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PROCESS OF FLOTATION SEPARATION OF ORE

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This invention relates to ore separation agents comprising admixtures of primary aliphatic amines having at least six carbon atoms with straight chain aliphatic nitriles having at least six carbon atoms, both of such substances being in substantial quantities, it further comprises processes wherein ores are subjected to a froth flotation in the presence of a mixture of primary aliphatic amines containing at least six carbon atoms and aliphatic nitriles containing at least six carbon atoms, and it more specifically comprises processes wherein siliceous minerals are separated from non-siliceous minerals by flotation in the presence of straight chain aliphatic nitriles and primary aliphatic amines, both of which contain at least six carbon atoms.

The higher primary aliphatic amines are important flotation agents because they show a high degree of selectivity for certain constituents in the ore mixture. It is not particularly important in any flotation separation process which of the mineral constituents concentrates in the float and which concentrates in the tailings. The major object of any separation process is that of separating the constituents into phases rich in one constituent.

The primary aliphatic amines, and to a lesser extent, the primary aliphatic amine salts, are highly effective for the separation of silica. They also show selective action when other ores are subjected to a flotation process. For example, the primary aliphatic amines containing six carbon atoms will cause silica to float away from a phosphate ore, leaving the phosphate behind as a tailing. On the other hand, such amines may be preferentially adsorbed by metalliferous ores, such as metallic sulfides, causing these to float and leaving the siliceous gangue behind as a tailing.

It has been shown experimentally that the higher primary aliphatic amines, and by that term in the present specification we mean to include those amines having at least six carbon atoms, and exclude those having a lesser number of carbon atoms, function quite differently from the higher primary aliphatic amine salts. The amine salts, as has been recognized by prior workers in this art, will ionize in water to form so-called cation-active surface agents. These surface-active agents act selectively upon certain constituents in the ore and are analogous to the so-called surface-active wetting agents, all of which depends upon ionization for their functioning. On the other hand, the primary aliphatic amines themselves are insoluble in water and do not undergo ionization. This holds true for all higher members of the series, namely those having twelve or more carbon atoms. It is an observed fact, however, that the higher primary amines do function differently from the corresponding amine salts. Undoubtedly, the primary amine is adsorbed by certain ore values as a kind of surface layer one or two moleclues thick. Experimental results show quite wide differences between the behavior of primary amines and primary amine salts. This is especially noticeable when comparisons are made between the amounts of these two agents which are necessary to give equal results. The flotation can be successfully practised with less primary amine per ton of ore than is required when primary amine salts are used. Moreover, the selective index for the separation is greater when primary amines are used.

However, those primary amines and their salts which have flotation properties are relatively expensive substances. Since they are prepared from the corresponding fatty acids they are thus more costly than the fatty acids themselves. It can be said categorically that the relatively high cost of the primary amines has, and probably will in the future, prevent the use of the primary amines alone as flotation agents. This is so in spite of the fact that they work very well indeed and give high selective indices. It can also be said that any process by which the cost per ton for the flotation agent could be reduced even though amines or amine salts are used would constitute an important step forward in this art.

Accordingly, we have set ourselves to the problem of discovering ways by which higher primary amines can be used for the flotation separation of ores under such conditions that the cost per ton of ore is greatly lessened. And as a result of our experiments we have discovered that the amount of such primary amines ordinarily required to perform some particular separation can be greatly reduced provided substantial quantities of higher primary aliphatic nitriles are used in admixture with the primary amine. Thus, for example, such an amine-nitrile mixture will contain approximately 50% to 80% by weight of primary aliphatic amines having six or more carbon atoms and 50% to 20% by weight of primary aliphatic nitriles having at least six carbon atoms.

But the use of nitriles in conjunction with the amines is not simply one of diluting the amount of amine by the addition of nitriles thereto. Indeed the nitriles themselves are relatively ex-

pensive materials since they must also be made from the fatty acids. What we have discovered is that when mixtures of amines and nitriles are employed the total quantity of amine-nitrile mixture is many times less than the quantity of primary amine which would be necessary to achieve the same degree of separation.

For example, some separations may require as much as six pounds per ton of a primary aliphatic amine having at least six carbon atoms. An even better separation of such an ore can be obtained when only one pound of a mixture of nitriles and amines is used. In every instance the amount of amine-nitrile mixture is always far less than the amount of primary amine which would be required if that substance were used alone. We emphasize this so that it will be clearly understood that we are not merely substituting a quantity of nitriles for a part of the primary amine ordinarily required for performing the separation when used alone.

Thus, in broad aspects, the present invention comprises as a new flotation agent a mixture of primary aliphatic amines and aliphatic nitriles, each of which contains at least six carbon atoms and in which both substances are present in substantial quantities. The pending application of Ralston et al., Serial No. 116,422, discloses mixtures of amines and nitriles but the quantities of nitrile therein is not more than about 4% or 5% and are simply small amounts of nitriles which have not been reduced to amines. The present invention differs from that co-pending application in that the amount of nitriles is substantial, never less than about 20%, and it is only when substantial quantities of nitriles are present that the particular function of the nitriles in reducing the amount of amines necessary comes into play.

In more specific aspects our invention embraces the flotation separation of ores by using the nitrile-amine mixtures of the present invention, and in still more specific aspects the present invention includes processes wherein silica is separated from non-siliceous minerals by means of the nitrile-amine mixtures of the present invention.

As stated, the amines which we use are all primary aliphatic amines containing at least six carbon atoms. These range from hexylamine, up to octadecylamine having eighteen carbon atoms. The amines may be either saturated or unsaturated, or mixtures of both. They are most conveniently prepared by converting fatty acids, such as cottonseed oil fatty acids, to the corresponding nitriles, and then reducing those nitriles to the corresponding amine. In such instances, the amines obtained will be a mixture of saturated and unsaturated amines in which the alkyl group is predominantly octadecyl or octadecenyl, together with minor quantities of secondary and tertiary amines. One such amine mixture may contain about 75% of primary aliphatic amines having, on the average, eighteen carbon atoms and 25% of secondary and tertiary amines.

The nitriles which we use all contain at least six carbon atoms and thus range from capronitrile to stearonitrile and unsaturated analogues thereof. These nitriles are advantageously prepared by reacting fatty acids with ammonia as described in certain Ralston patents.

The quantity of primary aliphatic amines and straight chain aliphatic nitriles can vary over reasonably wide limits but in every case there should be at least about 20% of nitriles in the mixture used as a flotation agent. Generally the amount of nitriles present does not exceed about 50%, but the operable range is from about 20% to about 65%, the rest being primary amines. The nitriles are soluble in the primary aliphatic amines, and, consequently, we prepare solutions of the nitriles in the amines and add these mixtures to the ore pulp to be separated. The flotation process itself differs in no way from that hitherto practised in the art.

In the foregoing we have generally emphasized admixtures of primary amines and aliphatic nitriles as the flotation agent in our process. We do not wish to exclude flotation in the presence of amine salts and the nitriles. But when amine salts are used it is best to add a mixture of primary amines and nitriles to the ore pulp and then acidify the pulp to such a point where the primary amines are converted to their corresponding salts. The nitriles are not soluble in primary amine salts, but it is possible, as an alternative method, to add the nitriles and the amine salts separately to the ore pulp to be treated. Since we have discovered that the amines function better than the amine salts in conjunction with substantial quantities of nitriles we prefer to use the amines in free base form rather than the amines as amine salts. But we do not wish the present invention to be so narrowly construed as to exclude flotation under such conditions that the added amines can be considered to exist as amine salts, or where the amine is directly added to the pulp in the form of its corresponding salt. Such salts are water-soluble and are hydrochlorides or acetates in most cases. But we also wish to emphasize that the amines are not the equivalents of the amine salts as will be pointed out in examples which we shall give presently.

We shall now describe a number of examples illustrating results which we have obtained on various types of ores so that those skilled in the art may understand the technical advantages residing in our process.

Example 1

36.459 grams of a deslimed phosphate ore which analyzed 15.25% P_2O_5, 20.96% CaO and 60.25% SiO_2 were placed in a Denver type flotation cell and 0.28 lb. per ton of a nitrile-amine mixture added. The mixture consisted of 64% amines prepared from palm oil nitriles and 36% nitriles prepared from cottonseed oil acids. Before the addition of the reagent the pH of the slurry was adjusted to 9.5 by the addition of sodium hydroxide solution. The flotation resulted in a concentrate which weighed 20.951 grams and a tailing which weighed 15.508 grams. The composition of the concentrate was as follows: SiO_2, 89.87%, CaO, 5.14%, and P_2O_5, 2.95%. The composition of the tailing was as follows: SiO_2, 15.07%, CaO, 44.25%, and P_2O_5, 32.42%. The percent B. P. L. of the tailing is, therefore, 70.8 and the percent recovery of the phosphate 89.05.

For comparison a similar sample was separated using octadecyl amine alone as the flotation agent. The sample required three pounds per ton of the amine and the phosphate recovery was 74.6%.

Thus from the above example it is apparent that only 0.28 pound per ton of the nitrile-amine mixture was necessary to get a percentage recovery of 89.05 whereas three pounds per ton of octadecyl-

amine alone gave a phosphate recovery of only 74.6%. This example clearly indicates that when substantial quantities of aliphatic nitriles are present in admixture with primary amines the total amount of nitrile-amine mixture is far less than the amount of octadecylamine required when this substance is used alone.

We shall now give an example wherein the amine is converted to an amine salt, namely the acetate, by the addition of acetic acid prior to performing the flotation.

Example 2

38.691 grams of the ore described in Example 1 were treated with 0.28 pound per ton of a nitrile-amine mixture. The mixture consisted of 66% of amines prepared by the hydrogenation of palm oil nitriles and 34% of nitriles prepared from cottonseed oil fatty acids. The flotation was conducted in the Denver type flotation cell which was mentioned under Example 1. The pH of the slurry was adjusted to 5.4 by the addition of acetic acid. This adjustment in pH was made after the nitrile-amine mixture had been added. The flotation resulted in a concentrate which weighed 28.120 grams and analyzed as follows: SiO_2, 71.13%, CaO, 38.95%, and P_2O_5, 28.75%. Under these conditions the phosphate recovery is 49.27%.

A comparison of this example with Example 1 shows that while the flotation using nitrile-amine mixtures conducted on the acid side are satisfactory as far as the amount of material floated is concerned, the selectivity is not as great as when the flotation is conducted on the alkaline side. In flotations conducted on the acid side the amine is present as an amine salt as distinguished from the undissociated amine which is present when the flotations are conducted on the alkaline side.

Examples 1 and 2 describe results obtained when primary amines, or amine salts having sixteen and eighteen carbon atoms are used. Example 3, which follows, shows results obtained when the primary amine contains sixteen carbon atoms and the nitrile contains eighteen carbon atoms. It may be stated at this point that it is not necessary that the nitrile and amine have the same number of carbon atoms. These can vary from six to eighteen.

Example 3

A sample of the same ore was treated in the flotation cell with 0.56 lb. per ton of a mixture which consisted of 75% of hexadecyl amine and 25% of octadecyl nitrile. The sample weighed 37.440 grams.

The concentrate weighed 9.983 grams and had the following composition: SiO_2, 96.66%, CaO, 1.99%, and P_2O_5, 1.35%. A further addition of reagent (0.28 lb. per ton) was made which resulted in a concentrate which weighed 10.819 grams and had the following composition: SiO_2, 81.18%, CaO, 9.72%, and P_2O_5, 7.16%. The tailing weighed 16.638 grams and analyzed as follows: SiO_2, 19.92%, CaO, 41.46%, and P_2O_5, 31.06%. This corresponds to a phosphate recovery of 85.03%.

Example 4

The ore treated was a deslimed "mud pond" sludge which had the following composition: SiO_2, 18.05%, CaO, 38.20%, R_2O_3, 5.04%, and P_2O_5, 28.40%. Considerable prior work had been done upon similar samples and it was determined that at least four pounds per ton of reagent was required to produce a satisfactory separation when amines such as dodecylamine or octadecylamine were employed. For example, in a typical run, four pounds per ton of octadecylamine gave a product which analyzed 71.2 percent B. P. L. The phosphate recovery in this instance was 68.89%.

A sample weighing 29.662 grams was floated with the equivalent of 2.2 pounds per ton of an amine-nitrile mixture. The mixture used consisted of 33% octadecylamine and 67% octadecylnitrile. The concentrate weighed 11.370 grams and had the following percentage composition: SiO_2, 30.40%, R_2O_3, 3.86%, CaO, 29.50%, and P_2O_5, 22.35%. The tailings weighed 18.292 grams and analyzed as follows: SiO_2, 6.30%, R_2O_3, 4.02%, CaO, 44.70%, and P_2O_5, 33.21%. The percent B. P. L. of the tailings is, therefore, 72.55 and the phosphate recovery 70.51%.

In Example 4 the amount of amine-nitrile mixture required is rather high, namely 2.2 pounds per ton of ore. This large amount in comparison with Example 3, is due to the very fine state of sub-division of the ore. We have found that when the ore is very finely divided somewhat larger quantities of flotation agents are necessary, regardless of the character of the flotation agent. Yet the example shows that only 2.2 pounds per ton of amine-nitrile is necessary to get an even higher recovery than can be obtained when four pounds per ton of octadecylamine alone is used.

Example 5

A deslimed sample of the same ore was floated with the equivalent of 1.6 lbs. per ton of a mixture which consisted of 33% nitriles prepared from coconut fatty acids and 67% amines prepared from cottonseed nitriles. The sample used weighed 30.658 grams. The flotation resulted in a concentrate which weighed 9.228 grams and a tailing which weighed 21.430 grams. The composition of the concentrate was as follows: SiO_2, 34.10%, R_2O_3, 3.66%, CaO, 27.30%, and P_2O_5, 20.34%. The tailings analyzed as follows: SiO_2, 6.70%, R_2O_3, 3.66%, CaO, 44.58%, and P_2O_5, 33.29%. This corresponds to a phosphate recovery of 79.17%. The percent B. P. L. of the tailings is 72.7.

Example 6

A deslimed sample of the same ore was treated with the equivalent of 1.1 lbs. per ton of a mixture which consisted of 33% palm oil amines and 67% of nitriles prepared from cottonseed acids. This flotation gave a concentrate which weighed 5.839 grams and had the following composition: SiO_2, 41.90%, R_2O_3, 3.66%, CaO, 25.60%, and P_2O_5, 18.35%. A further amount of reagent corresponding to 0.55 lb. per ton was then added and the flotation continued. This resulted in a concentrate which weighed 6.529 grams and had the following composition: SiO_2, 18.30%, R_2O_3, 4.30%, CaO, 36.62%, and P_2O_5, 27.42%. The tailings weighed 18.500 grams and analyzed as follows: SiO_2, 5.35%, R_2O_3, 3.77%, CaO, 44.35%, and P_2O_5, 32.98%. The distribution of the bone phosphate of lime, is, therefore, as follows: 72.01% in the tailings, 10.48% in the first concentrate and 17.51% in the second concentrate. The percent B. P. L. of the tailings was 72.03. The percentage distribution of the silica was as follows: 21.38% in the tailings, 55.21% in the first concentrate, and 23.41% in the second concentrate.

Example 7

49.567 grams of a fluorspar ore which analyzed 73.5% calcium fluoride and 21.6% silica was treated in the flotation cell with 0.25 lb. per ton of a nitrile-amine mixture. The mixture contained 60% octadecylamine and 40% lauronitrile. The concentrate weighed 29.736 grams and contained 94.8% calcium fluoride and 4.5% silica. The tailings weighed 19.831 grams and contained 42.39% silica and 41.92% calcium fluoride. This corresponds to a recovery of 77.14% of the calcium fluoride in the concentrate and a rejection of 87.48% of the silica present.

For purposes of comparison a sample of the same ore was separated by the use of octadecylamine. In the Denver type flotation cell the sample required two pounds of amine per ton of ore. This resulted in a separation of 75.78% of the calcium fluoride as a concentrate and a rejection of 85.72% of the silica in the tailing.

Example 8

A sample of calcite which contained 91.18% of calcium carbonate and 7.32% silica was placed in the flotation cell in the equivalent of 0.15 pound per ton of a mixture of dodecylamine and hexadecylnitrile. The mixture contained 50% by weight of dodecylamine. The original sample weighed 50.124 grams. Separation resulted in a concentrate which weighed 4.388 grams and which contained 31.18% silica. The tailings weighed 45.736 grams and analyzed 95.41% calcium carbonate and 3.72% silica. This corresponds to a separation of 95.48% of the calcium carbonate in the tailings and 53.41% of the silica in the concentrate.

A similar sample required 0.60 pound per ton of dodecylamine to obtain a comparable result.

The foregoing example illustrates the effectiveness of our amine-nitrile mixtures with a number of non-metalliferous ores from which it is desired to separate the silica. Good results are also obtained when the amine-nitrile mixtures of the present invention are used for the separation of constituents of metalliferous ores, such as the various copper sulfide ores. Examples 1 and 2 also illustrate the wide difference in behavior between the amines and the amine salts. Results are very much better when flotation in the presence of the free amines is insured by maintaining the slurry on the alkaline side. But for the sake of showing the scope of our invention we have included an example illustrative of results obtained when operating on the acid side.

Having thus described our invention, what we claim is:

1. The process of separating ores which comprises subjecting the ore to flotation separation in the presence of a flotation agent comprising a mixture of at least one primary aliphatic amine and at least one aliphatic nitrile, each containing at least six carbon atoms, the amount of nitrile being about 20% to about 65% of the combined quantity of amine and nitrile.

2. The process of separating siliceous gangue from ores containing the same which comprises subjecting the ore to flotation separation in the presence of a flotation agent comprising a mixture of at least one primary aliphatic amine and at least one aliphatic nitrile, each containing at least six carbon atoms, the amount of nitrile being about 20% to about 65% of the combined quantity of amine and nitrile.

3. The process of separating siliceous gangue from phosphate ores containing the same which comprises subjecting the ore to flotation separation in the presence of a flotation agent comprising a mixture of at least one primary aliphatic amine and at least one aliphatic nitrile, each containing at least six carbon atoms, the amount of nitrile being about 20% to about 65% of the combined quantity of amine and nitrile.

4. The process of separating ores which comprises subjecting the ore to flotation separation in the presence of a flotation agent comprising a mixture of at least one primary aliphatic amino compound chosen from the group consisting of primary aliphatic amines having at least six carbon atoms and water-soluble salts thereof, and at least one aliphatic nitrile containing at least six carbon atoms, the amount of nitrile being about 20% to about 65% of the combined quantity of amino compound and nitrile.

5. The process of separating phosphate ores which comprises subjecting the ore to flotation separation in the presence of a flotation agent comprising a mixture of at least one primary aliphatic amino compound chosen from the group consisting of primary aliphatic amines having at least six carbon atoms and water-soluble salts thereof, and at least one aliphatic nitrile containing at least six carbon atoms, the amount of nitrile being about 20% to about 65% of the combined quantity of amino compound and nitrile.

6. The process of separating ores which comprises subjecting an aqueous alkaline slurry of the ore to flotation separation in the presence of a flotation agent comprising a mixture of at least one primary aliphatic amine and at least one aliphatic nitrile, each containing at least six carbon atoms, the amount of nitrile being about 20% to about 65% of the combined quantity of amine and nitrile.

7. The process of separating phosphate ores which comprises subjecting the ore to flotation separation in the presence of a flotation agent comprising a mixture of at least one primary aliphatic amine and at least one aliphatic nitrile, each containing at least six carbon atoms, the amount of nitrile being about 20% to about 65% of the combined quantity of amine and nitrile.

8. The process as in claim 1 wherein the amine and nitrile contain sixteen to eighteen carbon atoms.

9. The process as in claim 2 wherein the amine and nitrile contain sixteen to eighteen carbon atoms.

10. The process as in claim 3 wherein the amine and nitrile contain sixteen to eighteen carbon atoms.

11. The process as in claim 4 wherein the amine and nitrile contain sixteen to eighteen carbon atoms.

12. The process as in claim 5 wherein the amine and nitrile contain sixteen to eighteen carbon atoms.

13. The process as in claim 6 wherein the amine and nitrile contain sixteen to eighteen carbon atoms.

14. The process as in claim 7 wherein the amine and nitrile contain sixteen to eighteen carbon atoms.

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