation separations, the steps of melting a minor quantity of a normally solid, high molecular weight aliphatic amine composition in a major quantity of water, and then introducing into the resultant liquor a sufficient amount of an acid to react with not more than a stoichiometric amount of the amine present in the liquor, and forming therewith a water soluble salt of the amine whereby to form a stabilized aqueous amine composition containing from about 1–5% by weight of the amine composition.

3. A process according to claim 2 in which about one-third equivalent of a stoichiometric amount of acid is used so as to form a stabilized composition.

4. A process according to claim 3 in which the acid is acetic acid.

5. A process according to claim 3 in which the acid is hydrochloric acid.

6. A process according to claim 3 in which the acid is nitric acid.

7. A process according to claim 3 in which the acid is formic acid.

8. A process according to claim 3 in which the acid is hydrobromic acid.

9. In a process for preparing a liquefied amine collector reagent for flotation separations, the steps of melting a minor quantity of a normally solid, high molecular weight aliphatic amine composition in a major quantity of water, and then introducing into the resultant liquor a stoichiometric amount of an acid which reacts with the amine present in the liquor to form a soluble salt thereof, whereby to form an aqueous stabilized amine salt solution.

10. A process according to claim 9 in which the acid is acetic acid.

11. A process according to claim 9 in which the acid is hydrochloric acid.

12. A process according to claim 9 in which the acid is formic acid.

13. A process according to claim 9 in which the acid is nitric acid.

14. A process according to claim 9 in which the acid is hydrobromic acid.

15. In a process for preparing a liquefied amine collector reagent for flotation separations, the steps of melting a minor quantity of a normally solid, high molecular weight aliphatic amine composition in a major quantity of water, and then introducing into the resultant liquor about 30% of a stoichiometric amount of acetic acid which reacts with the amine present in the liquor to form a soluble amine acetate salt, and thereby form an aqueous, stabilized amine composition containing at least about 1% of the amine composition by weight.

16. In a process for preparing a liquefied amine collector reagent for flotation separations, the steps of melting a minor quantity of a normally solid, high molecular weight aliphatic amine composition in a major quantity of water, and then introducing into the resultant liquor about 30% of a stoichiometric amount of hydrochloric acid which reacts with the amine present in the liquor to form a soluble amine chloride salt thereof, and thereby form an aqueous stabilized amine composition containing at least about 1% of the amine composition by weight.

17. In a process of preparing a liquefied amine collector reagent for flotation separations, the steps of melting a minor quantity of an aliphatic amine composition in a major quantity of water, and then introducing into the resultant liquor a sufficient quantity of acetic acid to react with substantially all of the amine whereby to form a stabilized amine acetate in water solution.

18. A process according to claim 17 in which the amount of amine is not more than about 5% by weight of the amount of water.

19. In a process of preparing a liquefied amine collector reagent for flotation separations, the steps of melting a minor quantity of an aliphatic amine composition in a major quantity of water, and then introducing into the resultant liquor substantially less than a stoichiometric amount of acetic acid to react with a portion of the liquefied amine whereby to form a stabilized emulsion of the aliphatic amine in an aliphatic amine acetate-water solution.

20. In a process of preparing a liquefied amine collector reagent for flotation separations, the steps of melting not more than about 5% by weight of an aliphatic amine composition in at least about 95% by weight of water, and then introducing into the resultant liquor substantially less than a stoichiometric amount of acetic acid to react with a portion of the liquefied amine whereby to form a stabilized emulsion of the aliphatic amine in an aliphatic amine acetate-water solution.

References Cited in the file of this patent

UNITED STATES PATENTS

2,816,870 Lentz ---------------- Dec. 17, 1957

FOREIGN PATENTS

1,096,459 France ----------------- Feb. 2, 1955

OTHER REFERENCES

The Chemistry of Fatty Amines, pamphlet pub. 1948 by Armour Chemical Division, Armour and Company, Chicago, Ill., 18 pages of text, 1 page reference.