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REMOVAL OF SILICA FROM NONMETALLIC ORES BY FROTH FLOTATION

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12 Claims. (Cl. 209—166)

This invention relates to an improved method of froth flotation of silica using certain classes of cationic reagents.

The flotation of silica by means of various cationic reagents has become of considerable importance, particularly in the beneficiation of phosphate ore from the Florida pebble phosphate field because of the fact that it is possible to obtain improved grade.

A number of cationic flotation reagents have been proposed, among which the condensation product of polyalkylene polyamines with fatty acids have proven to be extraordinarily useful, both by reason of their activity and the simpler and less critical flotation procedure which may be employed. The use of reagents of this type are described and claimed in the patent to Christmann, Jayne and Erickson, No. 2,278,060 of March 31, 1942. The reagents of that patent were obtained by reacting the materials at from about 130°–250° C. The present invention relates to an improvement in the process of floating silica using the abovementioned class of reagents.

In the flotation of silica, particularly in phosphate ores, the problem of slime is a critical one and in many cases it is not sufficient for best results to completely deslime a flotation feed because the flotation operation itself tends to produce secondary slime from the soft coated surfaces of the phosphate particles. This has led to a process in which the deslimed feed is subjected to polishing followed by a secondary desliming as described and claimed in the patent to Mead and Maust, No. 2,216,040 of September 24, 1940. Improved results are thereby obtained, but at the expense of further processing steps. It has been found that polishing may be eliminated or reduced if the flotation is carried out very rapidly before any time has elapsed in the flotation cell which would permit the formation of secondary slimes. This procedure is described and claimed in the copending application of Mead and Maust, Serial No. 322,771, filed March 7, 1940. High speed in flotation is therefore of great utility in the removal of silica.

The present invention is based on the discovery that when water solutions or dispersions of polyalkylene polyamine condensation products are prepared, considerable material which appears to be colloidal and which gives to the dispersion a kind of silky appearance is present. It has been found that if this silky appearance can be removed improved results are obtained and speed of flocculation is greatly increased.

The presence of colloidal material may be avoided in two different ways. Heat may be applied and on heating the water dispersion loses its silky appearance and is transformed into a clear solution, and the solution remains clear and gives improved results for a certain limited period of time after it has cooled down again. This method forms the subject matter of the copending application of Maust and Hollingsworth, Serial No. 440,986, filed April 29, 1942. The other method, which forms the basis of the present invention, is the filtering of the dispersion which also removes the silky appearance. The two processes effect improved results and each has advantages and disadvantages. The Mead and Hollingsworth process permits obtaining slightly higher grade but it is open to the disadvantage that the effect is not lasting and that the dispersion of the collector has to be used within a short time after heating, whereas the process of the present invention, while giving almost as high grade, is not open to the disadvantage that the effect is not lasting and considerable operating advantages are obtained by the possibility of treating the collector dispersion and using it for some period of time afterwards.

While it seems very probable that filtration may clarify the solution by the removal of colloidal material and that this is one of the main reasons for the improved results obtainable by the process of the present invention, it has not proven possible hitherto to determine definitely what adverse effect the colloidal material exerts and therefore it is not desired to limit the present invention to any theory of action.

Extensive tests undertaken in conjunction with the Maust and Hollingsworth invention referred to above have definitely shown that speed of flocculation is increased when the apparently colloidal material is removed or transformed into a clear solution and it seems probable that the increased speed of flocculation may be an important factor in the improved results. A corresponding increase of speed of flocculation is noted when the polyamine fatty acid promoters are filtered and it is to be presumed that the same factor of increased speed of flocculation will perform the same function in the present process as in that of the Mead and Hollingsworth application referred to above. It is not desired, however, to limit the invention to this particular theory of action and it is possible that other factors may be involved and may even be of greater importance than speed of flocculation.

It seems reasonably sure that the somewhat lower grade obtained when water dispersions of

polyalkylene polyamine fatty acid condensation products are used without treatment is due to at least two factors. The first, and apparently the most important, is the presence of the seemingly colloidal material, but some other factor must also be present because when the material is filtered in accordance with the general procedure of the present invention, the results can be still further improved, although by no means so greatly, by heating the filtered solution and this combination of filtering and the procedure of heating described by Maust and Hollingsworth constitutes a preferred procedure where maximum grade is all important and the operating difficulties incident to heating the collector dispersion very shortly before use are considered of minor importance. It should be noted that the combined procedure has the further advantage that any material variations in operating procedure which might result in standing long enough to eliminate the improvement obtained with unfiltered solution which has been heated will not have a similar adverse effect on a solution which has been filtered except after standing for several days. This additional safety factor is of considerable practical value in operations where the extremely close control which is possible in a laboratory operation is often impracticable. The preferred filtered and heated solution therefore has the advantage that it permits substantially a maximum grade with lower sensitivity to operating variations.

The invention will be described in greater detail in conjunction with the following specific example in which a typical Florida pebble phosphate feed of −35 mesh was deslimed, polished and again deslimed and then divided into three portions, each of which was conditioned with approximately 1½ pounds per ton of an acetate of a condensation product of coconut fatty acids with a mixture of polyethylene polyamine containing predominantly diethylene diamine, triethylene tetramine, and tetraethylene pentamine. The first portion was conditioned with cold 4% aqueous dispersion having a silky appearance. The second was conditioned with a solution which had been filtered which removed about 1% and the third was conditioned with a filtered solution which had then been heated and cooled and was used immediately after cooling.

The first portion gave a phosphate tailing containing 6.4% insoluble material. The froth was small and the bubbles large. The second portion gave a phosphate tailing containing 3.6% insoluble material. The froth was voluminous and very fine bubbles. The third portion which was treated with the filtered and heated material gave a phosphate tailing having 2.85% insoluble material and the froth was fine bubbled and slightly more voluminous than the second portion.

Similar results are obtained with other polyalkylene polyamine condensation products such as the condensation product of palm oil with the mixed polyethylene polyamines. Some variations are noted due to the fact that the different condensation products are of slightly different activity. The improvement is of the same order.

Tests of speed of flocculation were made with −48 mesh Florida pebble phosphate flotation feed which was polished and deslimed. In the test procedure the feed was conditioned at high solids with a 2% solution of the polyethylene polyamine coconut fatty acid condensation product described above, and six tests were made on six proportions, using various amounts of filtered and unfiltered reagent. The reagent solution was cold to eliminate any effect on speed of flocculation due to heating.

After conditioning, each portion of ore was diluted to froth flotation density, agitated for three seconds in a laboratory size Fagergren flotation cell, the air turned on, and silica floated for 10 seconds, and then a small sample of phosphate tailings removed from the bottom of the cell while it was running. Assays for insoluble content were made on the samples thus withdrawn. In general the nature of the froth produced by filtered and unfiltered reagent was quite different. The unfiltered reagent produced a small froth with relatively large bubbles, while the filtered reagent produced a relatively large froth with small bubbles. The metallurgical results appear in the following table:

Table

Insoluble	Reagent, lbs./ton feed	
	Unfiltered reagent	Filtered reagent
20.00	.45	.45
4.80		
14.00	.63	.63
2.10		
12.40	.81	.81
1.50		

It will be apparent from the table that a very marked increase in silica removal in the very short flotation time was effected by filtering the reagent, showing a marked increase in speed of flocculation as a test as is described above using so short a flotation time is primarily a measure of speed of flocculation. It is interesting to note that with larger amounts of reagent, in spite of the extraordinarily short flotation time, the silica removal is such as to produce a commercially useful phosphate tailing when filtered reagent is used, but no commercially useful results are obtained with unfiltered reagent in any concentration used.

The invention has been described in more detail in conjunction with the flotation of silica from phosphate rock as this is the most important commercial process at the present time. However, the action of the reagent is primarily on the silica and the presence of the phosphate except insofar as it tends toward slime formation is secondary. Comparable improved results are obtained in floating silica away from other non-metallic ores.

I claim:

1. A method of floating silica from a non-metallic ore which comprises conditioning an ore pulp with a solution of a condensation product, obtained at from about 130°–250° C., of higher fatty acids with polyalkylene polyamines said solution having been clarified by filtration and subjecting the conditioned pulp to froth flotation to produce a concentrate high in silica and a tailing low in silica.

2. A method of floating silica from phosphate ore which comprises conditioning the ore pulp with a solution of a condensation product, obtained at from about 130°–250° C., of higher fatty acids with polyalkylene polyamines said solution having been clarified by filtration and subjecting the conditioned pulp to froth flotation to produce a concentrate high in silica and a tailing low in silica.

3. A method of floating silica from non-metal-

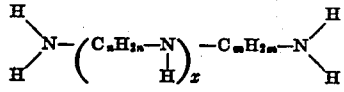
lic ore which comprises conditioning the ore pulp with a solution of a condensation product, obtained at from about 130°–250° C., of higher fatty acids with a mixture of polyalkylene polyamines said solution having been clarified by filtration and heated and subjecting the conditioned pulp to froth flotation promptly thereafter to produce a concentrate rich in silica and a tailing low in silica.

4. A method of floating silica from phosphate ore which comprises conditioning the ore pulp with a solution of a condensation product, obtained at from about 130°–250° C., of higher fatty acids with a mixture of polyalkylene polyamines said solution having been clarified by filtration and heated and subjecting the conditioned pulp to froth flotation promptly thereafter to produce a concentrate rich in silica and a tailing low in silica.

5. A method according to claim 2 in which the polyalkylene polyamines are polyethylene polyamines.

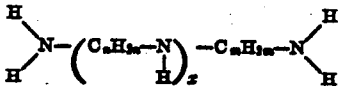
6. A method according to claim 4 in which the polyalkylene polyamines are polyethylene polyamines.

7. A method of floating silica from a nonmetallic ore which comprises conditioning an ore pulp with a solution of a promoter chosen from the group consisting of the reaction products, obtained at from about 130°–250° C., of polyalkylene polyamines, represented by the following general formula:



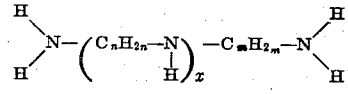
in which n, m, and x are small whole numbers with higher fatty acids or esters and acid addition salts thereof, said compounds being free from sulfonic groups, said solution having been clarified by filtration, and subjecting the conditioned pulp to froth flotation to produce a concentrate high in silica and a tailing low in silica.

8. A method of floating silica from a nonmetallic ore which comprises conditioning an ore pulp with a solution of a promoter chosen from the group consisting of the reaction products, obtained at from about 130°–250° C., of polyalkylene polyamines, represented by the following general formula:



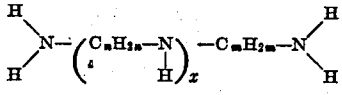
in which n, m, and x are small whole numbers with higher fatty acids or esters and acid addition salts thereof, said compounds being free from sulfonic groups, said solution having been clarified by filtration and subsequently heated, and subjecting the conditioned pulp to froth flotation to produce a concentrate high in silica and a tailing low in silica.

9. A method of floating silica from a phosphate ore which comprises conditioning an ore pulp with a solution of a promoter chosen from the group consisting of the reaction products, obtained at from about 130°–250° C., of polyalkylene polyamines, represented by the following general formula:



in which n, m, and x are small whole numbers with higher fatty acids or esters and acid addition salts thereof, said compounds being free from sulfonic groups, said solution having been clarified by filtration, and subjecting the conditioned pulp to froth flotation to produce a concentrate high in silica and a tailing low in silica.

10. A method of floating silica from a phosphate ore which comprises conditioning an ore pulp with a solution of a promoter chosen from the group consisting of the reaction products, obtained at from about 130°–250° C., of polyalkylene polyamines, represented by the following general formula:



in which n, m and x are small whole numbers with higher fatty acids or esters and acid addition salts thereof, said compounds being free from sulfonic groups, said solution having been clarified by filtration and subsequently heated, and subjecting the conditioned pulp to froth flotation to produce a concentrate high in silica and a tailing low in silica.

11. A method according to claim 8 in which the fatty acid is a coconut fatty acid.

12. A method according to claim 10 in which the fatty acid is a coconut fatty acid.

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