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FLOTATION PROCESS

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This invention relates to the froth flotation concentration of oxide compounds of the alkaline earth metals from argillaceous pulps, and more particularly to the use of aqueous emulsions of fatty acid collecting reagents. It is especially concerned with the flotation of calcite from finely divided pulps of argillaceous limestones, marls and chalks, to derive therefrom raw material mixtures, or lime components of mixtures, suitable for the production of desired types of Portland cement, and will be specifically described hereinafter in its application to such uses, but it will be understood that it is of more general utility.

In many of the natural limestones, marls and chalks, the constituent minerals are so fine that extremely fine grinding is required to free the bonds, or at least to release a sufficient proportion of the mineral or minerals occurring in excessive quantity, to permit the desired elimination. The resulting pulps are not readily amenable to froth flotation because the slimes constitute at least the major quantity. With some of these pulps, a limited de-sliming can be practiced, but frequently this is undesirable in view of weight losses and is impractical where the mineral sizes are such that the actual calcite separations are made in the lower micron ranges of particle size. Especially in cement manufacture, the calcite and quartz slimes should be recovered and utilized because intimate contact of fine particles is essential to produce uniform and complete reactions in burning the ultimate mixture to clinker.

With few exceptions, natural materials of the class described contain alumina in too great abundance to make them suitable for the manufacture of modern cements of the low-heat of hydration and sulphate resisting types, and in many the proportion of alumina is too large to permit production of cements of moderate heat of hydration suitable for ordinary uses, such as highway construction. In these materials, all tangible quantities of alumina are silicates, principally the micas, but other silicates, such as

kaolin or kaolinite and the feldspar minerals, etc., are common and may be present with one or more of the micas. The micaceous matter is readily released in grinding and the proportion in the slimes makes flotation separations difficult, as the froth is contaminated by particles trapped, probably mechanically, due to the fineness of the mica particles and their shapes, which give them a much slower settling rate than the other tailing minerals.

It has been discovered that light stage oiling flotation circuits are essential to effect a satisfactory differential separation of calcite from such pulps. In relatively warm pulps, oleic acid is a satisfactory collector, but as pulp temperatures are reduced, dispersion is incomplete and the consequent partial over-oiling causes decreased grades of concentrates due to partial heavy flocculation. Further, the relatively high cost of oleic acid makes its use objectionable for concentrating calcite, particularly in view of the low commercial value of cement. The high titre fatty acids, such as fish oil acids derived from fish scrap, are unsatisfactory as they cannot be uniformly dispersed and cause heavy flocculation, especially in cold water.

It has been proposed heretofore to employ emulsified fatty acids as collectors of other oxide ore minerals, but these lack utility in calcite pulps of the types described. Each of the three principal types have undesirable characteristics for the present purposes. Those stabilized by amine soaps produce heavy, matted froths of low-grade, difficult to clean by froth flotation and difficult to thicken, as heavy scum, carrying up to 5% of the weight of the calcite, floats on the surface of the thickener and cannot be destroyed by spraying or other convenient means. Further, these emulsions tend to form layers, i. e., are not as stable as those to be described hereinafter. The sodium soaps, used as stabilizers, produce excessive froths that cannot be controlled in stage oiling circuits and the emulsions are usually unstable. Emulsions stabilized by sulphonated alcohols produce low-grade con-

centrates and the froths are likewise too voluminous for practical purposes.

It is accordingly among the purposes of the invention to provide stable oil in water emulsions of the fatty acids, that can be used in high water dilutions to effect complete dispersion in the pulps, and to permit accurate and uniform control of the small quantities introduced at each of the oiled stages, whereby selective differential separations can be made of the calcite from the tailing minerals. It is a further objective to produce efficient collectors based on the cheaper fatty acids. It is a further purpose to provide emulsions of low frothing characteristics, whereby the froth balance of the cells can be controlled by additions of the usual frothing agents. It is also a purpose to provide collecting reagents that can be used at all ranges of pulp temperature, including temperatures just above freezing.

In general, the invention comprises the use of oil in water emulsions of fatty acids as collecting reagents for oxide ore minerals, particularly calcite. These emulsions are stabilized by rather critical quantities of a "sulphonated" oil of a class to be described hereinafter. The aqueous dispersions are relatively high, the ratio of oil to water being in a range of 1:10 to 1:30, and preferably within a range from 1:25 to 1:30, to permit accuracy in control of quantities and rapid dispersion in the pulps, particularly in stage oiling circuits. Greater ratios offer no apparent advantage in dispersion and the quantities involved are inconvenient. Ratios in the neighborhood of 1:5 are liable to inversion to water in oil emulsions in cold weather and are not readily controlled and dispersed.

The stabilizing agents used are of the class of "sulphonated" vegetable and animal oils, including fish oils. In this class, some are true sulphonated oils, of which sulphonated tea seed oil is probably an example, but others, such as sulphonated castor oil are sulphuric acid esters. The latter are commonly referred to and will be called sulphonated oils herein. The oils of the present invention are accordingly sulphonates or sulphates of glycerides of fatty acids, with more or less free acid.

The proportions of sulphonated oil required to produce dilute fatty acid emulsions, both stable at normal temperatures, and having desirable flotation characteristics, are rather critical and range from 5 to 7 parts, by weight, to 100 parts, by weight of the fatty acid oils. These proportions are not affected by the titre or the free fatty acid content of the oil. The preferred proportion is the minimum necessary to stabilize the emulsions, usually 5 parts, such emulsions remaining stable indefinitely at normal temperatures, some of the emulsions kept for three months showing no tendency to break down. Lesser quantities of the sulphonated oils do not produce complete stability, particularly in cold weather and in the lower ratios of water dilutions. Proportions above 7 parts are unsatisfactory, in the fine pulps described, as the excessive quantities result in poor selectivity, due to a pronounced tendency to produce heavy, matted froths, difficult to clean by froth flotation, with or without additional reagents or reagent quantities. Further, these tough froths are not effectively broken by spraying, and a considerable weight of the fine calcite is held in the scum

floating on the surface of the concentrates thickener.

These emulsions may conveniently be prepared by stirring the sulphonated oil in a drum of fatty acid, the latter being heated if it does not flow freely. The mixture may be drawn from the drum by a water eductor of the Venturi pipe, preferably equipped with a pressure gauge on the water inlet side. The quantity of water is proportional to the pressure required to syphon the oil mixture. The quantity of the oil, and consequently the degree of the oil in water dilution or dispersion, is controlled by varying the size of the orifice of the oil suction pipe. By these means, the desired ratio of oil to water can readily be obtained. The mixture of water and oil, as discharged from the eductor is partly emulsified, the dispersion being completed by passing the mixture preferably through a colloid mill, such as a "Premier paste mill", having a rotor clearance adjusted to about 0.003", although a homogenizer may be employed.

For a better understanding of the practice of the invention, reference is made to the following examples:

First example

The first example consists of a series of tests which illustrate the selectivity and collecting power of emulsions stabilized by representative sulphonated oils. It consists of nine tests in which substantially identical specimens of argillaceous limestone were treated under equivalent conditions. The flotation cell feed had the following physical analysis:

	Per cent
Plus 100 mesh-----	1.8
Minus 100 mesh plus 200 mesh-----	11.2
Minus 200 mesh plus 325 mesh-----	14.0
Minus 325 mesh-----	73.0

In each test, fish oil fatty acid of 78% free fatty acid content, by titration, was used as the collector in view of its low cost. The pulp temperatures were 60° F., whereby a blank test, No. 9, could be included for purposes of comparison. In this test unmodified (not emulsified) fish acid was used as the collector. This reagent is satisfactory only at elevated temperatures as its selectivity decreases rapidly as pulp temperatures decrease below 60° F. Test No. 8 was also included for purposes of comparison to show the low-grade of calcite concentrates obtained with emulsions stabilized by sulphonated alcohols, the agent used being a well-known wetting agent sold under the trade name "Aviroll-L144".

In all cases, in Tests Nos. 1 to 8 inclusive, five parts of stabilizing agent to one hundred parts of oil, by weight, were used in an oil in water dilution of 1:30. Flotation time in a Fagergren flotation machine was 5 minutes, the collecting reagent being added in stage oiling in five stages of rougher concentration at 1 minutes intervals. The frothing agent used was a mixture of branched and straight chain aliphatic monohydric alcohols boiling between about 152° C. and about 162° C. obtainable along with methanol by the catalytic hydrogenization of carbon oxides, hereinafter referred to for brevity as "F-1". It was emulsified with sulphonated alcohol ("Aviroll-L144") to permit stable dilution in water so that the small quantities introduced could be controlled accurately. The alkalinity of all pulps was normal, at pH 7.8. The calcite

(CaCO₃) content of all pulps was substantially identical, the average being 68% by titration.

tons each. The pulp was partially de-slimed by hydraulic classification but contained 20% of

Test No.	Concentrates			Rejects			Reagents lbs./ton		1:30 O/W emulsion of 100 parts fish oil 5 parts sulphonated oil
	Percent weight	Percent CaCO ₃	Percent weight CaCO ₃	Percent weight	Percent CaCO ₃	Percent weight CaCO ₃	Emulsion F-1	Fish oil	
1	69.5	85.2	87.4	30.5	28.2	12.6	0.067	0.515	Castor oil. *
2	77.3	81.0	91.6	22.7	25.6	8.4	0.067	0.515	Crude corn oil.
3	82.5	80.5	96.5	17.5	13.8	3.5	0.067	0.515	Olive oil.
4	81.4	83.6	96.6	18.6	12.6	3.4	0.067	0.515	Tea seed oil.
5	82.5	81.6	98.3	17.5	6.6	1.7	0.067	0.515	Cod oil.
6	79.5	80.4	93.0	20.5	20.3	6.0	0.067	0.515	Oleic acid.
7	82.9	80.5	96.9	17.1	12.6	3.1	0.067	0.515	Neat's-foot oil.
8	90.7	75.3	99.2	9.3	0.6	0.8	0.067	0.515	Sulphonated alcohol.
9	66.4	81.2	78.0	33.6	44.9	22.0	0.067	0.624	Fish acid unmodified.

It will be seen from the foregoing tests that the emulsion stabilized with sulphonated tea seed oil, produced the most satisfactory concentrates, with relation to both grade and weight recovery. This is closely followed by the emulsion stabilized by cod oil, Test No. 5, the lower grade being offset by the increased weight recovery of calcite. It should be understood that the concentrates of the first seven tests can readily be cleaned by froth flotation without additional reagents, if it is desired to improve the grade by discarding additional quantities of the tailing minerals. It will also be seen that the concentrates of Test No. 8, in which an emulsion stabilized by sulphonated alcohol was used are of the lowest grade. This low grade accounts for the extremely high weight recovery, and it will be understood that substantially all of the fine minerals were carried over in the excess of froth. The volume of froth was too great to permit effective cleaning. This lack of selectivity is characteristic of this emulsion, and the grades are not substantially improved by decreasing the quantity used. Blank Test No. 9, demonstrates that unmodified fish acid, even in a relatively warm pulp, produces a relatively low grade and a very low weight recovery. It is to be borne in mind that the heavy flocculation produced by this collector does not permit effective froth cleaning.

The identity of the sulphonated oils can best be understood by reference to the analysis of the sulphonated cod oil used in the emulsion of Test No. 5, and which is typical, the composition of the other sulphonated oils mentioned or included in the table being approximately the same:

pH (of 10% solution)	6.1
H ₂ O	25.0
Fatty acid (free)	30.0
Ash	3.5
SO ₃	3.6
Iodine (original)	137.0
Iodine (after sulphonation)	63.0

Second example

The second example comprises the essential results of four comparative tests in actual commercial operation. The material treated was argillaceous limestone taken from a tested storage pile of approximately 1600 tons to insure almost identical cell feeds for each test, of 400

the total solids in particle size ranges below 37 microns. The pulp temperatures varied from 65° to 68° F., and the alkalinity was substantially constant at pH 7.6. All tests were of 24 hours duration and were made in normal plant operation, using Fagergren flotation machines. In Tests Nos. 10 and 11, 0.01 lb. of F-1 alcohol was used as a frother, and in Tests Nos. 12 and 13, the quantity was 0.03 lb. per ton of solids.

Test No.	Conc. percent CaCO ₃	Percent weight recovery	Collector 1:27.5 O/W 5 parts sulph. castor oil 100 parts F. A.
10	88.0	87 to 88	Fish oil.*
11	88.0	84 to 85	Oleic acid.**
12	88.0	82 to 84	Unmodified oleic acid.
13	88.0	80 to 82	Unmodified fish acid.

* Fish oil of 80.2 percent free fatty acid.

** Oleic acid of 98 percent free fatty acid.

The foregoing are average results under usual conditions in actual cement mill operation, in which the objective was to maintain a constant grade of rougher concentrates closely approaching 88% CaCO₃. It will be seen that both of the emulsions, stabilized by sulphonated castor oil, were superior in weight recovery to the unmodified fatty acids. It is especially to be noted that in spite of its lower free fatty acid content, and particularly in view of the relatively low cost, the best results were obtained with emulsified fish oil, whereas the raw fish oil was inferior to the more expensive oleic acid.

To interpret the results of the foregoing tests properly, it should be borne in mind that for purposes of cement manufacture, it is not necessarily desirable to produce high grade concentrates, for both chemical and economical reasons. The ultimate cement raw material mixture required for burning consist of four essential constituents, three of which may be present in several mineral forms. To obtain favorable kiln reactions, the finest particle sizes of the essential constituents should be recovered and utilized, without disturbing the natural mixture, which has been improved in the course of grinding, more than necessary to effect the elimination of an excessive quantity of one or more of the constituents. Therefore, and depending upon the chemical composition of the limestone, the objectives are either to effect the minimum separations necessary in the entire supply of raw ma-

terials, with a minimum of equipment, processing steps and reagents, or, when the natural crystal sizes permit, to treat a minimum part of the natural raw materials. Further, because of the low commercial value of Portland cement, such practices are obviously desirable.

Although the calcium carbonate content of the desired raw material mixtures for all normal types of Portland cement is in the neighborhood of 76%, it will be realized that the grade of concentrates in most cases must be considerably higher, usually to permit the elimination of excessive micaceous matter, and so that the ultimate mixture can be corrected by "high ratio" silica derived from the tailings of the flotation operations, or supplied by a natural material high in silica, such as sandstone, or both.

In the second example, the purpose in maintaining a concentrate grade of 88% CaCO_3 was to achieve the foregoing objectives in a continuous process in which the ultimate mixture is made by combining the untreated fine particles and the flotation concentrates, the relative quantity of the cell feed increasing with respect to the untreated fines as the calcite content of the natural materials decreases, in accordance with the method of Breerwood Patent No. 2,028,313.

I claim:

1. A method of concentrating oxide ore minerals by froth flotation which comprises incorporating in a pulp of the mineral a quantity of an aqueous emulsion of a fatty acid stabilized by 5 to 7 parts of a sulphonated glyceride oil selected from the class consisting of the vegetable, animal and fish oils to 100 parts of fatty acid

oil, by weight, and subjecting the pulp to froth flotation.

2. A method of concentrating oxide ore minerals by froth flotation which comprises incorporating in a pulp of the mineral a quantity of an aqueous emulsion of a fatty acid stabilized by approximately 5 parts of a sulphonated glyceride oil selected from the class consisting of the vegetable, animal and fish oils to 100 parts of fatty acid oil, by weight, and subjecting the pulp to froth flotation.

3. A method of concentrating oxide ore minerals by froth flotation which comprises incorporating in a pulp of the mineral a quantity of an aqueous emulsion of a fatty acid stabilized by 5 to 7 parts of a sulphonated glyceride oil selected from the class consisting of the vegetable, animal and fish oils, to 100 parts of fatty acid oil, by weight, in which the oil in water ratio is within the range of 1:20 to 1:30, and subjecting the pulp to froth flotation.

4. A method of concentrating finely divided calcite by froth flotation from argillaceous pulps containing a substantial proportion of slimes, which comprises incorporating in a pulp, in a stage oiling froth flotation circuit, quantities of an aqueous emulsion of fish oil fatty acid stabilized by 5 to 7 parts of sulphonated glyceride oil selected from the class consisting of the vegetable, animal and fish oils, to 100 parts of fish oil, by weight, in which the oil in water ratio is within the range 1:20 to 1:30.

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