Patented Aug. 7, 1934 1,968,876

UNITED STATES PATENT OFFICE

1,968,876

COMPOSITION OF MATTER SUITABLE FOR USE IN FLOTATION

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No Drawing. Original application October 14, 1931, Serial No. 568,864. Divided and this application July 22, 1932, Serial No. 624,056

2 Claims. (Cl. 252—9)

This invention relates to compositions of matter suitable for use in flotation and is herein described as embodied in a composition which has proved useful in the flotation concentration of phosphate-bearing ores. This application is a division of Serial No. 568,864, filed Oct. 14, 1931.

Phosphates have already been sucessfully concentrated with the aid of fuel oil when agitated in aqueous pulps which also contained soap, but it has been supposed that the only soaps capable of successful use had to be made of fairly expensive materials, and it has hitherto been deemed impossible to commercially concentrate phosphate-bearing material with the aid of a soap made from such a substance as palm oil, fish oil, cotton-seed oil foots, and olive oil foots, oil foots being the organic matters that settle out on standing.

According to the present invention, as herein illustrated, the phosphate-bearing material is agitated in an aqueous pulp containing a substantially insoluble and unsaponifiable oil which carries a solid or substantially solid fatty acid in solution. It is found that, under these conditions, the fatty acids derived from such sources as have been mentioned above are not only almost as efficient as the more expensive oleic acid, but may even be more efficient.

The fatty acid is usually dissolved in warm fuel oil or warm Diesel engine oil and then the reagent thus obtained is added to the pulp of phosphate-bearing material in any suitable manner. Under these conditions it is found that a less quantity of the fatty acid will often suffice than that which has been hitherto added, either as oleic acid or in the form of soap, and it is also found that a less quantity of unsaponifiable insoluble oil than has hitherto been deemed necessary is effective. It has also been found possible to obtain larger recoveries than were hitherto deemed possible and yet obtain equally rich concentrates.

It has been found that the best results are obtained when the fatty acids used are the higher fatty acids which form substantially insoluble calcium soaps. The resin acids or the acids of American rosin have been found usually less effective than the other acids unless used in a larger quantity than is necessary when some other acids are used.

Some of the acids, such as palmitic, stearic, ricinoleic acid, usually fail to produce a sufficient quantity of bubbles in the pulp water to render the process efficient, and when such fatty acids are used it is often desirable to add pine oil, resin oil or a tar acid or other "frothing agent" to serve as a bubble-producing agent.

Satisfactory results have been obtained when the process was carried out with the fatty acids obtained from fish oil, menhaden oil, cotton-seed foots, olive foots, castor oil, and palm oil. In addition to the acids named above, these oils contain either linoleic, linolenic, myristic, clupanodonic or arachidic acids.

When suitable fatty acids are dissolved in the unsaponifiable oil, such as fuel oil, and then added to the pulp, it is found unnecessary to add soap as such, but the desired result can be obtained by agitating, in the presence of alkali, the pulp containing the fatty acids dissolved in fuel oil. Moreover, it is found that the alkali used may work satisfactorily even if it is some form of soda, despite the fact that it has hitherto been deemed necessary to use the potassium soaps of certain fatty acids because of the relative insolubility of the corresponding sodium soaps.

If the process is worked in Florida in hot weather, it has been found satisfactory to dissolve the solid fatty acids obtained from fish oil in a fuel oil of 20° Bé. and to use this solution in the phosphate pulp. In cold weather it was found advantageous to use a lighter gravity oil. The mixed fish oil fatty acids are solid at ordinary temperatures, but become perfectly fluid at a temperature of 100 to 125° F. If they are warmed until fluid and then stirred into the warm hydrocarbon oil there usually results a uniform and homogeneous mixture which throws down only a small amount of solids when cooled to atmospheric temperatures.

In commercial work fatty acids and fuel oil are usually mixed when received. For this purpose the pasty or solid fatty acids derived from fish oil are heated to between 100° and 150° F. in the tank car in which they are received, and fuel oil in a separate, usually somewhat larger, tank car is also heated to about the same temperature, thus lowering the viscosity of the already fluid fuel oil. The warm and liquid acids and fuel oil are drawn from the tank cars by separate pipes which unite in a T at a small centrifugal pump which serves as a mixer and delivers the mixed oil and acids to a reagent tank. Mixing is made more complete by later connecting the pump to recirculate the mixed oil and acids for about 24 hours after the tank cars have been unloaded.

It is found that the mixture of fuel oil and

solid fatty acids is so stable in Florida, even in winter, that only a trivial amount of sediment settles out of a sample removed and allowed to stand undisturbed in a beaker—no more settles than settles out of many standard commercial oils when subjected to a parallel test.

It is customary, by way of precaution, to recirculate the contents of a storage tank containing the mixture, by circulating it through a small centrifugal pump for about eight hours once a week. The coldest weather in a Florida winter failed to freeze out of the fuel oil any of the fatty acid material present, and the mixture remained liquid.

The best results have been obtained when a mixture of about equal parts of the fuel oil and fatty acids, prepared as just described, or in other ways, is introduced, in emulsion if desired, into an aqueous pulp of the phosphate-bearing material already treated with caustic soda. The best results have been obtained when the caustic soda was added in a 5 to 10% solution in sufficient quantity to produce a pH value of 8.0 to 9.6 in the pulp, though other alkalis, such as trisodium phosphate and ammonia and some amines give very good results.

It has been found most economical to first deslime the pulp so as to separate out all material smaller than 200 to 300 mesh and then treat the deslimed "sands" in a pulp containing from 30 to 60% water with the caustic soda and to add the solution of fatty acid and fuel oil after agitating the alkalinized pulp. Usually about 0.3 to 1.5 lbs. of caustic soda per ton of dry feed were satisfactory.

In treating Florida rock the debris or waste material from the rock washers, ranging in size from ¼'' down to slimes, was screened. The usual screen was a 20, 28 or 35-mesh sieve, and the over-size was ground in a rod mill to pass the same sieve, added to the original undersize and the whole re-agitated with water. The agitated pulp was allowed to stand for a short period and the suspended slime decanted off. In laboratory work decantation is usually carried out two or three times. The caustic soda was added to the deslimed pulp in solution as described above and enough of the solution of fatty acid and fuel oil was added so as to add from 0.25 to 2.0 lbs. of free acid per ton of feed, and the pulp agitated. Later further fuel oil was added, usually enough to bring up the total fuel oil to 1 to 7 lbs. per ton of dry feed. Then a frothing agent, such as a solution of 75 parts of crude rosin residue in 25 parts of kerosene oil, was added in an amount equal to 0.1 to 0.3 pounds per ton of dry feed. After further agitation the thick pulp was introduced into the flotation machine, diluted with tap water and a float formed rapidly when agitated to produce aeration. Under proper conditions in a minerals separation subaeration laboratory machine a satisfactory float was obtained in from one to four minutes.

Crystalline forms of calcium phosphate, such as crystalline apatite, which in the natural state are practically free from clay, may be successfully treated by grinding to —48 or —65 mesh and then thickening the product to 35 or 50% solids without decantation of slimes. Even under these conditions if much material finer than 300 mesh is present there is an increased consumption of reagents when a satisfactory concentration is obtained. Moreover, there is often required a longer time to obtain the float.

It is generally found best to keep the phosphate particles as much as possible between —35 mesh and +100 mesh and exclude substantially all of —300 mesh.

A series of tests were carried on in the laboratory with various fatty acids using as phosphate-bearing materials a well mixed sample of flotation feed from the Phosphate Recovery Corporation No. 2 Plant at Mulberry, Florida, which was of the type described above. In each case a rougher concentrate was floated off for one minute, the tailings withdrawn, the rougher concentrate replaced in the machine and diluted and refloated, without addition of further reagent, for one minute.

The tailings from the cleaning operation were weighed and assayed separately, but added to the rougher tailing in calculating the recovery of the tricalcium phosphate (B. P. L.).

Test No. 1.—Semi-solid free fatty acids of castor oil were dissolved in an equal volume of 20° Bé. fuel oil by warming and stirring, and added to the alkalinized pulp after cooling to room temperature. One pound of the fatty acids dissolved in fuel oil per ton of solids was added to a pulp made of the above-described flotation feed, and thereafter enough fuel oil added to bring the total fuel oil up to two pounds per ton. There was added 0.14 pounds per ton of Tarol #2 (a mixture of 75% steam distilled pine oil and 25% rosin oil by volume), the pulp agitated for one minute, and a rougher float concentrate separated. This concentrate was then diluted with further water, reagitated for a minute and a finished concentrate separated. The tailings from the cleaning operation were middlings capable of being retreated, but added to the other tailings in this test. The calculated heads contained 32.89 B. P. L., the concentrates contained 70.05% and the middlings and tailings contained 5.31% B. P. L., representing a recovery of 90.7 and a ratio of concentration of 2.35.

Test No. 2.—Solid free fatty acids of cotton seed oil foots were dissolved in an equal volume of 20° Bé. fuel oil, by warming and stirring, and added to the alkalinized pulp after cooling to room temperature. 0.4 lbs. of the fatty acids dissolved in fuel oil, per ton of solids, was added to a pulp made of the above-described flotation feed, and thereafter enough fuel added to bring the total fuel oil up to two pounds per ton. There was added 0.14 pounds per ton of Tarol #2, the pulp agitated for one minute, and a rougher float concentrate separated. This concentrate was then diluted with further water, reagitated for a minute and a finished concentrate separated. The tailings from the cleaning operation were middlings capable of being retreated, but added to the other tailings in this test. The calculated heads contained 33.03% B. P. L., the concentrates contained 73.91% and the middling and tailings contained 5.32% B. P. L., representing a recovery of 90.4% and a ratio of concentration of 2.48.

Test No. 3.—Solid free fatty acids of fish oil were dissolved in an equal volume of 20° Bé. fuel oil, by warming and stirring, and added to the alkalinized pulp after cooling to room temperature. 0.3 lbs. of the fatty acids dissolved in fuel oil, per ton of solids, was added to a pulp made of the above-described flotation feed, and thereafter enough fuel oil added to bring the total fuel oil up to two pounds per ton. There was added 0.14 pounds per ton of Tarol

#2, the pulp agitated for one minute, and a rougher float concentrate separated. This concentrate was then diluted with further water, reagitated for a minute and a finished concentrate separated. The tailings from the cleaning operation were middlings capable of being retreated, but added to the other tailings in this test. The calculated heads contained 32.7% of B. P. L., the concentrates contained 72.91% and the middling and tailings contained 5.45% B. P. L., representing a recovery of 90.1 and a ratio of concentration of 2.48.

Test No. 4.—Solid free fatty acids of palm oil were dissolved in an equal volume of 20° Bé. fuel oil, by warming and stirring, and added to the alkalinized pulp after cooling to room temperature. 0.75 lbs. of the fatty acids dissolved in fuel oil, per ton of solids, was added to a pulp made of the above-described flotation feed, and thereafter enough fuel oil added to bring the total fuel oil up to two pounds per ton. There was added 0.14 pounds per ton of Tarol #2, the pulp agitated for one minute, and a rougher float concentrate separated. This concentrate was then diluted with further water, reagitated for a minute and a finished concentrate separated. The tailings from the cleaning operation were middlings capable of being retreated, but added to the other tailings in this test. The calculated heads contained 33.% B. P. L., the concentrates contained 72.49% and the middling and tailings contained 3.44% B. P. L., representing a recovery of 94.% and a ratio of concentration of 2.34.

Test No. 5.—Semi-solid free fatty acids of peanut oil were dissolved in an equal volume of 20° Bé. fuel oil, by warming and stirring, and added to the alkalinized pulp after cooling to room temperatures. 0.7 lbs. of the fatty acids dissolved in fuel oil, per ton of solids, was added to a pulp made of the above-described flotation feed, and thereafter enough fuel oil added to bring the total fuel oil up to two pounds per ton. There was added 0.14 pounds per ton of Tarol #2, the pulp agitated for one minue, and a rougher float concentrate separated. This concentrate was then diluted with further water, reagitated for a minute and a finished concentrate separated. The tailings from the cleaning operation were middlings capable of being retreated, but added to the other tailings in this test. The calculated heads contained 32.64% B. P. L., the concentrates contained 73.93% and the middling and tailings contained 8.28% B. P. L., representing a recovery of 84.% and a ratio of concentration of 270.

Test No. 6.—Solid free fatty acids of tung oil were dissolved in an equal volume of 20° Bé. fuel oil, by warming and stirring, and added to the alkalinized pulp after cooling to room temperature. 0.5 lbs. of the fatty acids dissolved in fuel oil, per ton of solids, was added to a pulp made of the above-described flotation feed, and thereafter enough fuel oil added to bring the total fuel oil up to two pounds per ton. There was added 0.14 pounds per ton of Tarol #2, the pulp agitated for one minute, and a rougher float concentrate separated. This concentrate was then diluted with further water, reagitated for one minute and a finshed concentrate separated. The tailings from the cleaning operation were middlings capable of being retreated, but added to the other tailings in this test. The calculated heads contained 32.53% B. P. L., the concentrate contained 74.24% and the middling and tailings contained 4.84% B. P. L., representing a recovery of 91.1% and a ratio of concentration of 2.5.

Having thus described certain embodiments of the invention, what is claimed is:

1. A normally liquid composition of matter consisting of a heavy insoluble unsaponifiable oil carrying in solution about an equal amount of free fatty acid which is substantially solid at ordinary temperatures.

2. A normally liquid composition of matter consisting of a heavy insoluble unsaponifiable oil carrying in solution about an equal amount of the solid fatty acids of fish oil.

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