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ORE BENEFICIATION PROCESS

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The present invention generally relates to the beneficiation or concentration of ores. More particularly, the present invention relates to the concentration of phosphate minerals by froth flotation. Still more particularly, the invention relates to a froth flotation process effective, inter alia, to separate silica from phosphate minerals.

Phosphate rock is an ore which is a crude phosphatic material or mineral consisting of more or less impure noncrystalline calcium-fluorphosphate. Phosphate rock occurs widely in nature and normally occurs in association with silica as a major gangue constituent. In addition to the silica, other gangue constituents are silicates, calcium carbonate, carbonaceous material, heavy minerals, and the like, all of which, of course, contain no phosphorus and are of little, if any, nutritive value so far as plants and animals are directly concerned.

Many methods have been devised in the past for treating such ores to effect beneficiation or concentration of the phosphatic constituents by removing the siliceous, carbonaceous, and heavy mineral constituents therefrom. Several methods involve the desliming, dewatering and separation of either pulped of unpulped material in order to effect this beneficiation and concentration. One commonly used method involves the reagentizing and froth flotation of an aqueous pulp of the ore with an anionic collecting agent used in conjunction with a relatively high boiling hydrocarbon oil or liquid, together with the use of a basic component such as caustic (NaOH). When an aqueous suspension or pulp of phosphate rock is reagentized with a composition containing this combination and the same agitated and aerated in an aqueous suspension in a flotation cell, the phosphatic values of the rock are found to rise and become segregated in the upper portion of the suspension while the siliceous values are found to settle or deposit in the lower portion of the suspension. The beneficiated or enriched phosphatic material, which is withdrawn from the upper portion of the flotation cell, is usually called a rougher concentrate. The rougher concentrate normally contains from about 8% to about 20% by weight of silica. The rougher concentrate may be further beneficiated in a subsequent froth flotation.

Various methods of operating beneficiation and concentration processes of the flotation type to improve the recovery and the grade of the phosphate in the beneficiated product have been used in the past. Some of the factors which control the recovery and the grade of the phosphate flotation product are the properties of the ore, the pH of the slurry, the type and quantity of reagents and the type and quantity of "aeration." Because of the large scale character of the business of producing phosphate rock concentrates, and the highly competitive market existing in such a business, it is important that the reagentizing composition be relatively inexpensive. Great effort has been expended to discover collecting agents which will be more efficacious, yet which may cost even less than those heretofore employed. It is, however, not alone desirable to employ a less expensive collector or a collector which may be used in smaller quantities to effect an efficient segregation of the phosphatic values, but it is also important that the concentrate recovered be of relatively high purity, that is,

relatively free of solids other than the desired phosphatic material.

The tall oil collecting agents useful in the anionic, or so-called fatty acid, flotation stage are efficient and yield a satisfactory phosphate concentrate of satisfactory grade; however, the cost of such tall oil collecting agents constitutes a significant portion of the cost of phosphate mineral beneficiation. Accordingly, the art is continuously seeking more economical collecting agents which may be employed in lieu of the relatively expensive tall oil fractions with at least equivalent results.

It is, therefore, an object of the present invention to provide a process for the concentration of phosphate minerals by froth flotation.

It is a further object of the invention to provide a novel collector for use in the anionic flotation stage of a froth flotation process for the concentration of phosphate minerals.

These and other objects and advantages of the present invention will be apparent from the following description of the invention.

The crude tall oils or tall oil fractions conventionally used in froth flotation processes for the concentration of phosphate minerals are fatty acid in character. The crude tall oil is obtained as a by-product of the chemical digestion of wood as practiced in the paper industry. The tall oil material conventionally used is either a high grade crude tall oil, or a "heart-cut" or middle fraction resulting in a crude tall oil distillation. In a crude tall oil distillation, a light tall oil fraction, usually called a light end or distillation head, is also produced. This light end, when compared to the middle fraction, or the entire crude tall oil, has a relatively lower boiling range. The distillation of the crude tall oil also produces a heavy tall oil fraction. This heavy fraction, when compared to the middle fraction, or the entire crude tall oil, or the light end, has a relatively higher boiling range.

The use of tall oil as a collector in flotation processes provides one of the chief markets for tall oil. Many of the heavy and "heart-cut" tall oil fractions and many of the crude tall oils, however, are not satisfactory as flotation collectors, and the price of these so-called low grade materials is relatively low. The light ends are also generally unsatisfactory as flotation collectors and the price of the light ends is also low, compared to the price of the high grade tall oils and "heart-cut" fractions. The light ends, in fact, are considered as waste product from tall oil distillations.

Light ends, heavy tall oils and so-called low grade crude tall oils, and many tall oil "heart-cut" fractions have, accordingly, generally found little if any use as a collector in a froth flotation process. The price of these materials, however, has been considerably lower than high grade crude tall oils and high grade "heart-cut" fractions. It has now been discovered, and the present invention is generally based on this discovery, that these materials, when mixed together or blended in certain proportions, produce a product, hereinafter denominated a blend, which has good flotation properties. It has been determined that the blend generally has excellent handling characteristics and metallurgy superior to any component of the blend. It has also been determined that the blend is more economical to use in a froth flotation than a good quality tall oil and more economical than any component of the blend.

In accordance with this invention, it has been discovered that silica-containing phosphate minerals can be concentrated efficiently by froth flotation in the presence of a collecting agent comprising the blend obtained by admixing a tall oil material and a relatively lower boiling tall oil fraction, the relatively lower boiling tall oil frac-

tion having a weight ratio of rosin acids to fatty acids less than about 0.6. The tall oil material preferably has a weight ratio of rosin acids to fatty acids greater than about 1.2. The tall oil material and the relatively lower boiling tall oil fraction are preferably present in said final blend in relative amounts to provide a weight ratio of rosin acids to fatty acids within the range of from about 0.5 to about 1.1. These ranges of ratios are preferred since it has been determined that particularly good results are obtained when operating within these ranges. However, the invention generally contemplates blending the relatively lower boiling tall oil fraction with relatively higher boiling tall oil material in all proportions. In general, the blend contains at least 5% by weight of the relatively lower boiling tall oil fraction and more preferably at least 10% by weight.

When the relatively lower boiling tall oil fraction is admixed with a heavy fraction of tall oil or with a "heart-cut" fraction of tall oil, it is preferred that the relatively lower boiling tall oil fraction be present in the final blend in an amount to provide a weight ratio of light ends to heavy fraction or "heart-cut" fraction greater than the ratio of light ends to heavy or "heart-cut" fraction existing in the original crude undistilled tall oil. In other words, for example, when a crude tall oil containing about 4% light ends, 50% "heart-cut" fraction and 46% heavy fraction, is distilled to produce a heavy fraction, and the heavy fraction is used in the preparation of a flotation reagent in accordance with this invention, the weight ratio of light ends to heavy fraction in the final blend should be greater than 4/46.

As is well known, tall oil is a mixture of fatty acids, rosin acids, and unsaponifiable material. The composition of tall oil, either crude tall oil or any tall oil distillation fraction, is usually reported as the weight percent of rosin acids, the weight percent of fatty acids, and the weight percent of unsaponifiable material. It has been determined that the weight ratio of rosin acids to fatty acids is very important in evaluating the tall oil as a flotation reagent.

A good grade of tall oil, that is a tall oil which has good flotation properties, generally contains at least 35% by weight of fatty acids and has a weight ratio of rosin acids to fatty acids within the range of from about 0.8 to about 1.0.

Many crude tall oils or tall oil heavy or "heart-cut" fractions, especially those having a weight ratio of rosin acids to fatty acids greater than about 1.2, and more especially those having the weight ratio greater than about 1.6, even though containing at least 35% by weight of rosin acids, are generally unsatisfactory for use as a flotation reagent. Therefore, as hereinbefore mentioned, such tall oil materials are of relatively low price. Tall oil material having a weight ratio of rosin acids to fatty acids greater than about 1.2 is commercially available and preferably contains at least 35% by weight of rosin acids. This tall oil material is either an entire crude tall oil or a selected fraction thereof, usually a heavy or "heart-cut" fraction.

The light ends are also generally unsatisfactory as flotation reagents. The light ends usually contain a relatively high weight percent of fatty acids, generally greater than 60 weight percent; however, the ratio of rosin acids to fatty acids is usually below about 0.6 and frequently below about 0.25. The light end tall oil material having a weight ratio of rosin acids to fatty acids less than about 0.6 has a relatively lower average boiling point and preferably contains at least 35% by weight of fatty acids and more preferably at least 45% by weight of fatty acids, and still more preferably at least 60% by weight of fatty acids. This light end material is obtained from the distillation of a crude tall oil and is generally the overhead product of the distillation.

The tall oil material having a weight ratio of rosin acids to fatty acids greater than about 1.2 is blended with the relatively lower boiling tall oil fraction in any suitable manner. As performed on a large scale, the materials are mixed together in a blending tank provided with a rotating propeller. The materials are preferably blended in relative amounts to provide a final blend having at least 5% by weight of the lower boiling tall oil fraction and more preferably at least 10% by weight, and the final blend preferably also has a weight ratio of rosin acids to fatty acids within the range of from about 0.5 to about 1.1 and preferably within the range of from about 0.75 to about 0.95. The resultant blend preferably contains at least 35% by weight of fatty acids. It has been determined that such blends have good flotation properties and handling characteristics and metallurgy superior to either component of the blend.

In addition to the essential values in the tall oil blend, the usual reagentizing composition also contains a basic material such as caustic soda, soda ash, KOH, or the like, in order to regulate the pH of the suspension or pulped slurry above 7.0 and preferably between about 8.0 and about 9.0. A third component, which is usually used in the reagentizing composition, is a froth controller which is normally a liquid hydrocarbon component which is a liquid under the conditions obtaining. Suitable substances in this category are diesel oil, fuel oil, kerosene, the heavier solvent naphthas, crude oil, and the like, as well as mixtures of two or more of these liquid hydrocarbon components.

The tall oil blend, the basic material, and the liquid hydrocarbon component of the reagentizing composition may be added separately to the ore or they may be added as a previously prepared admixture to the dewatered phosphatic material. Also, it is possible to obtain substantial results in beneficiating the phosphatic rock ore, if the hydrocarbon component of the reagentizing composition is omitted entirely.

A typical composition is given below, the amounts being in pounds per ton of solids treated:

A. Tall oil blend in an amount between about 0.25 and about 3.0.
B. Diesel or fuel oil in conventional amounts, usually between about 0.1 and about 6.0.
C. Caustic soda or any other suitable basic material in conventional amounts, usually between about 0.2 and about 1.5.

The tall oil blends of this invention are employed in conventional manner and generally in conventional proportions known to the art. In general, and in accordance with conventional practice, phosphate rock reagentized with a composition as above described may be subjected to a separation or segregation step, or sequence of such steps in a number of ways, all of which effect a marked beneficiation or concentration of the desired phosphatic values of the ore. Such a reagentized feed may be treated by slurrying in water to form an aqueous suspension, aerating the suspension, and allowing the froth layer and agglomerate layer to collect at the top of the flotation cell, while the siliceous impurities and other undesirable values sink to the bottom of the cell. In this manner, the floated phosphatic values are segregated from the siliceous bodies and the like. The concentrate or partially concentrated phosphatic material may then be subjected to a further flotation or series of flotation steps employing the same reagentizing composition, or a different one, to further beneficiate the phosphatic values.

The novel reagentizing composition may also be applied in processes designed to beneficiate or concentrate phosphatic ores in which froth flotation is not involved. Thus, for example, the reagentized phosphatic feed, either at an original or intermediate step in the beneficiation, may be subjected to a conventional tabling operation designed to permit the collection and segregation of phosphatic material on the one hand, and siliceous material on the other hand. Also, the phosphatic material reagentized with the

novel reagentizing composition may be successfully beneficiated as to its phosphatic content in a spiraling operation in which the reagentized feed is passed downwardly in a spiraling path. In the spiral operation, the phosphatic material is selectively moved to the outer side of the spiral pathway while the siliceous bodies and other impurities are collected from the inner portion of the spiral pathway.

As illustrative of the characteristics of the instant invention, but in no wise intending to be limited thereby, the following example is given:

EXAMPLE

A series of runs was conducted under substantially the same standard conditions of treatment and involved the same amounts of ore or rock and the like, and except as indicated in the table, all conditions, reagents, and treatments remained constant so that a set of strictly comparable results were obtained with the exceptions noted in the table. The runs were all conducted so as to achieve substantially a 90% recovery of the BPL content in the rock feed, except as noted in the table.

In each instance, Florida pebble phosphate rock of about −28 mesh was deslimed and dewatered to about eighty percent solids, placed in a mixing chamber with reagent, and agitated. The reagentized rock was then diluted with water, and passed to a flotation cell of conventional type with the various types of reagents in the amounts specified below in the table. Runs 1, 5, 9, and 13 were made using a standard high grade tall oil. These runs were made for the purpose of comparing the blends of this invention with a standard high grade tall oil when used in a flotation operation. It should be noted that in all runs the blends of this invention were superior to the standard.

Table

Run No.	Flotation collector	Analysis of collector			Lbs. reagent per ton feed	Percent compared with blend		Percent BPL in concentrate
		Percent, RA	Percent, FA	RA/FA		Reagent consumption	Cost	
1	Standard high grade tall oil	40.62	45.59	0.891	0.494	89	107.0	62.98
2	Low grade crude tall oil	56.43	28.39	1.988	0.635	114	115.0	62.08
3	Light ends	5.28	83.28	0.0634	0.700	126	124.1	67.38
4	Blend of 2 parts crude tall oil and 1 part light ends.	39.39	47.31	0.833	0.556	100	100.0	63.75
5	Standard high grade crude tall oil.	40.6	45.6	0.89	0.86	103	162	65.0
6	Heavy end fraction (pitch)	32.0	44.0	0.73	1.20	144	139	67.6
7	Light ends	5.3	83.3	0.06	0.94	113	117	67.3
8	Blend of 1 part heavy ends and 1 part light ends.	18.7	63.7	0.29	0.83	100	100	73.2
9	Standard high grade crude tall oil.	40.6	45.6	0.89	0.56	95	127	65.0
10	Middle cut fraction	26.5	71.6	0.37	0.49	82	128	66.1
11	Light ends	5.3	83.3	0.06	0.94	159	127	67.3
12	Blend of 1 part middle cut and 3 parts light ends.	10.8	80.4	0.14	0.59	100	100	67.9
13	Standard high grade crude tall oil.	40.6	45.6	0.89	1.04	102	135	54.0
14	#2 crude tall oil [1]	54.6	18.0	3.04	2.00	197	216	50.7
15	Light ends	5.3	83.3	0.06	1.34	133	118	57.0
16	Blend of 2 parts crude tall oil and 1 part light ends.	38.2	39.8	0.96	1.01	100	100	56.4

[1] Crude tall oil from Bahama woods—90% BPL recovery not obtained; 83% recovery used this sample only.

The present invention provides a process which is effective materially to reduce the cost of the froth flotation concentration of phosphate materials and accordingly constitutes a significant contribution to the art.

The description of the invention utilized specific reference to certain process details; however, it is to be understood that such details are illustrative only and not by way of limitation. Other modifications and equivalents of the invention will be apparent to those skilled in the art from the foregoing description.

Having now fully described and illustrated the invention, what is desired to be secured and claimed by Letters Patent is set forth in the appended claims.

We claim:

1. A process for preparing a reagent for use in a process for beneficiating ores which comprises admixing (A) and (B);

(A) A tall oil material selected from the group consisting of tall oil, middle fractions of tall oil, heavy tall oil fractions and mixtures thereof;

(B) A tall oil fraction having a fatty acid content of at least 35% by weight, having a boiling range relatively lower than said tall oil material (A), and having a weight ratio of rosin acids to fatty acids less than about 0.6;

said (B) lower boiling tall oil fraction being used in an amount of at least 5% by weight of the resulting admixture of (A) and (B) to produce a resulting admixture of (A) and (B) having a fatty acid content of at least 35% by weight and a weight ratio of rosin acids to fatty acids less than 1.1.

2. The process of claim 1 wherein the relatively lower boiling tall oil fraction has a weight ratio of rosin acids to fatty acids less than about 0.25.

3. The process of claim 1 wherein said relatively lower boiling tall oil fraction is used in an amount of at least about ten percent by weight of the resulting admixture.

4. A process for preparing a reagent for use in a process for beneficiating ores which comprises admixing a tall oil material selected from the group consisting of tall oil, middle fractions of tall oil, heavy tall oil fractions and mixtures thereof with a tall oil fraction having a fatty acid content of at least 35% by weight, having a boiling range relatively lower than said tall oil material and having a weight ratio of rosin acids to fatty acids less than about 0.6, said tall oil material and said relatively lower boiling tall oil fraction being used in relative amounts to provide in the resulting admixture a weight ratio of rosin acids to fatty acids within the range of from about 0.5 to about 1.1.

5. The process of claim 4 wherein said tall oil material comprises crude tall oil.

6. The process of claim 4 wherein said tall oil material comprises a heart-cut fraction resulting from the distillation of a crude tall oil.

7. The process of claim 4 wherein said tall oil material comprises a high boiling fraction resulting from the distillation of a crude tall oil.

8. A process for preparing a reagent for use in a process for beneficiating ores which comprises admixing a tall oil material obtained from crude tall oil and selected from

the group consisting of tall oil, middle fractions of tall oil, heavy tall oil fractions and mixtures thereof having a weight ratio of rosin acids to fatty acids greater than about 1.2 with a tall oil fraction having a fatty acid content of at least 35% by weight, having a boiling range relatively lower than said tall oil material and having a weight ratio of rosin acids to fatty acids less than about 0.6, said tall oil material and said relatively lower boiling tall oil fraction being used in relative amounts to provide in the resulting admixture a weight ratio of rosin acids to fatty acids within the range of from about 0.5 to about 1.1 and to provide a weight ratio of said relatively lower boiling tall oil fraction to said tall oil material greater than in the crude tall oil from which said tall oil material was obtained.

9. The process of claim 8 wherein said tall oil material and said relatively lower boiling tall oil fraction are used in amounts to provide in the resulting admixture a weight ratio of rosin acids to fatty acids within the range of from about 0.75 to about 0.95.

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