

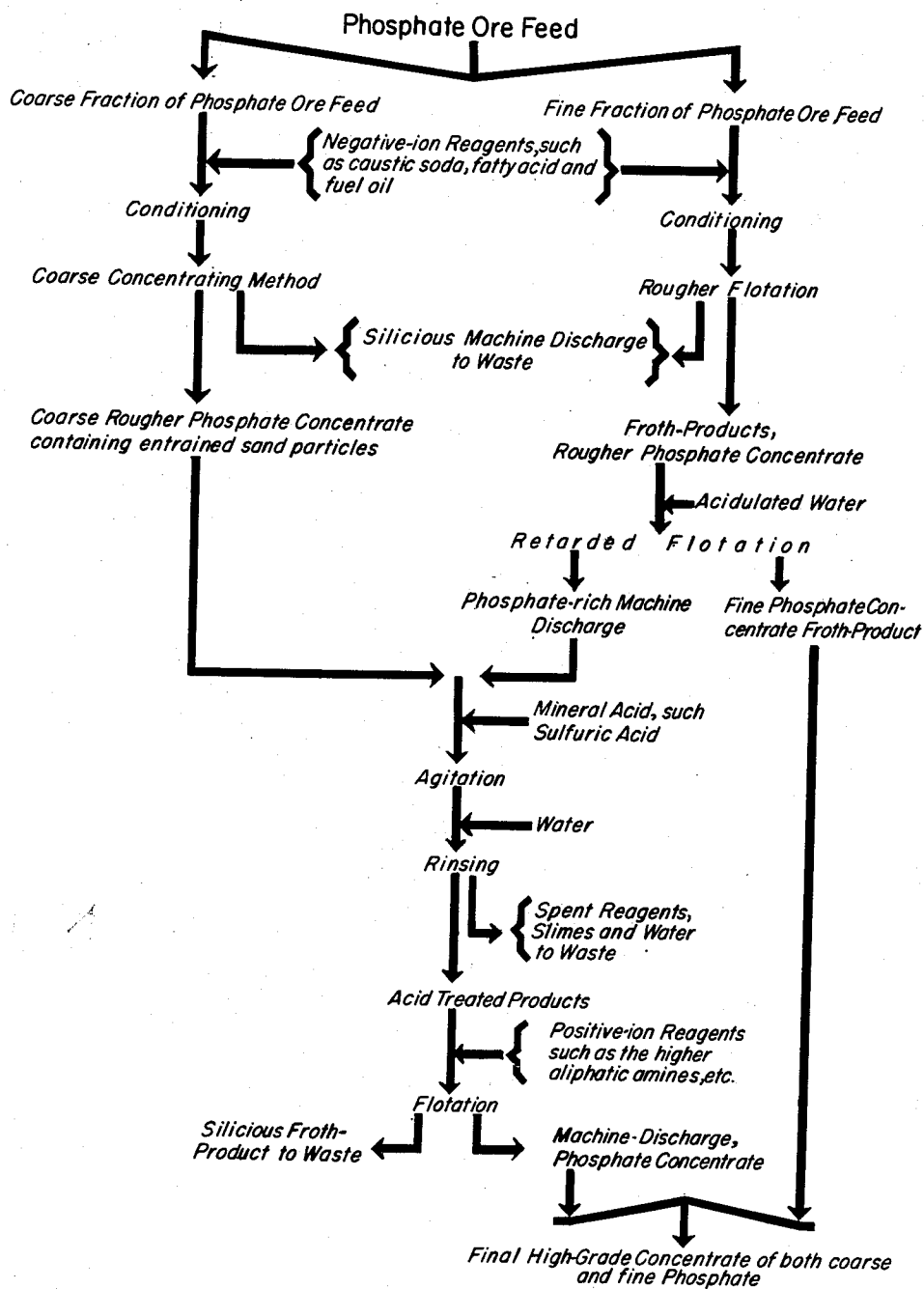
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CONCENTRATION OF PHOSPHATE ORES

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## CONCENTRATION OF PHOSPHATE ORES

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1 Claim. (Cl. 209—166)

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The present invention relates to the concentration of phosphate minerals from their ores, and may be regarded as an improvement upon the method described in our co-pending application, Serial No. 177,374, which is assigned to the assignee of the present application.

The general object of the present invention is to obtain from a phosphate ore, containing ore particles which are too coarse for froth-flotation treatment as well as particles which are fine enough for froth-flotation treatment, a final high-grade concentrate containing a high percentage of both the coarse and fine phosphate particles; and to achieve this result with economy in the reagents employed, particularly the positive-ion reagents which are expensive. To this end, the invention involves separate appropriate treatments with the use of negative-ion reagents of the coarse and fine fractions of the phosphate ore, followed by de-oiling and then by froth-flotation treatment with the use of positive-ion reagents of a mixture of the products resulting from said initial treatments. Some of the advantages of the invention are economy in the positive-ion reagents employed, and the production of a final high grade phosphate concentrate containing both coarse and fine particles from the whole of the phosphate ore, and a considerable increase in the usual recovery of the phosphate particularly in the coarse fraction of the ore. The manner in which these advantages are achieved will be understood from the following description of methods embodying the invention.

The invention will be understood from the following description, taken in connection with the accompanying drawing which is a simplified general flow-sheet of a typical plant practicing the invention. It will be understood that this flow-sheet merely contributes to an understanding of the invention, and that various modifications in the methods used and the apparatus employed may be resorted to without departing from the spirit of the invention as defined in the claims hereto appended.

The operations represented in the flow-sheet will now be described. The phosphate ore feed is divided into coarse and fine fractions.

As indicated at the upper left part of the flow-sheet, the coarse fraction of the phosphate ore feed is treated with negative-ion reagents such as caustic soda, fatty acid and fuel oil, and is then subjected to a separating treatment, (including, if advantageous, a cleaning retreatment of the concentrate) resulting in a siliceous machine-discharge (which is sent to waste) and a coarse rougher phosphate concentrate containing entrained sand particles. This separating treatment may be carried out in any suitable

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apparatus, such as belt separators such as are described in U. S. patents to Greene and Wilbur Nos. 2,047,773 and 2,231,066; or helical separators such as are described in U. S. patents to Humphreys Nos. 2,431,559 and 2,431,560; or shaking tables which are customarily used for the concentrating treatment of a phosphate ore having particles too large to permit the ore to be advantageously treated in froth-flotation cells. This operation produces from the coarse fraction of the feed a coarse rougher phosphate concentrate containing the finer entrained sand particles; and a siliceous machine discharge, containing most of the coarser siliceous particles, which is sent to waste. It will be understood that this coarse phosphate rougher concentrate may be submitted to a cleaning operation if desirable.

As shown at the upper right-hand portion of the flow-sheet, the fine fraction of the phosphate ore feed is also conditioned with negative-ion reagents, such as those which have been mentioned; and is then subjected to flotation treatment in flotation cells of any well known kind. This flotation treatment results in a froth-product which is a rougher phosphate concentrate, and a siliceous machine discharge which is sent to waste. This rougher phosphate concentrate is then subjected to retarded-flotation treatment, by which is meant a treatment which restrains the normal floatability of the phosphate and produces a fine phosphate concentrate froth-product of such high grade that it is treated as a part of the final phosphate concentrate; the machine discharge from the retarded flotation treatment being a phosphate-rich product. This retarded-flotation treatment may be carried out in several ways, as explained in our prior co-pending application above mentioned. As represented in the flow-sheet, the retarded-flotation treatment is made possible by the fact that to the rougher phosphate concentrate which is the feed to that treatment is added acidulated water having a low pH, say about 3. However, as pointed out in our prior application, instead of using acidulated flotation water having a low pH, it is possible to obtain retarded-flotation by subjecting the feed to that operation to agitation and scrubbing with ordinary (neutral) flotation water; or retarded-flotation may be accomplished merely by maintaining the level of the pulp in the flotation cells so low that only the top portion of the froth-product is removed.

As illustrated in the lower half of the flow-sheet, the coarse rougher phosphate concentrate containing entrained sand particles, obtained from the coarse fraction of the feed, is combined with the phosphate-rich residue obtained from the retarded-flotation treatment of the rougher

phosphate concentrate from the fine fraction of the feed. This mixture is the feed to the operations which will now be described. In order to remove the effect of the negative-ion agents, this feed is treated with a mineral acid and rinsed. (As in the method of the patent to Arthur Crago 2,293,640 issued August 18, 1942, now owned by the assignee of the present application.) As shown in the flow-sheet this acid-treated material is conditioned with positive-ion reagents, such as the higher aliphatic amines, etc. and is then subjected to froth-flotation treatment in flotation cells which results in a siliceous froth-product which is removed and sent to waste, and a machine discharge which is a high-grade phosphate concentrate, which is combined with the high-grade phosphate concentrate which was the froth-product from the retarded-flotation treatment. Thus, from the original phosphate ore, is produced a final high-grade phosphate concentrate containing a high proportion of both the coarse and the fine phosphate particles in the original ore.

The method which is the present invention will be understood from the foregoing description, but an example of the practicing of the invention will now be described in order to show the advantages thereof.

#### Example

A deslimed phosphate ore feed was classified into two size fractions: a coarse fraction which was substantially -14+65 mesh and represented 25% by weight of the original feed; and a fine fraction which was substantially -35 mesh and represented 75% by weight of the original feed.

The coarse fraction of the deslimed phosphate ore feed was conditioned in an aqueous pulp for 2 minutes at 70% solids with negative-ion reagents consisting of 0.4 pound of caustic soda, 4.5 pounds of fuel oil, and 0.7 pound of tall oil, all in pounds per ton of the dry coarse fraction of the feed. This conditioned feed was then treated in a minerals separation laboratory belt separator apparatus in the usual way, thereby producing a coarse rougher phosphate concentrate, and a sand tailing which was discarded. This rougher concentrate was returned to the belt separator for re-treatment, without the addition of reagents, and was subjected to a cleaning separation, thereby producing a phosphate-sand middling product which was sent to waste but might have been recirculated to the feed; and a coarse rougher phosphate concentrate containing entrained sand particles which was retained for the further treatment hereafter described.

The finer fraction of the deslimed phosphate ore feed was conditioned in an aqueous pulp for 2 minutes at 70% solids with negative-ion reagents consisting of 0.4 pound of caustic soda, 3 pounds of fuel oil, and 0.25 pound of tall oil, all in pounds per ton of the dry fine fraction of the feed. This conditioned feed was diluted with tap water to about 20% solids in a minerals separation laboratory airflow flotation machine, agitated and aerated to produce a sand tailing in the machine-discharge which was discarded; and a froth-product which was a rougher phosphate concentrate.

This rougher phosphate concentrate was de-watered and repulped in the flotation machine at about 10% solids with water to which sufficient sulfuric acid had been added to produce a pH of 3, employing for that purpose approximately 1.8 pounds of  $H_2SO_4$  per ton of the fine fraction of the feed. The rougher concentrate was agitated

briefly and then aerated and refloated in this acid pulp, thereby producing a retarded-flotation of a high-grade final phosphate concentrate containing a minimum sand content; and a phosphate-rich machine-discharge consisting of both phosphate and sand particles.

The coarse rougher phosphate concentrate containing entrained sand particles, obtained from the belt separator, was then combined with the phosphate-rich residue obtained from the retarded-flotation step. This mixture was agitated for 3 minutes at approximately 50% solids with 4.0 pounds of sulfuric acid per dry ton of said mixture, and was then washed and rinsed substantially free of acid and spent negative-ion reagents. This acid-treated and rinsed mixture was repulped in a flotation cell, conditioned for about 15 seconds with positive-ion reagents consisting of 0.36 pound of "Armec T" (a tallow amine acetate made by Armour & Company), 0.4 pound of kerosene and 0.23 pound of pine oil frother, all in pounds per ton of the mixture which was the feed to this operation, and then was aerated and a low-grade siliceous froth-product was removed and sent to waste, leaving a high-grade final phosphate concentrate in the machine discharge, which was combined with the finer high-grade final phosphate concentrate obtained from the retarded-flotation step; thereby producing from the original ore a final high-grade phosphate concentrate containing a high proportion of both the coarse and fine particles in the original ore.

The metallurgical results of the above described operations, and the quantities of reagents employed, are recorded in the following tables:

| Products                                                                        | Percent Wt. | Percent BPL | Percent Insol | Percent BPL Distribution |
|---------------------------------------------------------------------------------|-------------|-------------|---------------|--------------------------|
| Total Feed.....                                                                 | 100.0       | 40.5        | -----         | 100.0                    |
| Belt Separation (Coarse Fraction of Ore):                                       |             |             |               |                          |
| 1. Feed.....                                                                    | 25.0        | 47.1        | -----         | 29.1                     |
| 2. Belt Concen.....                                                             | 15.0        | 76.9        | 5.6           | 28.5                     |
| 3. Siliceous Tailing to Waste.....                                              | 10.0        | 2.6         | -----         | 0.6                      |
| Rougher Phosphate Flotation, (Fine fraction of Ore):                            |             |             |               |                          |
| 4. Feed.....                                                                    | 75.0        | 38.2        | -----         | 70.9                     |
| 5. Rougher Conc. Froth-Product.....                                             | 37.0        | 71.5        | -----         | 67.3                     |
| 6. Siliceous Machine Disch. to Waste.....                                       | 38.0        | 3.8         | -----         | 3.6                      |
| Retarded Phosphate Flotation:                                                   |             |             |               |                          |
| 7. Phosphate Conc. Froth-Product.....                                           | 25.4        | 79.7        | 2.7           | 50.0                     |
| 8. Phosphate-rich Machine Disch.....                                            | 11.6        | 60.2        | -----         | 17.3                     |
| Sand Flotation from Belt Cleaner Concentrate and Cell Middling (items 2 and 8): |             |             |               |                          |
| 9. Siliceous Froth-product to Waste.....                                        | 4.0         | 13.7        | -----         | 1.4                      |
| 10. Machine Discharge, Phosphate Conc.....                                      | 22.6        | 79.3        | 2.6           | 44.4                     |
| Overall Results:                                                                |             |             |               |                          |
| Total Phosphate Conc. (items 7 and 10).....                                     | 48.0        | 79.5        | 2.7           | 94.4                     |
| Total Tailing (items 3, 6 and 9).....                                           | 52.0        | 4.3         | -----         | 5.6                      |

Includes circulating middling 5.3% by weight and 35.4% BPL.

#### Total reagents employed

| Reagents           | Lbs./Ton of Total Feed |
|--------------------|------------------------|
| Caustic Soda.....  | 0.40                   |
| Fuel Oil.....      | 3.37                   |
| Tall Oil.....      | 0.37                   |
| Sulfuric Acid..... | 2.36                   |
| Armec T.....       | 0.10                   |
| Kerosene.....      | 0.11                   |
| Pine Oil.....      | 0.09                   |

The excellent results and the economy in reagents employed in the example are obvious from the above tables. The overall recovery of the phosphate values from this feed was excellent, being 94.4% of the total fine and coarse phosphate in the feed. Particularly noteworthy was the recovery of BPL values from the coarse fraction of the ore, represented in the belt concentrate, item No. 2 in the table. This high recovery amounted to  $(28.5 \times 100) / 29.1$  or 97.9% and is largely attributed to the fact that a maximum grade belt concentrate is not required in this process. Along with these excellent recoveries, a maximum grade of 79.5% BPL was obtained in the final combined concentrate which contained only 2.7% insoluble.

There are several reasons why the method, as described and illustrated in the example results in a very high recovery of a high-grade phosphate concentrate above mentioned. One reason is that the phosphate particles in the rougher phosphate concentrate (resulting from the initial treatment of the coarse fraction of the ore feed) are so coarse that they have little tendency to float with the silica in the final froth-flotation treatment with positive-ion reagents. Another reason is that the phosphate-rich machine discharge (resulting from the initial treatment of the fine fraction of the ore feed) has been very largely freed of very fine phosphate particles which if present might float with the silica in the final froth-flotation treatment with positive-ion reagents. Therefore, the mixture which is subjected to de-oiling and then to froth-flotation treatment with positive-ion reagents is particularly well suited to that treatment.

The economy achieved in the quantity of expensive positive-ion reagents employed is largely due to the reduction of the weight of the material which is subjected to froth-flotation treatment with those reagents. It will be noted from the example that the weight of the material mixture subjected to de-oiling and then to froth-flotation treatment with positive-ion reagents was only 26.6% of the weight of the original phosphate feed. In the tabulation, see percent weight in items 3 and 8.

What is claimed is:

The method of jointly concentrating both

coarse and fine particles from a phosphate ore feed, containing both coarse and fine particles, which comprises dividing said ore feed into finer and coarser fractions; subjecting said finer and coarser fractions separately in aqueous pulps to concentrating operations with negative-ion reagents, thereby removing from each fraction of the ore a siliceous machine discharge which is sent to waste, and separate coarse and fine rougher phosphate concentrates; subjecting said fine rougher concentrate in an aqueous pulp to agitation and froth-flotation treatment, thereby producing a fine phosphate froth-product of high-grade which is a part of the final concentrate and a fine phosphate-rich machine-discharge; mixing said fine phosphate-rich machine-discharge and said coarse rougher phosphate concentrate and subjecting that mixture to treatment with a mineral acid, followed by rinsing with water, thereby removing from said mixture substantially all of said negative-ion reagents; and subjecting said acid-treated mixture to a concentrating operation in an aqueous pulp with positive-ion reagents, thereby producing a siliceous froth-product which is sent to waste, and a residue which is a high-grade phosphate concentrate which is the other part of the final concentrate; thereby producing a final high-grade concentrate containing a high proportion of both the coarse and fine phosphate particles in the original ore feed.

#### References Cited in the file of this patent

#### UNITED STATES PATENTS

| Number    | Name     | Date          |
|-----------|----------|---------------|
| 1,480,884 | Dolbear  | Jan. 15, 1924 |
| 2,293,640 | Crango   | Aug. 18, 1942 |
| 2,350,943 | Thompson | June 6, 1944  |
| 2,461,813 | Duke     | Feb. 15, 1949 |

#### OTHER REFERENCES

Milling Methods for 1934, published by the A. I. M. M. E., New York, N. Y., 1935, pages 452 and 460.

Taggart, Handbook of Mineral Dressing © 1945, section 12, pages 75 and 100.