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# PHOSPHATE FLOTATION PROCESS

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This invention relates to the novel process for beneficiating phosphate ores by flotation.

In summary, this invention is directed to the flotation of phosphate ore slurries by the steps of treating the phosphate ore with flotation agents comprising an alkali metal salt of an aromatic sulfonic acid having a molecular weight above 360 and below about 600 and a hydrocarbon oil having a viscosity of from 33 to 10,000 sec. Saybolt measured at 100° F., and separating the phosphate contained in the slurry by froth flotation.

Certain preferred embodiments of this invention include the following: (1) The hydrocarbon sulfonate comprises a mixture of benzene and naphthalene sulfonates having an average molecular weight in the range of from about 400 to 500 in amounts equivalent to the addition of from 0.025 to 0.80 lb. $NaSO_3$ per ton of ore and preferably from 0.04 to 0.35 lb. $NaSO_3$ per ton of ore. (2) The hydrocarbon oil has a viscosity greater than 200 sec. Saybolt measured at 100° F. and is employed in an amount of from 0.1 to 5.0 lb. per ton of ore. (3) The phosphate ore slurry is conditioned at a solids concentration of from about 68 to 76 percent solids and preferably from about 71 to 76 percent solids. (4) The pH of the slurry during conditioning is above 6 and below 10 and is preferably about neutral. (5) The conditioning time is at least 2.5 minutes at ambient temperature. (6) The separated phosphate obtained by the initial flotation is subjected to a second flotation in the presence of a frother, preferably a higher alcohol. (7) The slurry concentration is adjusted to about 20 percent solids for flotation.

One known method for separating phosphates from phosphate ores involves the use of an anionic flotation procedure such as disclosed in Patent Nos. 2,373,688, 2,571,866, 2,643,770 and 2,682,337. This method involves the steps of conditioning a washed, sized phosphate rock with a mixture of an anionic flotation agent such as a petroleum sulfonate, a hydrocarbon oil such as crude oil or a fuel grade oil, and an alkaline agent for pH adjustment such as sodium hydroxide. However, this method has not been satisfactory to produce the degree of phosphate ore beneficiation desired.

As a result, an anionic flotation has usually been employed together with a later reverse cationic flotation procedure such as is shown in Patent No. 2,922,522. This procedure has several disadvantages. The cationic flotation agent, usually an amine, is relatively expensive. Furthermore, the rougher concentrate from the anionic flotation step must be deoiled prior to conditioning with the cationic reagent. This deoiling is usually achieved by means of a sulfuric acid treatment followed by a fresh water wash, and adds further cost disadvantages to the method. Not only are further reagents required but additional equipment must be provided in the system.

One object of this invention is the elimination of the need for an inverse flotation procedure using amines.

One object of this invention is to achieve beneficiation of the phosphate ores by flotation using low cost flotation agents.

Another object of this invention is a process for the beneficiation of phosphate ores comprising the steps of conditioning an aqueous slurry of the phosphate ore with flotation agents comprising an alkali metal salt of an aromatic sulfonic acid having a molecular weight above 360 and below about 600 and a hydrocarbon oil having a viscosity of from 33 to 10,000 sec. Saybolt measured at 100° F., and separating the phosphate contained in the slurry by froth flotation.

Another object of this invention is a process for the beneficiation of conditioning an aqueous slurry of the phosphate ore having a solids content of from about 68 to 76 percent solids and having a pH in the range of about from 6 to 10 with flotation agents comprising an alkali metal salt of a hydrocarbon aromatic sulfonic acid having a molecular weight above 360 and below about 600 in an amount equivalent to the addition of 0.025 and 0.80 lb. of $NaSO_3$ per ton of ore and a hydrocarbon oil having a viscosity of from 33 to 10,000 sec. Saybolt measured at 100° F. in an amount of from about 0.1 to 5.0 lb. per ton of ore, and separating the slurry by froth flotation.

Still another object of this invention is a process for the beneficiation of phosphate ores comprising the steps of conditioning an aqueous slurry of the phosphate ore having a solids content of about from 71 to 76 percent solids and having a pH in the range of about from 6 to 10 with flotation agents comprising an alkali metal salt of an aromatic sulfonic acid having a molecular weight in the range of about from 400 to 500 in an amount equivalent to the addition of 0.04 to 0.35 lb. of $NaSO_3$ per ton of ore and a hydrocarbon oil having a viscosity of from 33 to 10,000 sec. Saybolt at 100° F. in an amount of from about 0.1 to 5.0 lbs. per ton of ore.

A further object of this invention is a process for the beneficiation of phosphate ores comprising the steps of conditioning an aqueous slurry of the phosphate ore with flotation agents comprising an alkali metal salt of an aromatic sulfonic acid having a molecular weight above 360 and below about 600 and a hydrocarbon oil having a viscosity of from 200 to 10,000 sec. Saybolt measured at 100° F. separating the phosphate contained in the slurry by froth flotation, and subjecting the separated phosphate to a second flotation in the presence of a frother agent.

Prior to beneficiation of the phosphate ore by flotation, the ore must be washed and sized. The ore may be prepared by conventional techniques such as those disclosed in Patent No. 2,571,866. The washed and sized ore is introduced into a conditioner where it is mixed with sufficient water to provide a solids concentration of from 68 to 76 weight percent solids, and preferably from 71 to 76 percent solids. The conditioner may be any conventional mixing means which is capable of uniformly mixing slurries of this high concentration. For example, the conditioner may be a vertical mixing tank with a cruciform impeller or it may be a horizontal rotary drum with flights for lifting the feed. This solids concentration is critical; concentration outside of this range will not provide the desired beneficiation in the flotation cells.

The flotation agents are then introduced into the slurry, and the conditioning treatment is continued for at least 2.5 minutes and preferably for at least 5 minutes. The minimum of 2.5 minutes is critical at ambient water temperatures as hereinafter explained. The flotation agents comprise an aromatic sulfonate, a hydrocarbon oil, and an alkaline or acidic reagent for pH adjustment. The aromatic sulfonate can be a hydrocarbon sulfonate having a molecular weight of from above 360 to 600 and preferably from 400 to 500. Examples of suitable hydrocarbon sulfonates are the sodium salts of: trioctylbenzenesulfonate, decanylnaphthalenesulfonate, didecanylnaphthalenesulfonate, and propylheptyldecanylnaphthalenesulfonate. Mixtures of any of these compounds are suitable. A mixture of sodium alkylbenzenesulfonates and alkylnaphthalenesulfonates having an average molecular weight of from about 450–470 and an average number of carbon atoms per molecule of about from 25–30 has been found to be especially suitable. The amount of sulfonate employed will vary depending upon the phosphate content of the ore; a higher phosphate content will require the use of a greater quantity of the sulfonate. However, amounts less than those equivalent to 0.025 lb. $NaSO_3$ per ton of ore are ineffectual. Amounts equivalent to the addition of 0.04 to 0.35 $NaSO_3$ per ton of ore are preferred. Employing the alkylbenzenesulfonate-alkylnaphthalenesulfonate mixture mentioned above, amounts of from about 0.40 to 0.60 lb. per ton for an ore having a feed assay of about 6 percent $P_2O_5$ and of from about 0.20 to 0.40 lb. per ton of an ore having a feed assay of about 5 percent $P_2O_5$ have been found to be optimum.

The hydrocarbon oil must have a viscosity greater than 33 sec. Saybolt measured at 100° F. and must be sufficiently fluid to be dispersed. Oils having a viscosity greater than 10,000 sec. Saybolt measured at 100° F. have been found to be unsuitable. Where a second cleaner flotation is employed, the oil viscosity must be greater than 200 sec. Saybolt at 100° F. in order to provide effective flotation without a reconditioning. The hydrocarbon oil can be employed in amounts of from 0.1 to 5 lbs. per ton of ore. The preferred hydrocarbon oil has a viscosity within the range of about 300 to 500 sec. Saybolt at 100° F.

The alkaline reagent may be any conventional water soluble alkaline or acidic material such as sodium hydroxide or sulfuric acid, respectively, for example. The sole purpose of these reagents is to provide pH adjustment. The pH should be adjusted to a range of above 6.0 and below 10.0. Below 6.0 insufficient flotation is obtained, and above 10.0 the silica is floated. A pH of neutrality is preferred.

The conditioned phosphate ore slurry is then introduced into a flotation machine or bank of rougher cells. The slurry concentration should be adjusted to about 20 percent solids for optimum flotation. Any suitable rougher flotation unit such as a Fagergren or Mineral Separation type unit may be employed. The beneficiated phosphate ore is removed as the rougher concentrate. The rougher concentrate is then subjected to a further flotation in a cleaner unit which may be any suitable flotation unit such as a Denver-Sub A type unit. A frothing agent is added to the rougher concentrate prior to the cleaner flotation. Any conventional frother such as a higher alcohol can be employed. Methylisobutylcarbinol and pine oil are suitable examples. The rougher concentrate should be adjusted to about 20 percent solids for flotation in the cleaner cells. The beneficiated phosphate product is obtained as cleaner cell concentrate, and the cleaner cell tails are recycled for further processing.

The following examples are included for the purpose of illustration only, and are not to be construed as limitations of the invention claimed herein:

## EXAMPLE 1

This example shows the critical effect of the pulp density in the conditioning step. The experiments were conducted at a constant sulfonate addition of 0.48 lb. per ton, a natural water pH of 7.3 to 8.0 and a constant oil addition of 0.4 lb. per ton. The sulfonate employed was the preferred alkylbenzenesulfonate-alkylnaphthalenesulfonate mixture described above. The results are shown in Table I.

*Table I*

| Run No. | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Pulp density | 61.4 | 68.3 | 72.3 | 74.8 | 75.7 | 76.8 |
| Phosphate recovery in rougher cell, wt. percent | 40.7 | 57.1 | 79.9 | 90.6 | 87.2 | (1) |

[1] Such a large amount of the total feed floated that no assay of the product was make, no effective separation being obtained.

As can be seen, the pulp solids concentration should be between 71 and 76 for effective operation.

## EXAMPLE 2

This series of tests show the effect of the oil viscosity. The experiments were conducted at a natural water pH and a sulfonate concentration of about 0.27 lb. of the sulfonate employed in Example 1 per ton of ore. The ore contained about 5 percent phosphate as $P_2O_5$. Methylisobutylcarbinol was employed as the frothing agent in the cleaner cells. The results are shown in Table II.

*Table II*

| Test No. | Oil Viscosity, sec. (Saybolt at 100° F.) | Quantity of Oil Added, lb. per ton | Phosphate Recovery in Rougher Cell, Wt. Percent | Wt. Percent Feed Recovered in Cleaner Cell |
|---|---|---|---|---|
| 1 | No oil | 0.00 | 68.8 | 1.8 |
| 2 | 32.5 | 0.40 | 75.3 | 1.8 |
| 3 | 33.8 | 0.36 | 75.1 | 1.1 |
| 4 | 378.0 | 0.46 | 92.7 | 8.1 |
| 5 | 407.0 | 0.46 | 89.9 | 9.9 |

These results demonstrate the critical nature of the oil viscosity when employed with the aromatic sulfonates of this invention. An abrupt improvement is obtained in the phosphate recovery in the rougher cells, but the improved recovery in the feed recovery in the cleaner cells is even more unexpected. Unless the higher viscosity oils of this invention are employed, virtually no phosphate recovery in the cleaner cells is obtained.

## EXAMPLE 3

This example is a further illustration of the criticality of the hydrocarbon oil viscosity. These experiments were conducted at a pH of 7.5, a sulfonate concentration of 1.4 lb./ton of ore employing the sulfonate of Example 1 with an ore containing about 15 percent $P_2O_5$. The pulp density during conditioning was about 71% solids. The results are shown in Table III.

*Table III*

| Oil viscosity, sec. (Saybolt at 100° F.): | Phosphate recovery in rougher cell, weight percent |
|---|---|
| No oil | 10.8 |
| 32.5 | 35.7 |
| 54 | 65.4 |
| 407 | 74.4 |

## EXAMPLE 4

This example demonstrates that the molecular weight of the aromatic sulfonate employed as the collector is critical. The sulfonates employed were sodium salts of aromatic hydrocarbon sulfonates. The experiments were conducted at a pH of 7.5, with a sulfonate concentration of 0.22 lb. per ton, with a hydrocarbon oil having a viscosity of 407 sec. Saybolt at 100° F., and with a solids concentration during conditioning of about 74 percent solids. The results are shown in Table IV.

*Table IV*

| Molecular weight of aromatic sulfonate, approximate: | Phosphate recovery in rougher cell, weight percent |
|---|---|
| 230 | (1) |
| 310 | (1) |
| 320 | (1) |
| 330 | (1) |
| 360 | (1) |
| 420 | 86.9 |
| 455 | 85.1 |
| 460 | 93.6 |
| 460 | 93.8 |

[1] No flotation was obtained.

As shown by the results in Table IV, the molecular weight of the sulfonate is critical. It must be above 360 and is preferably above about 380.

## EXAMPLE 5

This example illustrates the importance of the conditioning time employing sulfonates and oils. The experiments were conducted at a constant sulfonate addition of about 0.26 lb. of the sulfonate of Example 1 per ton of ore, a natural water pH and temperature and a constant oil addition of 0.46 lb. per ton of ore of an oil having a viscosity of 378 sec. Saybolt at 100° F. The results are shown in Table V.

*Table V*

| Run No. | Conditioning time, min. | Phosphate recovery in rougher cell, weight percent |
|---|---|---|
| 1 | 1 | 68.0 |
| 2 | 2.5 | 82.0 |
| 3 | 5 | 92.7 |
| 4 | 10 | 89.7 |

As these results clearly indicate, the conditioning time is a critical feature of this invention.

As can be seen from the above examples and the types of reagents used in the flotation process, the method of this invention provides a superior phosphate recovery with low cost reagents. With the process of this invention it is no longer necessary to follow the anionic flotation step with a reverse flotation using cationic flotation agents. This avoids the necessity for intermediate deoiling steps and the necessary equipment for performing these steps. Of course, the process of this invention can be followed with a reverse, cationic flotation step if desired.

All concentrations stated herein are in units of weight.

I claim:

**1.** A process for the beneficiation of phosphate ores comprising the steps of conditioning for at least about 2.5 minutes an aqueous slurry of the phosphate ore having a solids content of from about 71 to 76 percent solids and having a pH in the range of about from 6 to 10 with flotation agents comprising an alkali metal salt of a hydrocarbon aromatic sulfonic acid having a molecular weight above 380 and below about 600 in an amount equivalent to the addition of 0.025 to 0.80 lb. of $NaSO_3$ per ton of ore and a hydrocarbon oil having a viscosity of from 200 to 10,000 sec. Saybolt measured at 100° F. in an amount of from about 0.1 to 5.0 lb. per ton of ore, and separating the slurry by froth flotation.

**2.** The process according to claim **1** wherein the alkali metal salt of the hydrocarbon aromatic sulfonic acid has an average molecular weight in the range of from about 400 to 500.

**3.** The process according to claim **1** wherein the alkali metal salt of the hydrocarbon aromatic sulfonic acid is employed in an amount equivalent to the addition of 0.04 to 0.35 lb. of $NaSO_3$ per ton of ore.

**4.** A process for the beneficiation of phosphate ores comprising the steps of conditioning for at least about 2.5 minutes an aqueous slurry of the phosphate ore having a solids content of from 71 to about 76 percent solids and having a pH in the range of about from 6 to 10 with flotation agents comprising an alkali metal salt of an aromatic sulfonic acid having a molecular weight in the range of about from 400 to 500 in an amount equivalent to the addition of 0.04 to 0.35 lb. of $NaSO_3$ per ton of ore and a hydrocarbon oil having a viscosity of from 200 to 10,000 sec. Saybolt measured at 100° F. in an amount of from about 0.1 to 5.0 lb. per ton of ore.

**5.** The process according to claim **4** wherein the alkali metal salt of the aromatic sulfonic acid is a mixture comprising alkylbenzenesulfonates and alkylnaphthalenesulfonates having an average molecular weight of about from 450 to 470 and having an average number of carbons per molecule of from about 25 to 30.

**6.** A process for the beneficiation of phosphate ores comprising the steps of conditioning for at least about 2.5 minutes an aqueous slurry of the phosphate ore having a solids content of from 71 to about 76 percent solids and having a pH range of about 6–10 with flotation agents comprising an alkali metal salt of an aromatic sulfonic acid having a molecular weight above 380 and below about 600 and a hydrocarbon oil having a viscosity of from 200 to 10,000 sec. Saybolt measured at 100° F., separating the phosphate contained in the slurry by froth flotation, and subjecting the separated phosphate to a second flotation in the presence of a frother agent.

**7.** The process of claim **6** wherein the hydrocarbon oil has a viscosity above 300 sec.

**8.** The process according to claim **6** wherein the aromatic sulfonic acid salt is employed in an amount equivalent to the addition of 0.025 to 0.80 lb. of $NaSO_3$ per ton of ore.

**9.** The process according to claim **8** wherein the hydrocarbon oil is employed in an amount of from about 0.1 to 5.0 lbs. per ton of ore.

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