# PATENT SPECIFICATION

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COMPLETE SPECIFICATION

## Improvements in or relating to Processes of Concentrating Phosphate-bearing Minerals

Communication from PHOSPHATE RECOVERY CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, of 61, Broadway, City and State of New York, United States of America.

I, ARTHUR HAROLD STEVENS, B.Sc. (Lond.), F.C.S., Fellow of the Chartered Institute of Patent Agents, a Subject of the King of Great Britain, of the firm of Stevens, Langner, Parry & Rollinson, of 5—9, Quality Court, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the concentration of phosphate-bearing minerals and is herein illustrated in connection with the examples given as applied to the concentration of Florida phosphate rock.

In accordance with the invention, concentration of such minerals is carried out by a selective collecting action effected on the silicious constituents of the ore treated by the use of bone oil and an acid capable of forming with water a distinctly acid solution readily titratable with an aqueous solution of a base, by agitating a pulp of the ore containing the phosphate mineral to undergo concentration in the presence of these agents, as a result of which a material relatively rich in silicious gangue and relatively poor in phosphate values may subsequently be separated from the pulp, the material remaining being collected as the concentrate by reason of its retention therein of the greater proportion of the phosphate values. Instead of bone oil, crude quinoline may be employed, the same separating effect on the silicious impurities normally associated with phosphatic material being obtained by the use of the latter substance in conjunction with an acid of the character stated.

In the process of the present invention as above defined, the bone oil or crude quinoline functions as a collector for the silicious constituents of the ore treated, while the acid functions as an activating agent causing the bone oil or crude quinoline to have a preferential affinity for such constituents.

We are aware that phosphate-bearing minerals have already been concentrated by the use of bone oil. In all of these instances, however, that oil has been used without acid and as a collector for the phosphate values, a procedure from which the process of the present invention obviously differs. We are also aware that phosphate-bearing minerals have been concentrated by a collecting action on the silicious gangue, but we are not aware that either bone oil or crude quinoline has ever been used to effect that collecting action.

As made apparent by the foregoing statement of the invention, all water-soluble acids yielding distinctly acid solutions readily titratable with an aqueous solution of a base are qualified for use in the process of the present invention, satisfactory results having thus been obtained with sulphuric acid, sulphurous acid, hydrochloric acid, hydrofluoric acid, hydrofluorsilicic acid, arsenic acid, selenic acid, acetic acid, and lactic acid. In addition to acids of this character, however, it has been found that some inorganic salts reacting acid in solution with water are also capable of use in the process of the present invention, the most effective of these salts being sodium silicofluoride, ammonium silicofluoride, stannic chloride, phosphorous trichloride, silicon tetrachloride, thionyl chloride, and potassium bisulphate. It is uncertain, however, whether the activating effect of such salts is wholly due to the acids liberated, since others also reacting acid when dissolved in water have proved totally ineffective. When a salt is used in the process of the present invention, therefore, it should not only be capable of dissolving in water with an acid reaction, but it should also be adapted to function as an activating agent enabling the bone oil or crude quinoline to have a preferential affinity for the

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siliceous constituents of the ore treated, that is, the nature of the salt employed should not be such as to prevent the activating effect of the liberated acid.

The use of an activating agent is apparently essential to the process of the present invention, the siliceous gangue being probably so conditioned by such agent that it is enabled to properly react with the bone oil or crude quinoline. When either acid or salt is used as the activating agent, the pulp is undoubtedly of an acid character, although a decidedly acid pulp is not necessary, particularly in the case of a salt. Moreover, caustic soda may in certain cases be used along with the other agents.

In carrying out the invention, the bone oil or crude quinoline and the activating agent may each be added separately to the pulp, best results being obtained in most cases when the activating agent is added after the bone oil or crude quinoline. When bone oil is used, however, this oil may first be treated with an acid of the aforementioned character, a reaction product being obtained which has been found capable of use without further addition of acid to the pulp. If desired, this product may be dissolved in alcohol prior to use. Or, the bone oil may be dissolved in alcohol prior to its treatment by the acid.

If the product resulting from the aforementioned acid treatment of bone oil is thereafter treated with water so as to extract its water-soluble fraction, this extracted fraction may also be used to effect separation of siliceous gangue from phosphatic material. This fact seems to indicate that the effective ingredients in bone oil enabling this substance to operate as a collector for such gangue are amine bases or impurities associated therewith. The water-soluble fraction of acid-treated bone oil also requires no further addition of acid to the pulp.

The process of the present invention may be carried out by well-known physical forms of concentration, such as flotation and tabling. When flotation is employed, of course, it is the siliceous gangue which is caused to accumulate in the material floated, which is removed as a tailing or waste product, leaving the greater proportion of the phosphate values in the non-floated material as the concentrate. And when tabling is employed, the siliceous constituents are caused to be discharged at the side of the table and the phosphate values at the end, contrary to ordinary tabling practice applied to phosphate-bearing ores.

It is understood that the process of the present invention is not limited to the exclusive use of the agents which have been designated. For example, a mineral oil may be used as a cooperating collector. Also, any well-known frother may be used when flotation is employed.

The separation of siliceous gangue from phosphatic material as carried out by the process of the present invention enables excellent results to be obtained with relation to both content and recovery of phosphate values in the concentrate or material remaining after the separation, the process of the present invention being almost identical in mechanical characteristics with the usual processes of separating the phosphate values. In the same manner the pulp thickens in the preliminary operation of mixing it with the reagents. And when the subsequent step of separating the siliceous gangue is carried out by froth flotation, there is obtained the same type of froth float, which is removed in the usual manner in a very short period of time. On the other hand, whereas by increasing the amount of collector the grade of concentrate is lowered and the recovery of values made higher when floating the phosphate values, it has been found that the reverse situation holds true for the process of the present invention. That is, the content of the phosphate values in the non-floated material is caused to increase and the recovery of such values to decrease, with increasing amount within reasonable limits of bone oil or other collector admixed with the pulp.

In preparing the ore for treatment by the process of the present invention, it is in general desirable that it be both comminuted to a particle size most suitable for efficient operation and that it be largely deslimed, its desliming greatly minimizing the consumption of the reagents. Ordinarily, the crude ore is first subjected to a preliminary grinding operation and thereafter screened or classified to remove all particles other than those desired. The undersize may then be deslimed, and the oversize reground, deslimed, and added to the deslimed undersize; or the oversize may be reground, added to the undeslimed undersize, and the whole then deslimed.

The following examples describe certain tests which have been made in carrying the invention into effect, the reagent proportions in each being figured on the basis of the dry weight tonnage (2000 pounds) of the material treated.

silicious constituents of the ore treated, that is, the nature of the salt employed should not be such as to prevent the activating effect of the liberated acid.

The use of an activating agent is apparently essential to the process of the present invention, the silicious gangue being probably so conditioned by such agent that it is enabled to properly react with the bone oil or crude quinoline. When either acid or salt is used as the activating agent, the pulp is undoubtedly of an acid character, although a decidedly acid pulp is not necessary, particularly in the case of a salt. Moreover, caustic soda may in certain cases be used along with the other agents.

In carrying out the invention, the bone oil or crude quinoline and the activating agent may each be added separately to the pulp, best results being obtained in most cases when the activating agent is added after the bone oil or crude quinoline. When bone oil is used, however, this oil may first be treated with an acid of the aforementioned character, a reaction product being obtained which has been found capable of use without further addition of acid to the pulp. If desired, this product may be dissolved in alcohol prior to use. Or, the bone oil may be dissolved in alcohol prior to its treatment by the acid.

If the product resulting from the aforementioned acid treatment of bone oil is thereafter treated with water so as to extract its water-soluble fraction, this extracted fraction may also be used to effect separation of silicious gangue from phosphatic material. This fact seems to indicate that the effective ingredients in bone oil enabling this substance to operate as a collector for such gangue are amine bases or impurities associated therewith. The water-soluble fraction of acid-treated bone oil also requires no further addition of acid to the pulp.

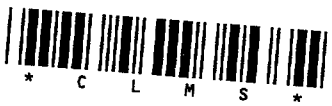
The process of the present invention may be carried out by well-known physical forms of concentration, such as flotation and tabling. When flotation is employed, of course, it is the silicious gangue which is caused to accumulate in the material floated, which is removed as a tailing or waste product, leaving the greater proportion of the phosphate values in the non-floated material as the concentrate. And when tabling is employed, the silicious constituents are caused to be discharged at the side of the table and the phosphate values at the end, contrary to ordinary tabling practice applied to phosphate-bearing ores.

It is understood that the process of the present invention is not limited to the exclusive use of the agents which have been designated. For example, a mineral oil may be used as a cooperating collector. Also, any well-known frother may be used when flotation is employed.

The separation of silicious gangue from phosphatic material as carried out by the process of the present invention enables excellent results to be obtained with relation to both content and recovery of phosphate values in the concentrate or material remaining after the separation, the process of the present invention being almost identical in mechanical characteristics with the usual processes of separating the phosphate values. In the same manner the pulp thickens in the preliminary operation of mixing it with the reagents. And when the subsequent step of separating the silicious gangue is carried out by froth flotation, there is obtained the same type of froth float, which is removed in the usual manner in a very short period of time. On the other hand, whereas by increasing the amount of collector the grade of concentrate is lowered and the recovery of values made higher when floating the phosphate values, it has been found that the reverse situation holds true for the process of the present invention. That is, the content of the phosphate values in the non-floated material is caused to increase and the recovery of such values to decrease, with increasing amount within reasonable limits of bone oil or other collector admixed with the pulp.

In preparing the ore for treatment by the process of the present invention, it is in general desirable that it be both comminuted to a particle size most suitable for efficient operation and that it be largely deslimed, its desliming greatly minimizing the consumption of the reagents. Ordinarily, the crude ore is first subjected to a preliminary grinding operation and thereafter screened or classified to remove all particles other than those desired. The undersize may then be deslimed, and the oversize reground, deslimed, and added to the deslimed undersize; or the oversize may be reground, added to the undeslimed undersize, and the whole then deslimed.

The following examples describe certain tests which have been made in carrying the invention into effect, the reagent proportions in each being figured on the basis of the dry weight tonnage (2000 pounds) of the material treated.



EXAMPLE 1.

Deslimed phosphate feed to plant No. 4 of the Phosphate Recovery Corporation in Florida, consisting mainly of tricalcium phosphate and silica and of a particle size to pass through a screen of 28 meshes to the lineal inch, was made up with water into a thick pulp of about 70% solids. To this pulp were added during agitation in an impeller-type mixer, first 44 lbs. per ton of crude bone oil obtained from the Texas Chemical Company and then 18.4 lbs. per ton of concentrated sulphuric acid, the mixer speed being from 300 to 400 r.p.m. Addition of the reagents mentioned required about one minute, subsequent to which agitation in the mixer was continued for about two minutes, small amounts of water being added to maintain a consistency that permitted ready mixing. After this conditioning the pulp was transferred to a laboratory subaeration flotation machine, where it was diluted and agitated for a period of one minute, during which a floating froth mainly carrying the silica particles was produced and separated. The following table indicates the results of the test:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate | Ratio of Concentration |
|---|---|---|---|---|---|
| Feed | 100 | 40.13 | 49.29 | | |
| Floated | 50.0 | 8.82 | 87.07 | 11.0 | |
| Non-Floated | 50.0 | 71.44 | 11.50 | 89.0 | 2.0 |

EXAMPLE 2.

A sample of the same feed was processed in the same manner as in Example 1, but in this instance the proportion of the bone oil was increased to 48 lbs. per ton and that of concentrated sulphuric acid decreased to 7.4 lbs. per ton. As shown by the following table, a higher grade of tricalcium phosphate concentrate was obtained, but the tricalcium phosphate recovery was slightly lowered.

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate | Ratio of Concentration |
|---|---|---|---|---|---|
| Feed | 100 | 39.94 | 49.72 | | |
| Floated | 53.8 | 8.92 | 87.38 | 12.0 | |
| Non-Floated | 46.2 | 76.05 | 5.87 | 88.0 | 2.06 |

EXAMPLE 3.

Again the identical procedures of Example 1 were repeated, except that 52 lbs. per ton of the bone oil and 3.6 lbs. per ton of the acid were employed, the following results being obtained.

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate | Ratio of Concentration |
|---|---|---|---|---|---|
| Feed | 100 | 40.09 | 48.18 | | |
| Floated | 54.1 | 7.62 | 86.05 | 10.3 | |
| Non-Floated | 45.9 | 78.36 | 3.55 | 89.7 | 1.96 |

EXAMPLE 4.

A sample of the same feed as before was made up with water into a pulp of 70% solids, which pulp was agitated in the mixer first with 26 lbs. per ton of crude bone oil obtained from the Eastman Kodak Company and then with 1.84 lbs. per ton of concentrated sulphuric acid, the pulp being acid to litmus after this conditioning operation. As before, the conditioned pulp was treated in the flotation machine for the production of a floating froth, but in this instance, upon removal of the non-floated material (constituting the finished concentrate), the floated material was retreated in the machine, without further addition of reagents. The results are given in the following table, in which the non-floated material obtained by the cleaning operation stated is indicated as a middling:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate | Ratio of Concentration |
|---|---|---|---|---|---|
| Feed | 100 | 41.26 | 48.92 | | |
| Refloated | 56.0 | 11.72 | 84.53 | 15.9 | |
| Middling | 1.8 | 64.23 | 20.56 | 2.8 | |
| Non-Floated | 42.2 | 79.49 | 2.86 | 81.3 | 2.47 |

COMPARATIVE TEST 1.

A pulp of the same feed and of the same consistency as in the preceding examples was agitated in the mixer with 320 lbs. per ton of crude Eastman Kodak Company bone oil, no acid being employed. Subsequently treating the pulp in the flotation machine, no flotation whatever could be effected.

EXAMPLE 5.

Deslimed phosphate feed to plant No. 2 of the Phosphate Recovery Corporation in Florida, also of a particle size to pass through a screen of 28 meshes to the lineal inch, was made up with water into a pulp of 70% solids, which pulp was conditioned in the mixer with the following agents separately introduced therein in the order in which they appear: 2.78 lbs. of fuel oil, 34 lbs. of bone oil obtained from Eimer & Amend and known as "Animal oil foetida, tech", and 2.24 lbs. of concentrated sulphuric acid, all per ton of dry feed. The pulp thus conditioned was then processed in the flotation machine in the same manner as in Example 4. The results are shown in the following table, the middling product referring to the non-floated material obtained by retreatment in the machine:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 28.18 | | |
| Refloated | 65.0 | 2.57 | | 5.7 |
| Middling | 1.3 | 66.43 | | 3.0 |
| Non-floated | 33.7 | 76.16 | 2.02 | 91.3 |

EXAMPLE 6.

A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned in the mixer with the following agents separately introduced therein in the order in which they appear: 54 lbs. per ton of concentrated sulphuric acid, 6.24 lbs. per ton of fuel oil, 52 lbs. per ton of crude Texas Chemical Company bone oil, and 0.14 lb. per ton of a frothing agent consisting of 3 parts of crude rosin residue dissolved in 1 part of kerosene oil. Treatment of the conditioned pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 36.33 | | |
| Floated | 36.3 | 2.51 | | 2.5 |
| Non-floated | 63.7 | 55.61 | 29.06 | 97.5 |

EXAMPLE 7.

For the purpose of this example caustic soda was employed in addition to the agents enumerated in Example 6. A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned in the mixer with the following agents separately introduced therein in the order in which they appear: 0.8 lb. of caustic soda, 6.24 lbs. of fuel oil, 94 lbs. of the same bone oil, 36.8 lbs. of concentrated sulphuric acid, and 0.28 lb. of the same kerosene-rosin frothing agent, all per ton of dry feed. The pulp thus conditioned was treated in the flotation machine, the non-floated material was removed, and the floated material was retreated without further addition of reagents. The results are shown in the following table, in which the non-floated material obtained by the cleaning operation stated is indicated as a middling, it being observed that a much higher grade of tricalcium phosphate concentrate was obtained than in the preceding example:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 39.98 | 50.26 | |
| Refloated | 53.4 | 10.12 | 85.97 | 13.5 |
| Middling | 3.0 | 59.22 | 26.89 | 4.4 |
| Non-floated | 43.6 | 75.25 | 8.12 | 82.1 |

EXAMPLE 8.

A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned in the same manner as in Example 7, but with the proportions of the bone oil and acid reduced to 40 lbs. per ton and 18.4 lbs. per ton, respectively. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 40.08 | 49.97 | |
| Floated | 60.0 | 15.83 | 79.11 | 23.7 |
| Non-floated | 40.0 | 76.45 | 6.25 | 76.3 |

EXAMPLE 9.

For the purpose of this example a solution of acid-treated bone oil in alcohol was used as a flotation collector for the silica, which solution was prepared in the following manner:—

To 100 g. of crude Eastman Kodak Company bone oil, 30 cc. of concentrated sulphuric acid were added slowly with stirring. The oil heated considerably and thickened to a tarry mass, stirring being continued until the oil cooled. The oil thus treated was dissolved in an equal volume of alcohol, the solution being employed in the following test:—

A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned in the mixer with the following agents separately introduced therein in the order in which they appear: 0.8 lb. per ton of caustic soda, 6.24 lbs. per ton of fuel oil, 14 lbs. per ton of the above alcohol solution, and 0.14 lb. per ton of the kerosene-rosin frothing agent previously indicated. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 40.13 | 50.42 | |
| Floated | 36.9 | 6.81 | 91.54 | 6.3 |
| Non-floated | 63.1 | 59.62 | 26.37 | 93.7 |

EXAMPLE 10.

Here a flotation collector was employed consisting of water-soluble constituents of acid-treated bone oil, this collector being obtained as follows:—

100 g. of crude Texas Chemical Company bone oil were treated with 30 cc. of concentrated sulphuric acid in the manner indicated in the preceding example. To this treated oil 100 cc. of water were added, and the mixture stirred. The water took much of the products of the treated oil into solution, the solid material sinking to the bottom of the container. The water solution was decanted and filtered. To the residue another 100 cc. of water were added with stirring, and the water solution was again decanted and filtered, this procedure being successively repeated until in all 500 cc. of water were used in leaching the solid material. The solution obtained by these successive leaching and filtering operations was employed in the following test:

A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned in the mixer with the following agents separately introduced therein in the order in which they appear: 0.8 lb. per ton of caustic soda, 6.24 lbs. per ton of fuel oil, a proportion of the above water solution corresponding to 34 lbs. per ton of the constituents dissolved therein, and 0.14 lb. per ton of the kerosene-rosin frothing agent previously indicated. Treatment of the conditioned pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 40.00 | 30.50 | |
| Floated | 42.8 | 4.41 | 93.72 | 4.7 |
| Non-floated | 57.2 | 66.63 | 17.82 | 95.3 |

EXAMPLE 11.

The identical procedures indicated in the preceding example were repeated, except for the following differences: In the preparation of the solution obtained by acid treatment of bone oil and subsequent leaching of the same, crude Eastman Kodak Company bone oil and 1000 cc. of wash water were employed; and in the flotation test, 96 lbs. per ton of the solution thus obtained were employed, without caustic soda. The following results were obtained:

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 39.61 | 51.22 | |
| Floated | 37.5 | 3.41 | 94.88 | 3.2 |
| Non-floated | 62.5 | 61.32 | 25.02 | 96.8 |

EXAMPLE 12.

In exactly the same manner as in Example 10, 100 g. of crude Texas Chemical Company bone oil were treated with 30 cc. of concentrated sulphuric acid and subsequently leached with 500 cc. of water. The water extract was used in the proportion of 50 lbs. per ton in the flotation test, which was otherwise carried out in the same manner as in Example 10, the following results being obtained:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate | Ratio of Concentration |
|---|---|---|---|---|---|
| Feed | 100 | 39.25 | 51.40 | | |
| Floated | 39.4 | 5.01 | 94.34 | 5.0 | |
| Non-floated | 60.6 | 61.52 | 23.49 | 95.0 | 1.65 |

COMPARATIVE TEST 2.

The residue obtained in Example 12 by the acid and water treatment of bone oil was further washed to remove all soluble ingredients. It may here be noted that these ingredients color water intensely so that, as a criterion of their complete removal, washing was continued until the water was colorless. A total of 8500 cc. of water, including the 500 cc. employed in Example 12, was required before no coloration could be detected. The residue from this further leaching was then treated with enough alcohol to produce a mixture containing approximately 95 parts of alcohol to 5 parts of residue, most of the residue dissolving in the alcohol. This mixture was filtered and the solution thus obtained employed as a reagent in the following test:—

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated with the same agents as in Example 12, except that 20 lbs. per ton of the above alcohol solution were employed instead of the water extract. Subsequently treating the pulp in the flotation machine, substantially no flotation effect was produced on the silica.

EXAMPLE 13.

This example is intended to show that the residue obtained by acid and water treatment of bone oil will also cause the silica to float if the soluble ingredients are not all removed.

Crude Texas Chemical Company bone oil was treated with one-third its weight of concentrated sulphuric acid and the resulting material treated with wash water in amount sufficient to produce a water solution of approximately 5 parts of dissolved ingredients therein to 95 parts of water, this solution being separated from the residue. To this residue alcohol was added in the approximate amount of 85 parts of alcohol to 15 parts of residue, much of the residue dissolving in the alcohol. This mixture was filtered, the filtrate being employed in the following test:—

A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned in the mixer with the following agents separately introduced therein in the order in which they appear:—0.3 lb. per ton of caustic soda, 7.5 lbs. per ton of fuel oil, 90 cc. per ton of the above filtrate, and 0.14 lb. per ton of the kerosene-rosin frothing agent already described. The pulp thus conditioned was treated in the flotation machine, the non-floated material was removed, and the floated material was retreated without further addition of reagents. The non-floated material resulting from this last operation is indicated as a middling in the following table, it being observed that a much higher grade of tricalcium phosphate concentrate was obtained than in Examples 10, 11, and 12, in neither one of which was the leaching of acid-treated bone oil carried out to remove all water-soluble constituents therefrom.

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 39.74 | 50.77 | |
| Refloated | 53.7 | 10.12 | 87.76 | 13.7 |
| Middling | 4.0 | 57.71 | 28.64 | 5.8 |
| Non-floated | 42.3 | 75.65 | 5.88 | 80.5 |

EXAMPLE 14.

Here a flotation collector was prepared by first dissolving 200 g. of crude Texas Chemical Company bone oil in 200 cc. of alcohol. This solution was treated with 250 cc. of concentrated sulphuric acid and then with 1000 cc. of water, the resulting material being filtered. The filtrate was used in the following test:—

A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned in the mixer with the following agents separately introduced therein in the order in which they appear:—0.6 lb. of caustic soda, 2 lbs. of fuel oil, 100 cc. of the above filtrate, and 0.14 lb. of the kerosene-rosin frothing agent already indicated, all per ton of the dry feed. Subsequently treating the pulp in the flotation machine, a concentrate as a non-floated material was obtained assaying 51.13% tricalcium phosphate, the tricalcium phosphate recovery being 98%.

EXAMPLE 15.

Repeating the identical procedures of Example 14, but with the proportions of the fuel oil and filtrate increased to 4 lbs. per ton and 115 cc. per ton, respectively, the non-floated material assayed 57.63% tricalcium phosphate, the tricalcium phosphate recovery being 97.7%.

EXAMPLE 16.

Here crude quinoline derived from coal tar and obtained from the Eastman Kodak Company was used as a flotation collector for the silica, the test being carried out as follows:—

A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned in the mixer with the following agents separately introduced therein in the order in which they appear:—16 lbs. per ton of the above quinoline material, 3.68 lbs. per ton of concentrated sulphuric acid, 5.56 lbs. per ton of fuel oil, 1.84 lbs. per ton more of concentrated sulphuric acid, and 12 lbs. per ton more of the above quinoline material. The pulp thus conditioned was treated in the flotation machine, the non-floated material was removed, and the floated material was retreated without further addition of reagents, the non-floated material obtained by this cleaning operation being indicated as a middling in the following table:—

| Product | % Weight | % Assay | | % Recovery |
|---|---|---|---|---|
| | | Tricalcium Phosphate | Insolubles | Tricalcium Phosphate |
| Feed | 100 | 42.16 | | |
| Refloated | 9.0 | 2.02 | | 0.4 |
| Middling | 19.6 | 3.97 | | 1.8 |
| Non-floated | 71.4 | 57.71 | 28.66 | 97.8 |

EXAMPLE 17.

A much higher grade of concentrate was obtained with crude quinoline by the following procedures:—

To a pulp of the same feed as in Example 1 and of the same consistency as before were added, during agitation in the mixer, first 22 lbs. per ton of crude quinoline and then 3.68 lbs. per ton of concentrated sulphuric acid. The pulp thus conditioned was transferred to the flotation machine, where subsequent to dilution 7.2 lbs. per ton of kerosene were introduced through the air duct and a sand float removed in the usual manner by agitation. Thereafter, 7.2 lbs. per ton of kerosene were once more introduced through the air duct and a second sand float removed. The results of the test are indicated in the following table:—

| Product | % Weight | % Assay | | % Recovery |
|---|---|---|---|---|
| | | Tricalcium Phosphate | Insolubles | Tricalcium Phosphate |
| Feed | 100 | 41.01 | | |
| 1st floated | 40.0 | 4.41 | | 4.3 |
| 2nd floated | 4.5 | 15.91 | | 1.8 |
| Non-floated | 55.5 | 69.43 | 14.75 | 93.9 |

In each of the following ten examples acid other than sulphuric acid was used as an activating agent.

EXAMPLE 18.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 48 lbs. of crude Texas Chemical Company bone oil and then with 10 lbs. of glacial acetic acid, both per ton of dry feed. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate | Ratio of Concentration |
|---|---|---|---|---|---|
| Feed | 100 | 40.40 | 48.62 | | |
| Floated | 54.9 | 9.13 | 85.67 | 12.4 | |
| Non-floated | 45.1 | 78.47 | 3.52 | 87.6 | 2.22 |

EXAMPLE 19.

The procedures employed were the same as in the preceding example, except that the proportion of acetic acid was reduced to 6 lbs. per ton and the floated material retreated in the flotation machine, the non-floated material obtained by the latter operation being indicated as a middling in the following table:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate | Ratio of Concentration |
|---|---|---|---|---|---|
| Feed | 100 | 40.44 | 49.10 | | |
| Refloated | 52.4 | 7.32 | 88.64 | 9.5 | |
| Middling | 3.1 | 64.42 | 20.39 | 4.9 | |
| Non-floated | 44.5 | 77.76 | 4.55 | 85.6 | 2.24 |

EXAMPLE 20.

By further reducing the proportion of the acetic acid of Example 18 to 4 lbs. per ton, but otherwise following the identical procedures of that example, the following results were obtained:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate | Ratio of Concentration |
|---|---|---|---|---|---|
| Feed | 100 | 40.22 | 48.52 | | |
| Floated | 44.8 | 14.85 | 77.89 | 16.5 | |
| Non-floated | 55.2 | 60.82 | 24.69 | 83.5 | 1.81 |

EXAMPLE 21.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 10 lbs. of crude Eastman Kodak Company bone oil and then with 1.6 lbs. of hydrofluoric acid, both per ton of dry feed. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 48.98 | | |
| Floated | 52.3 | 6.72 | | 8.6 |
| Non-floated | 47.7 | 78.17 | 2.51 | 91.4 |

EXAMPLE 22.

Here the activating agent was hydrofluorsilicic acid, obtained from Eimer and Amend as a solution of 27% to 28% acid strength. To a pulp of the same feed as in Example 1 and of the same consistency as before were added, during agitation in the mixer, first 8 lbs. per ton of crude Eastman Kodak Company bone oil and then an amount of the above solution corresponding to 0.8 lb. per ton of the hydrofluorsilicic acid dissolved therein, subsequent treatment of the pulp in the flotation machine yielding the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 39.53 | 50.86 | |
| Floated | 51.6 | 4.81 | 93.64 | 6.3 |
| Non-floated | 48.4 | 76.55 | 5.24 | 93.7 |

EXAMPLE 23.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 8 lbs. of crude Eastman Kodak Company bone oil and then with 8 lbs. of chemically pure arsenic acid, both per ton of dry feed. Subsequent treatment of the pulp yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 37.10 | 52.87 | |
| Floated | 52.9 | 9.03 | 86.87 | 12.9 |
| Non-floated | 47.1 | 68.63 | 14.70 | 87.1 |

EXAMPLE 24.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 8 lbs. of crude Eastman Kodak Company bone oil and 5.6 lbs. of chemically pure selenic acid, both per ton of dry feed. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 40.10 | 50.42 | |
| Floated | 49.6 | 5.21 | 93.14 | 6.4 |
| Non-floated | 50.4 | 74.45 | 8.45 | 93.6 |

EXAMPLE 25.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 40 lbs. of crude Texas Chemical Company bone oil and then with 10 lbs. of lactic acid, both per ton of dry feed. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 39.88 | | |
| Floated | 48.7 | 2.72 | | 3.3 |
| Non-floated | 51.3 | 75.17 | 8.04 | 96.7 |

EXAMPLE 26.

With a pulp of the same feed as in Example 1 and of the same consistency as before were thoroughly admixed first 30.2 lbs. of crude Texas Chemical Company bone oil and then 26 lbs. of hydrochloric acid, both per ton of dry feed. The pulp was then transferred to the flotation machine, where it was treated in the usual manner. The tricalcium phosphate assay of the non-floated material was 78.48% and the tricalcium phosphate recovery therein 91.3%.

EXAMPLE 27.

The activating agent in this instance was sulphurous acid formed by bubbling sulphur dioxide gas through water. A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned first with 30.2 lbs. per ton of crude Texas Chemical Company bone oil and then with an undetermined amount of the above formed acid. Subsequent frothing of the pulp yielded a non-floated material assaying 73.35% tricalcium phosphate, the tricalcium phosphate recovered therein being 94.9%.

Inorganic salts were employed as activating agents in the following fifteen examples.

EXAMPLE 28.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 8 lbs. per ton of crude Eastman Kodak Company bone oil and then with 0.8 lb. per ton of sodium silicofluoride as a 2.5% solution in water. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 39.94 | 48.96 | |
| Floated | 51.9 | 3.68 | 91.68 | 4.8 |
| Non-floated | 48.1 | 79.07 | 2.86 | 95.2 |

EXAMPLE 29.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 10 lbs. per ton of crude Eastman Kodak Company bone oil and then with 1 lb. per ton of ammonium silicofluoride as a 2.5% solution in water. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 39.67 | 49.42 | |
| Floated | 52.1 | 3.48 | 92.01 | 4.6 |
| Non-floated | 47.9 | 79.04 | 3.10 | 95.4 |

EXAMPLE 30.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 20 lbs. per ton of crude Eastman Kodak Company bone oil and then with 4 lbs. per ton of stannic chloride as a 5% solution in water. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 38.87 | 51.15 | |
| Floated | 54.3 | 6.63 | 90.47 | 9.3 |
| Non-floated | 45.7 | 77.17 | 4.43 | 90.7 |

EXAMPLE 31.

A sample of the same feed as in Example 1 was subjected to froth flotation with 16 lbs. per ton of crude Eastman Kodak Company bone oil and 4 lbs. per ton of stannous chloride. While the non-floated material assayed 76.36% tricalcium phosphate, the tricalcium phosphate recovery therein was only 11.2%.

EXAMPLE 32.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 20 lbs. per ton of crude Eastman Kodak Company bone oil and 8 lbs. per ton of silicon tetrachloride. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 39.58 | 50.12 | |
| Floated | 53.5 | 6.42 | 89.61 | 8.7 |
| Non-floated | 46.5 | 77.74 | 4.69 | 91.3 |

EXAMPLE 33.

A sample of the same feed as in Example 1 was subjected to froth flotation with 54 lbs. per ton of crude Eastman Kodak Company bone oil and 20 lbs. per ton of nickel sulphate. The tricalcium phosphate assay of the non-floated material was 79.02%, but the tricalcium phosphate recovery was only 20%.

EXAMPLE 34.

A sample of the same feed as in Example 1 was subjected to froth flotation with 20 lbs. per ton of crude Texas Chemical Company bone oil and 4 lbs. per ton of zinc sulphate. The tricalcium phosphate assay of the non-floated material was 75.66%, but the tricalcium phosphate recovery was only 17.6%.

EXAMPLE 35.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 64.52 lbs. per ton of phosphorous trichloride and then with 30.2 lbs. per ton of crude Texas Chemical Company bone oil. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 39.55 | | |
| Floated | 50.0 | 6.84 | | 8.6 |
| Non-floated | 50.0 | 72.25 | 12.15 | 91.4 |

EXAMPLE 36.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 64 lbs. per ton of phosphorous pentachloride and then with 30.2 lbs. per ton of crude Texas Chemical Company bone oil. By subsequent treatment of the pulp in the flotation machine a non-floated material was obtained assaying 57.66% tricalcium phosphate, the tricalcium phosphate recovered therein being 89.4%.

EXAMPLE 37.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 20 lbs. per ton of cupric chloride and then with 30.2 lbs. per ton of crude Texas Chemical Company bone oil. By subsequent treatment of the pulp in the flotation machine a non-floated material was obtained assaying 53.56% tricalcium phosphate, the tricalcium phosphate recovered therein being 71.7%.

EXAMPLE 38.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 30.2 lbs. per ton of crude Texas Chemical bone oil and then with 3.36 lbs. per ton of thionyl chloride. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 41.45 | | |
| Floated | 50.5 | 6.93 | | 8.4 |
| Non-floated | 49.5 | 76.67 | 7.2 | 91.6 |

EXAMPLE 39.

A pulp of the same feed as in Example 1 and of the same consistency as before was agitated in the mixer first with 68 lbs. per ton of crude Texas Chemical Company bone oil and then with 40 lbs. per ton of potassium bisulphate. Subsequent treatment of the pulp in the flotation machine yielded the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 40.66 | | |
| Floated | 46.9 | 4.67 | | 5.4 |
| Non-floated | 53.1 | 72.45 | 10.71 | 94.6 |

EXAMPLE 40.

A sample of the same feed as in Example 1 was subjected to froth flotation with 68 lbs. per ton of crude Texas Chemical Company bone oil and 40 lbs. per ton of sodium dihydrogen phosphate. While the tricalcium phosphate assay of the non-floated material was only 50.34%, the tricalcium phosphate recovered therein was 95.1%.

EXAMPLE 41.

A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned with 44 lbs. per ton of crude quinoline, 6.48 lbs. per ton of sulphur monochloride, and 7.2 lbs. per ton of kerosene. Subsequent frothing of the pulp yielding the following results:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 41.10 | | |
| Floated | 46.9 | 7.07 | | 8.1 |
| Non-floated | 53.1 | 71.14 | 12.72 | 91.9 |

EXAMPLE 42.

A sample of the same feed as in Example 1 was subjected to froth flotation with 22 lbs. per ton of crude quinoline, 6.72 lbs. per ton of thionyl chloride, and 7.2 lbs. per ton of kerosene. The tricalcium phosphate assay of the non-floated material was 59.08% and the tricalcium phosphate recovery therein 92.8%.

In an endeavor to determine the effect of fuel oil on the process of the present invention the following tests were carried out:—

EXAMPLE 43.

A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned in the mixer with the following agents separately introduced therein in the order in which they appear:—3 pounds of fuel oil, 16 pounds of crude Eastman Kodak Company bone oil, and 1.84 pounds of concentrated sulphuric acid, all per ton of dry feed. Subsequent treatment of the pulp in the flotation machine yielded a concentrate as a non-floated material assaying 78.77% tricalcium phosphate, the tricalcium phosphate recovery being 77.3%.

EXAMPLE 44.

Repeating the procedures of Example 43, but with the proportion of fuel oil decreased to 2 pounds per ton, the tricalcium phosphate assay of the non-floated

material was 77.05% and the tricalcium phosphate recovery 86.0%.

EXAMPLE 45.

Here no fuel oil was employed, the procedures being otherwise the same as in Example 43, the bone oil being added before the acid. The non-floated material assayed 76.16% tricalcium phosphate, the tricalcium phosphate recovery being 90.4%.

The % assays and recoveries obtained in Examples 43, 44, and 45 are recorded in the following table, from which it is seen that the effect of fuel oil is to increase the grade of concentrate, but to lower the recovery:—

| | % Assay Tricalcium Phosphate | % Recovery Tricalcium Phosphate |
|---|---|---|
| Ex. 43 (3 lbs. of fuel oil) | 78.77 | 77.3 |
| Ex. 44 (2 lbs. of fuel oil) | 77.05 | 86.0 |
| Ex. 45 (no fuel oil) | 76.16 | 90.4 |

The effect produced by employing different amounts of bone oil was also investigated, the following test being carried out for comparison with Example 43.

EXAMPLE 46.

The conditions were the same as in Example 43, except that the proportion of bone oil was decreased to 10 pounds per ton. The non-floated material assayed 63.82% tricalcium phosphate, the tricalcium phosphate recovery being 79.8%.

The following table records the % assays and recoveries obtained in Examples 43 and 46, it being observed that the grade of concentrate increases and the recovery decreases, with increasing amount of bone oil:—

| | % Assay Tricalcium Phosphate | % Recovery Tricalcium Phosphate |
|---|---|---|
| Ex. 43 (16 lbs./ton of bone oil) | 78.77 | 77.3 |
| Ex. 46 (10 lbs./ton of bone oil) | 63.82 | 79.8 |

Experimental work was also carried out with fuel oil, bone oil, and acid to determine the effect of the order of addition of these agents, the following tests being carried out for comparison with Example 44:—

EXAMPLE 47.

The procedures were the same as in Example 44, but here the bone oil was introduced before the fuel oil, the acid being introduced last. The non-floated material assayed 77.85% tricalcium phosphate, the tricalcium phosphate recovery being 78.9%.

EXAMPLE 48.

Here the acid was introduced first, then the fuel oil, then the bone oil, the procedures being otherwise the same as in Example 44. The non-floated material assayed 51.47% tricalcium phosphate, the tricalcium phosphate recovery being 75.6%.

The % assays and recoveries obtained in Examples 44, 47, and 48 are recorded in the table below. From this table it is apparent that the bone oil should be added before the acid in order to obtain best results with regard to both grade of concentrate and recovery. As to the fuel oil, it should be added after the bone oil in order to obtain the highest grade of concentrate, and before the bone oil in order to obtain the highest recovery:—

| | 1st Agent | 2nd Agent | 3rd Agent | % Assay Tricalcium Phosphate | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|---|
| Ex. 44 | Fuel oil | Bone oil | Acid | 77.05 | 86.0 |
| Ex. 47 | Bone oil | Fuel oil | Acid | 77.85 | 78.9 |
| Ex. 48 | Acid | Fuel oil | Bone oil | 51.47 | 75.6 |

With the view to determine what the effect might be by diluting the acid prior to introduction into the mixer, the following test was carried out for comparison with Example 44:—

EXAMPLE 49.

The procedures were the same as in Example 44, but here the acid was introduced as a 5% solution. The non-floated material assayed 78.77% tricalcium phosphate, the tricalcium phosphate recovery being 79.8%.

The % assays and recoveries obtained in Examples 44 and 49 are recorded in the following table, it being apparent that the use of concentrated acid lowers the grade of concentrate and increases the recovery, and that the use of dilute acid increases the grade of concentrate and lowers the recovery.

| | % Assay Tricalcium Phosphate | % Recovery Tricalcium Phosphate |
|---|---|---|
| Ex. 44 (concentrated acid) | 77.05 | 86.0 |
| Ex. 49 (diluted acid) | 78.77 | 79.8 |

The following examples are intended to show the applicability of the process of the invention to tabling.

EXAMPLE 50.

A pulp of the same feed as in Example 1 and of the same consistency as before was conditioned in the mixer with the following agents separately introduced therein in the order in which they appear: 30 pounds per ton of crude Texas Chemical Company bone oil and 10 pounds per ton of acetic acid. These agents were added to the pulp during agitation, this addition requiring about one minute and agitation being thereafter continued for two minutes more. Subsequent to this conditioning, the pulp was fed to a laboratory-size Wilfley table with the results indicated in the following table, wherein the product termed "Tailing" refers to the material which came off the side of the table near the feed end, the product termed "Concentrate" refers to the material which in large part came off the discharge end, and the product termed "Middling" refers to the material which came off the side between the concentrate and tailing products.

| Product | % Weight | % Assay Tricalcium Phosphate | % Recovery Tricalcium Phosphate |
|---|---|---|---|
| Feed | 100 | 42.59 | |
| Tailing | 32.3 | 2.31 | 1.7 |
| Middling | 27.2 | 52.25 | 33.4 |
| Concentrate | 40.5 | 68.23 | 64.9 |

EXAMPLE 51.

The identical procedures of the preceding example were repeated, but with the amounts of the bone oil and acid increased to 35.75 pounds per ton and 12.21 pounds per ton, respectively. The results are given in the following table, wherein the product terms have the same significance as in the preceding example:—

| Product | % Weight | % Assay Tricalcium Phosphate | % Assay Insolubles | % Recovery Tricalcium Phosphate |
|---|---|---|---|---|
| Feed | 100 | 44.88 | | |
| Tailing | 16.5 | 2.33 | | 0.8 |
| Middling | 35.7 | 22.11 | | 17.6 |
| Concentrate | 47.8 | 76.59 | 7.32 | 81.6 |

EXAMPLE 52.

A sample of the same feed as in Example 1 was subjected to a tabling operation with 14.4 lbs. per ton of kerosene, 65.7 lbs. per ton of crude quinoline, and 24 lbs. per ton of acetic acid. The material which came off the discharge end of the table assayed 76.57% tricalcium phosphate.

It will be appreciated that other impurities may be present in the phosphate ores treated, the process according to the present invention being concerned only with the concentration of the phosphate mineral with respect to the silicon constituents.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A process of concentrating phosphate-bearing minerals utilizing the preferential adherence of a collecting agent to the silicious gangue, which comprises agitating a pulp of the ore containing the phosphate-bearing mineral in the presence of crude quinoline, or bone oil, and an acid capable of forming with water a distinctly acid solution readily titratable with an aqueous solution of a base, separating from the pulp a material relatively rich in silicious gangue and relatively poor in phosphate values, and collecting the remaining material as the concentrate.

2. A process of concentrating phosphate-bearing minerals utilizing the preferential adherence of a collecting agent to the silicious gangue, which comprises agitating a pulp of the ore containing the phosphate-bearing minerals in the presence of acid-treated

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bone oil, the oil-treating acid being capable of forming with water a distinctly acid solution readily titratable with an aqueous solution of a base, separating from the pulp a material relatively rich in silicious gangue and relatively poor in phosphate values, and collecting the remaining material as the concentrate.

3. A process as claimed in claim 1, in which the pulp is first agitated with the bone oil or crude quinoline and thereafter with the acid.

4. A process as claimed in claim 2, in which only water soluble constituents of the acid-treated bone oil are used.

5. A process as claimed in claims 1 to 4, in which the acid used is sulphuric acid.

6. A process as claimed in either of claims 1 and 3, in which in the place of the acid there is employed an inorganic salt capable of dissolving in water with an acid reaction and incapable of preventing the activating effect of the liberated acid, *i.e.* which is adapted to function as an activating agent to cause the crude quinoline or bone oil to have a preferential affinity for the silicious gangue.

7. A process as claimed in claim 6, in which the salt used is an inorganic halide.

8. A process as claimed in any one of the preceding claims, in which the pulp is agitated in the presence of a mineral oil.

9. A process as claimed in any one of the preceding claims, in which the pulp is treated to cause a froth relatively rich in silicious gangue and relatively poor in phosphate values, and the non-floated material is collected as the concentrate.

10. The improved process of concentrating phosphate-bearing materials, substantially as hereinbefore described.

Dated the 16th day of August, 1937.

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