

- [54] **BENEFICIATION OF PHOSPHATE ORES**
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- [51] Int. Cl. .... **B03b 9/00**
- [58] Field of Search ..... **209/12, 161, 167, 209/2, 17; 241/20, 24**

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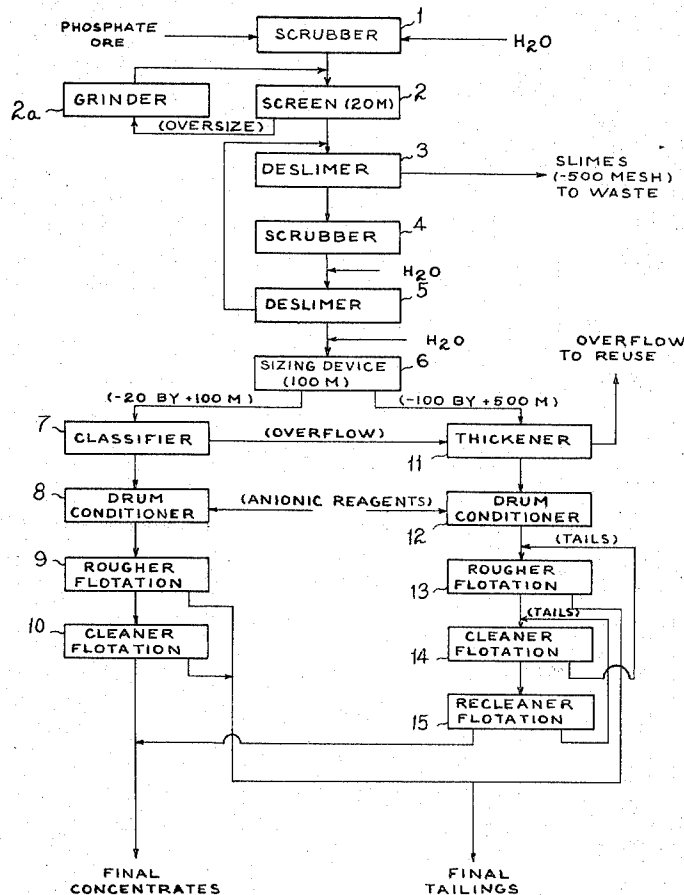
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[57] **ABSTRACT**

A process for beneficiating phosphate ores in which the ore is scrubbed and deslimed prior to separation into a coarse fraction and a fine fraction, each of which is subjected to a plurality of anionic flotation steps and screening steps to obtain high recovery and high grade phosphate product whereby the acid cleaning and cationic flotation steps previously used are eliminated.

**8 Claims, 2 Drawing Figures**

- [56] **References Cited**
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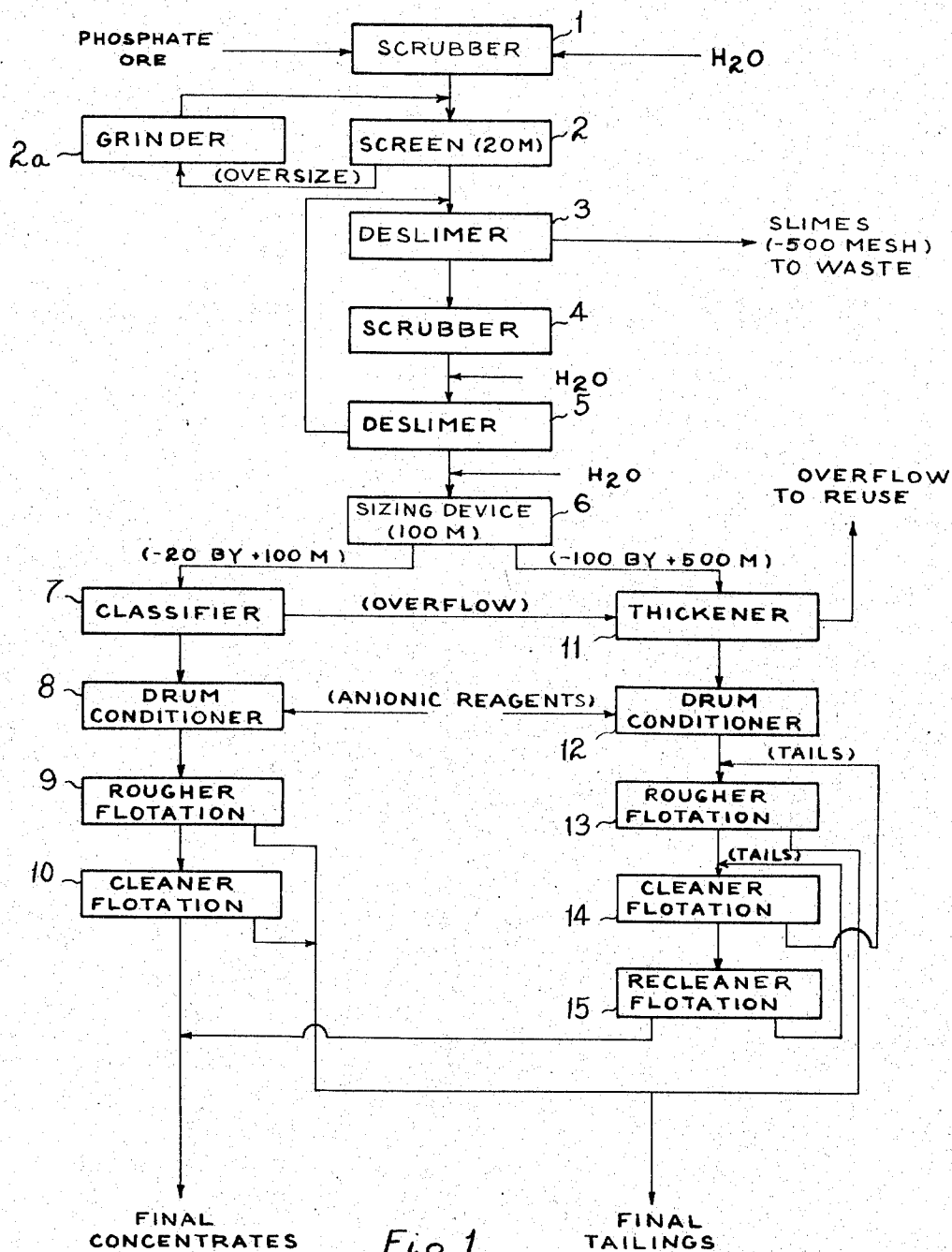


Fig. 1

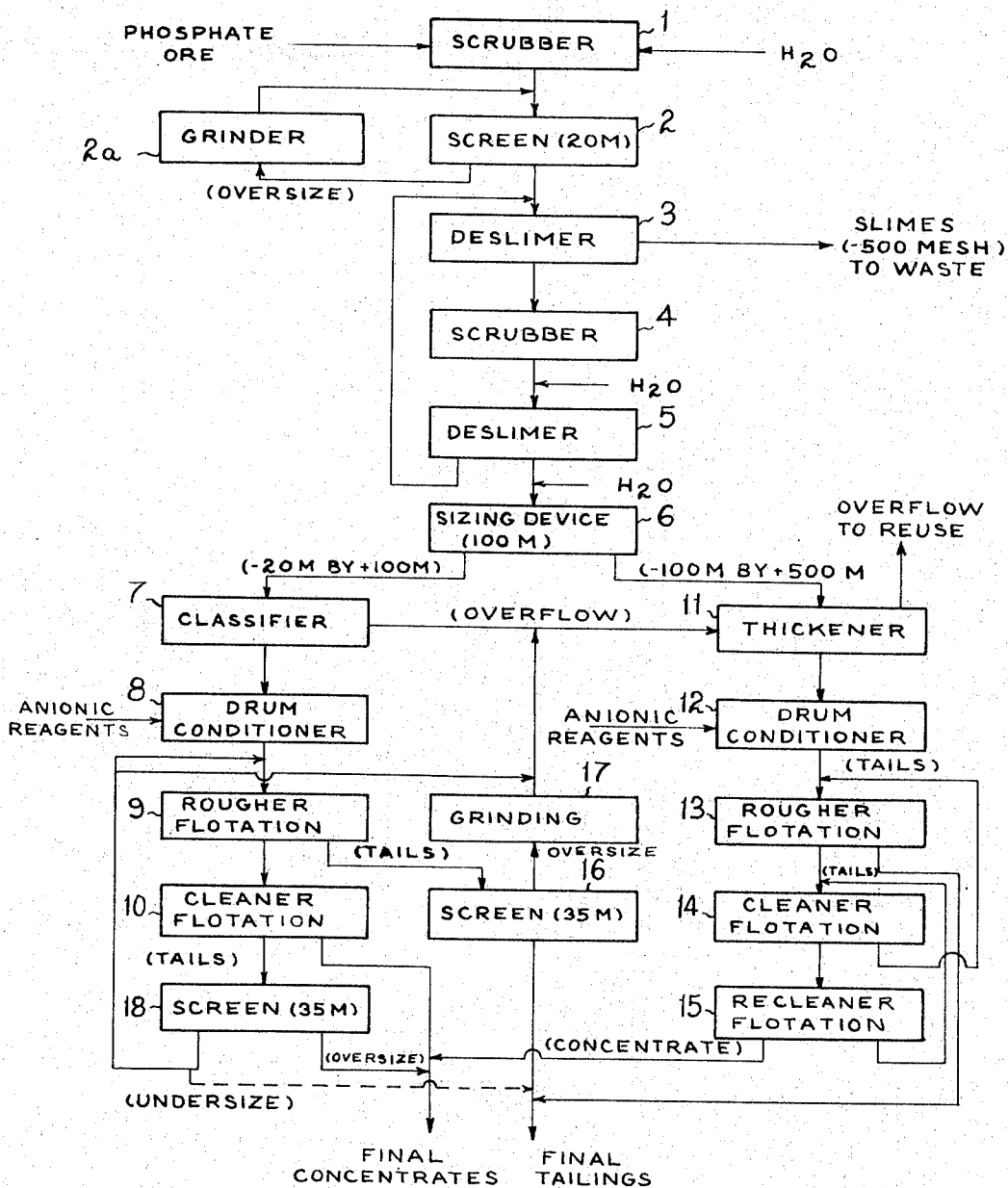


Fig. 2

## BENEFICIATION OF PHOSPHATE ORES

This invention relates to the beneficiation of certain phosphate ores by which not only is a remarkable amount of the total phosphate in the ore recovered in the final product but also the product is at least as rich in phosphate values as obtained by present processes but is frequently richer. In addition, the present process eliminates at least two of the essential steps of the principal process now in commercial use, thus reducing costs to a substantial extent as will be explained more fully hereinafter.

As is known, virgin phosphate ores differ in numerous respects depending on their geographical location and a process which is suitable for an ore in one area, such as the well known Florida ores, may not be suitable, nor even operable for ores in another area. These differences in the ores are not too well understood and may be attributed to physical as well as chemical differences in the gangue materials since in most phosphate ores the phosphate values, commonly referred to as B.P.L. (Bone phosphate of lime) is in the form of apatite, such as fluorapatite, having the formula  $Ca_4(CaF)(PO_4)_3$ , or other apatites in which the F is replaced by Cl or OH. The non-phosphate portions of the ores usually consist of clay, silica and the like, which may be present in different physical forms which affect the beneficiation of the ores. How the physical forms affect the treatment of the ores is not well known since it is usually more economical to test the ores from new deposits by various known processes to determine the one process which gives the best results as to total phosphate recovery and grade of product.

A process frequently used in treating Florida ores includes a first flotation step with anionic reagents followed by an acid ( $H_2SO_4$ ) scrubbing treatment to remove the first reagent and a subsequent flotation step with a cationic reagent for final separation of the gangue materials from the phosphate values, such as is described in U.S. Pat. No. 2,293,640 to Arthur Crago. This process is hereinafter referred to as the Florida Process.

A general representative metallurgical balance of the Florida Process is shown below:

Product	% Weight	% B.P.L.	% B.P.L. Recovery Based on Ore	% Based on Flot Feed
Crude Ore (Matrix)	100.0	20.0	100.0	—
Slime	30.0	20.0	30.0	—
Flot. Conc.	16.2	69.0	56.0	80.0
Slimes + Flot. Tails	83.8	10.5	44.0	20.0

In addition to the substantial phosphate ore deposits in Florida, there are substantial deposits in Tennessee, North Carolina and elsewhere, which may be beneficiated by similar processes. Another known deposit of importance is to be found in Angola, West Africa and more precisely in the District of Cabinda. Major deposits are located 35 to 30 kilometers from the Atlantic coast port city of Ladana, in the Massabi Formation and consists of interbedded sand, clay, silt, foraminifera limestone, granular calcite and/or dolomite, with phosphate occurring as pellets or nodules, with organic remains. The phosphate is believed to be in the form of fluorapatite.

The Florida process was first used on the ores found in Angola and gave very poor results in that not only was much of the phosphate values lost to the slimes, but of even greater significance, the cationic flotation step which normally floats the remaining silica did not do so on this ore. Various modifications and variations of the main process were attempted with little or no improvement in the results. Finally it was discovered that a process, i.e. the process of the present invention, obtained excellent results and gave, in some respects, results superior to the results obtained on the Florida ores treated by the Florida processes.

The reasons for the failure of the Florida process on the Angola ores are not known with certainty, although it is believed that the silica particles may have unusually "glassy" surfaces which were not coated by the cationic reagents and thus did not float. According to the present process as used on Angola ores, it was found that fine silica accompanied larger phosphate particles occurring in the tailing from the cleaner flotation stages as will be described hereinafter and that a separation of one from the other was possible by a screening step.

Although the present process will be described as used on the above mentioned Angola ores, it will be understood that this process may be used advantageously on any ore having characteristics similar to the Angola ores, wherever found and that while the critical characteristics which determine the usefulness of this process are not known and cannot be easily determined analytically, nevertheless the value of the present process in treatment of such ores can be easily determined by comparing results of the Florida process, or other known processes, with the results of the process of the present invention.

In most non-metallic flotation processes, it has been found that if a coarse particle is once floated, as in a rougher flotation operation, it is reluctant to float again, if at all, in a cleaner flotation operation. Therefore, a low grade concentrate must be expected with high recovery or a loss of coarse concentrate in the middlings must be expected if a cleaner operation is used in non-metallic flotation. The other alternative is an expensive anionic flotation-acid scrubbing-cationic flotation operation used for phosphate recovery as is described above.

It was discovered, that a saponified fatty acid concentrate could be cleaned one or more times and that the coarser fraction of the middlings could be screened away from the finer fraction leaving a high grade coarse middling that could report to the final concentrate, and a low grade fine middling that could either report to tailings or back to the head of the circuit. The resultant savings in reagent alone could amount to about \$0.20/ton of originally mined crude ore and this would be in addition to the savings in labor, and in the auxiliary capital equipment required for additional scrubbing, washing, conditioning and flotation.

In addition to the increased recovery of high grade phosphate product of the present process compared to the Florida Process, the capital and operating costs of the present process are drastically reduced because of (1) the elimination of the acid step for removing the anionic agent which reduces production costs by about 3.75 cents to 5.0 cents per ton of crude ore based on a cost of \$25.00 per ton of  $H_2SO_4$ , and (2) the elimination of the cationic reagent which reduces production costs by about 6.0 to 12.0 cents per ton of crude ore

based on costs of about 30 cents per pound for the cationic reagents.

Based on the above and the present production figures for beneficiating Florida ores, the total reagent savings alone due to the elimination of the acid step would amount to about \$1¼ million per year and the savings due to the elimination of the cationic reagent would be about \$¾ million a year.

The process of the present invention will now be described with reference to the attached drawings in which:

FIG. 1 illustrates a flow diagram of one method of carrying out the process, and

FIG. 2 illustrates a second form of a flow diagram for carrying out the present invention.

FIG. 1 illustrates the process in which the phosphate ore as mined is first crushed to about 20 mesh and is then treated with water in a first scrubber 1 for about 2 minutes and then is subject to a screening 2 at about 20 mesh (Standard Tyler screen sizes). Any oversized material at about +20 mesh may be reground in a grinder 2a and returned to the scrubber while the undersize material at -20 mesh is fed to a deslimer 3. The desliming step may be carried out in cyclone separators or by very fine screens so as to effect a separation at about 500 mesh. The undersized material at about -500 mesh is slime and is discarded to waste. The oversized ore material having a size of +500 mesh is preferably passed to a second scrubber 4 and scrubbed for about 2 minutes and then passed to a second deslimer 5, the slime overflow from which may be recycled to the first deslimer. If found desirable for the particular ore being treated, the second scrubber 4 and second deslimer 5 may be eliminated so that the +500 mesh material from the first deslimer 3 may be passed directly to a sizing device. The sand material from deslimer 5 at about +500 mesh is diluted with water and the slurry passed through the sizing device or screen 6 to make a separation at about 100 mesh. The sizing device or screen 6 separates the deslimed ore into two fractions one comprising a coarse fraction of about -20 by +100 mesh and the other a finer fraction of about -100 by +500 mesh.

The coarser fraction is passed to a classifier 7 in which some of the water and possibly a small amount of fine particles is removed leaving an underflow sand fraction comprising about 75 percent solids. This fraction is passed to a drum conditioner 8 to which is added an anionic flotation reagent and certain other reagents to be described further hereinafter. After the ore material is thoroughly conditioned with the anionic flotation reagents it is passed to the rougher flotation cells 9. The flotation tailings, or underflow from the cells 9 are discarded along with other tailings as described further below. The flotation concentrate, without any further addition of reagents is passed to the cleaner flotation cells 10, the flotation tails from which are discarded and the flotation concentrate from which forms a portion of the final concentrate.

The finer fraction from screen 6 having a size of from -100 by +500 mesh is passed to a thickener 11. To this thickener may be added the overflow from classifier 7, if desired, and the overflow from the thickener 11 is removed for reuse in the process wherever dilution is called for as for example to scrubber 1, deslimer 5 or sizing device 6. The ore pulp coming from the underflow of the thickener 11 comprises about 75 percent

solids. This pulp is passed to drum conditioner 12 to which anionic flotation reagents are added as will be described further hereinafter. After this ore fraction has been thoroughly conditioned with the anionic reagents it is passed to the rougher flotation cells 13, the flotation tailings or underflow from which is discarded with the tailings from rougher flotation cells 9. The flotation concentrate, without any further addition of reagents is passed to cleaner flotation cells 14. The cleaner flotation tailings from these cells are preferably recycled to the rougher flotation cells 13 for retreatment. The flotation concentrate from the cleaner flotation cells 14 without the addition of further reagents may be passed to recleaner flotation cells 15 for further upgrading and concentration of phosphate values in the ore. The flotation tails from the recleaner cells 15 are preferably recycled to the cleaner flotation cells 14 and the flotation concentrate is combined with the final concentrate from the cleaner flotation cells 10 obtained from the treatment of the coarse ore fraction.

According to FIG. 2, the same procedure is followed through elements 1 - 6 and the finer fraction, i.e. -100 by +500 mesh, is treated in the same fashion through elements 11 - 15. However, the coarser fraction, after passing through elements 7 - 9 is subjected to a different and more refined treatment. The tailings from the rougher flotation cells 9 are passed through a fine screen 16 which may be a DSM type screen provided with a knocking device to facilitate screening. If desirable the screen may be from about 28 mesh to about 65 mesh, and the oversized material is passed through a grinder 17 such as a wet hammer mill or rod mill and returned to the thickener 11 for the finer fraction, while the undersized material is passed to the final tailings. On the other hand, the concentrate from the rougher flotation cells 9 are passed, as before, to cleaner flotation cells 10. The tails therefrom are passed through a screen 18 of the types mentioned above for screen 16. The undersized fraction therefrom is recycled to the rougher flotation cells 9 or alternatively passed with the material from grinder 17 to thickener 11, or, if desired, passed directly to final tailings. The oversized material is passed to the final concentrate. Whenever flotation cells have been referred to in the foregoing it will be understood that any group of such cells may, as is customary in the art, be referred to as flotation machines.

Wherever in this application mention is made of the use of screening as a sizing device this step may be carried out by the use of a fixed, flat or curved screening surface, mounted on an incline, and of the Dutch State mines type of screen. To the rear side of the frame of the screen there may be attached a knocking device to prevent the screen from blinding.

With reference to FIG. 1 pertinent analyses of the various fractions throughout the process are shown in the following Table I:

TABLE I

Product	% Weight	% B.P.L.	% Recovery B.P.L.
1. Calculated ore feed	100.00	24.69	100.00
2. -20 × 100 M Rougher conc.	19.76	71.52	57.27
3. Do. tails	20.48	4.59	3.78
4. Do. feed	40.24	37.46	61.05
5. Do. cleaner conc.	17.82	76.87	55.46
6. Do. tails	1.94	22.48	1.81
7. Do. feed	19.76	71.52	57.27
8. 100 × 500 M Rougher conc.	11.47	48.95	22.69
9. Do. tails	26.50	2.56	2.77

10. Do.	feed	37.97	16.56	25.46
11. Do. cleaner conc.		8.06	68.03	22.19
12. Do.	tails	3.41	3.84	0.50
13. Do.	feed	11.47	48.95	22.69
14. Do. Recleaner conc.		7.28	72.29	21.29
15. Do.	tails	0.78	27.85	0.90
16. Do.	feed	8.06	68.03	22.19
17. total flot. feed		78.21	27.31	86.51
18. total flot. conc.		25.10	75.54	76.75
19. total rougher tails		46.98	3.43	6.55
20. total cleaner-recleaner tails		6.13	12.82	3.21
21. total slimes		21.79	15.29	13.49

With reference to FIG. 2 analyses of the various fractions are shown in the following Table II:

TABLE II

Product	% Weight	% B.P.L.	% Recovery B.P.L.
1. Calculated ore feed	100.00	23.37	100.00
2. -20 × 100 M Rougher conc.	14.77	80.61	50.95
3. a. Do. tails, +48M	7.01	5.29	1.73
b. Do. tails, -48M	0.94	6.99	0.30
4. Do. feed	22.72	54.33	52.98
5. -100 × 500 M Rougher conc.	14.91	35.89	22.90
6. Do. tails	53.68	2.08	4.77
7. Do. feed	68.59	9.44	27.67
8. Do. cleaner conc.	8.69	57.82	21.46
9. Do. tails	6.22	5.42	1.44
10. Do. feed	14.91	35.89	22.90
11. Do. Recleaner conc.	7.90	62.50	21.16
12. Do. tails	0.79	8.87	3.30
13. Do. feed	8.69	57.82	21.46
14. total flot. feed	84.54	21.82	78.91
15. total flot. conc.	22.67	74.27	72.11
16. total rougher tails	54.62	2.16	4.97
17. total cleaner-recleaner tails	7.01	5.92	1.74
18. total slimes	15.46	31.87	21.09

The various percentage values shown above are based on the original mined ore, and not, as is usually customary, on the deslimed ore as it is passed to the flotation cells.

It is to be noted that the desliming steps are performed at about 500 mesh instead of the conventional 150-200 mesh and this has the immediate effect of reducing phosphate losses from about 30 percent to about 15 - 20 percent.

The anionic reagents employed in the foregoing processes are comprised of fatty acid tall oil and fuel oil. While the ratio of fatty acid tall oil and fuel oil may vary within rather wide limits, the ratio is generally maintained at from about 1.5 to 1 to about 2.5 to 1. In Table I relating to FIG. 1, 4.9 lbs. of the fatty acid tall oil and 2.2 lbs of fuel oil were used per dry short ton of crude ore while in Table II relating to FIG. 2 the anionic reagents comprises 5.5 lbs. of fatty acid tall oil and 3.2 lbs. of fuel oil per dry short ton of crude ore.

It was found advantageous to flotation efficiencies in all respects to control the alkalinities of flotation feed pulps. The control was obtained by the addition of caustic soda, as required, to produce flotation feed pulps having pH values between about 7.5 and about 9.5. Sodium carbonate or lime could be used for the same purpose.

According to current practice, the Florida ores when subject to the anionic flotation-acid scrubbing-cationic flotation procedure commonly used as mentioned above give a final recovery of phosphate values from about 50 percent - 60 percent based on the crude ore, whereas according to the present process the final recovery of phosphate values is in the range of 65 percent - 80 percent.

I claim:

1. A process for the beneficiation of phosphate ore comprising scrubbing the ores at least once, desliming the scrubbed ore at about 500 mesh after each of said at least one scrubbing steps, separating the deslimed ore at about 100 mesh to produce a coarse fraction and a fine fraction, passing the coarse fraction through a classifier to produce an overflow and a coarse slurry containing about 75 percent solids, conditioning the coarse slurry with anionic flotation reagents, subjecting said conditioned coarse slurry to treatment in at least one rougher flotation machine to produce rougher tailings and a rougher concentrate, treating the concentrate in at least one cleaner flotation machine to produce tailings and a final concentrate, passing the fine fraction through a thickener to produce a fine slurry containing about 75 percent solids, conditioning the fine slurry with anionic flotation reagents, subjecting the conditioned fine slurry to treatment in at least one rougher flotation machine to produce tailings and a concentrate, treating the concentrate in at least one cleaner flotation machine to produce tailings and a second concentrate, recycling said tailings to the at least one rougher flotation machine, treating the second concentrate in at least one recleaner flotation machine to produce tailings and a final concentrate, recycling the last mentioned tailings to the at least one cleaner flotation machine and combining the last mentioned concentrate with the final concentrate obtained from the coarse slurry and combining at least a portion of the tailings from the first mentioned at least one rougher flotation machine with the tailing from the second mentioned at least one rougher flotation machine.

2. A process as claimed in claim 1 and further comprising screening at about 20 mesh the scrubbed ore, grinding the oversized material from said screening step and recycling said ground oversized material to said screening step and further comprising a second scrubbing step of the deslimed ore material and a second desliming step, the slime from said second desliming step being recycled to the first desliming step.

3. A process as claimed in claim 1 and further comprising passing the tailings from the at least one rougher flotation machine for the coarse slurry to a screening step having an effective mesh of separation from about 28 to about 65 mesh, passing the undersized material to final tailings, grinding the oversized material and passing the ground material to the thickener for the fine fraction.

4. A process as claimed in claim 3 and further comprising passing the tailings from the at least one cleaner flotation machine for the coarse fraction to a screen having an effective mesh of separation from about 28 to about 65 mesh and recycling the undersized material to the at least one rougher flotation machine for the coarse fraction.

5. A process as claimed in claim 4 and further comprising passing the tailings from the at least one cleaner flotation machine for the coarse fraction to a screen having an effective mesh of separation from about 28 to about 65 mesh and passing the undersized material to the thickener for the fine fraction.

6. A process as claimed in claim 1 and further comprising passing the tailings from the at least one cleaner flotation machine for the coarse fraction to a screening step on a fixed flat inclined or curved screen of the Dutch State mines type and to which is attached on the rear side of the frame of said screen a knocking device

7

to prevent screen blinding and having an effective mesh of separation from about 28 mesh to about 65 mesh, and passing the oversize material to the final coarse concentrate fraction and the undersize to final tailings, or recycling the undersize fraction to the head of the coarse rougher flotation circuit or to the thickener at the head of the fine rougher flotation circuit.

7. A process as claimed in claim 1 wherein the an-

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ionic reagents comprise fatty acid tall oil and fuel oil in the ratio of from about 1.5 to 1 to about 2.5 to 1.0.

8. A process as claimed in claim 1 wherein the said flotation operations are performed at controlled alkalinities wherein the pH of the flotation feed pulps are held between about 7.5 and about 9.5 with the use of caustic soda, lime or sodium carbonate.

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