Patented Feb. 15, 1949 2,461,817

# UNITED STATES PATENT OFFICE

2,461,817

## CONCENTRATION OF PHOSPHATE MINERALS FROM THEIR ORES

Ernest W. Greene and James B. Duke, Lakeland, Fla., assignors to Minerals Separation North American Corporation, New York, N. Y., a corporation of Maryland

No Drawing. Application December 8, 1945, Serial No. 633,862

2 Claims. (Cl. 209—166)

1

The present invention relates to concentration of phosphate minerals from their ores in which the phosphate is mixed with siliceous gangue and may be regarded as an improvement in a step of the method covered by the patent to Arthur Crago No. 2,293,640, issued August 18, 1942, now owned by the assignee of the present application.

That Crago patent describes and claims a method of concentrating phosphate minerals from their ores, which comprises subjecting the ore in an aqueous pulp to a concentrating operation with reagents to separate a rougher concentrate of the phosphate values admixed with entrained silicious gangue, treating the rougher concentrate with a mineral acid to remove the effect of the reagents used in its production, and thereafter subjecting the rougher concentrate in an aqueous pulp to a concentrating operation to separate a collected material largely composed of the entrained silicious gangue, thereby producing a final phosphate concentrate.

The reagents, described in the Crago patent as useful in the first step of that method, are such negative-ion agents as the higher fatty acids, such as fish-oil fatty acid and oleic acid and their soaps, the resin acids and their soaps, wood by-product fatty acids, naphthenic acids and their salts, the higher sulpho-fatty acids and their salts with the proper bases, the acid esters of high-molecular-weight aliphatic alcohols with inorganic acids and their alkali-metal and alkaline-earth-metal salts, the higher xanthates, etc. The reagents described as useful in the last step of that method are of the positive-ion type such as the higher aliphatic amines and their salts with water-soluble acids, the esters of amino-alcohols with high-molecular-weight fatty acids and their salts with water-soluble acids, the higher alkyl-O-substituted isoureas and their salts with water-soluble acids, the resin amines and their salts with water-soluble acids, the higher aliphatic quaternary ammonium bases and their salts with water-soluble acids, the higher alkyl pyridinium salts of water-soluble acids, the higher alkyl quinolinium salts of water-soluble acids, etc. It is also stated in that patent that the use of an anionic active fatty acid compound is preferred in the carrying out of the first concentrating operation, while the use of a cationic-active amine compound is preferred in the carrying out of the second concentrating operation. In performing the intermediate step between the two concentrating operations, the mineral acid employed is described in that patent as preferably sulfuric acid because of its low cost. These various reagents are useful in the improved method of the present invention.

2

The Crago patent also states that in the carrying out of the concentrating operations used in practicing the method of that patent, any concentrating device may be used which is capable of discharging the collected material in such forms as floating froth, skin or surface float, individual agglomerates, etc.; and that such devices include flotation machines and gravity-concentrating tables, the collected material being discharged in the case of the former in the form of a floating froth over the lip of the machine, and in the case of the latter in the form of skin float and suspended agglomerates at the table side. Such devices may be used in practicing the improved method of the present invention.

In the commercial practice of the process of the Crago patent it sometimes occurs that, while the final phosphate concentrate produced is of high grade, the percentage of the available phosphate in the feed which appears in the final phosphate concentrate is not as high as desired. That is, although a phosphate concentrate of high grade is obtained, a considerable percentage of the phosphate in the feed has been collected with the silicious gangue and sent to waste in the last step of the process.

Difficulty in obtaining recovery in the final phosphate concentrate of a satisfactory percentage of the phosphate in the feed. as above mentioned, seems to be due to a number of causes which are more likely to occur in plant operation than in laboratory practicing of the method of said Crago patent. Our belief is that when the unsatisfactory percentage of recovery just mentioned is encountered it is due to failure adequately to treat the rougher concentrate with a mineral acid to remove the effect of the reagents used in its production. In a plant operation, that failure may be due to the use of insufficient mineral acid or to lack of adequate mixing of the acid with the rougher concentrate or to both, or to other reasons. Various attempts have been made to insure a high percentage of phosphate recovery in practicing the method of the Crago patent, but these attempts have either been more or less unsuccessful or have required the use of additional reagents or apparatus or both, which has increased the cost and complexity of the plant and its operation.

The general object of the present invention is to make more certain the obtaining of a high grade and a high percentage recovery of phos-

phate in the final phosphate concentrate produced by the method of said Crago patent.

According to the present invention, the desired end is achieved, with economy in use of reagents and without a substantial increase in the apparatus employed in the plant, by the use of new and improved methods of acid-treating the rougher phosphate concentrate to remove the effect of the reagents used in the production of that rougher phosphate concentrate. These new and improved methods consist not only in agitating but also in aerating the rougher concentrate in an aqueous pulp with a mineral acid without removing the froth thereby formed and until said pulp is substantially free of froth, and in subjecting the thus acid-treated rougher concentrate to a dewatering operation and preferably to a rinsing operation, after which the acid treated rougher concentrate is subjected to a concentrating operation to separate a collected material largely composed of entrained silicious gangue, according to the last step of the method of the Crago patent; thereby in the residue of that operation producing a final phosphate concentrate. According to our understanding of the phenomena involved, this acid-treatment of the rougher phosphate concentrate, under conditions providing for aeration as well as agitation, causes quick removal from some of the phosphate particles of the reagents used in the production of the rougher concentrate and sinking of those particles while other phosphate particles, owing to the reagents still carried by them, rise into the froth where they remain temporarily until the acid-treatment of them is complete, whereupon these phosphate particles sink into the pulp below the froth and are discharged along with the first-mentioned phosphate particles.

The agitation and aeration of the acid-treated rougher concentrate, in the manner just described, may advantageously be carried out in a sub-aeration froth-flotation cell, the feed to which and the discharge therefrom are so regulated that the froth produced does not rise high enough to overflow the lip of the cell. In practice, it has been found that by operating such a cell with its tank from one-third to one-half full of pulp so that the froth is retained, desirable results are obtained. It has also been found that the agitation and aeration of the acid-treated rougher phosphate concentrate may advantageously be carried on in two sub-aeration froth-flotation cells arranged so that the discharge from the bottom of the first cell goes to the second cell from the bottom of which the completely acid-treated pulp is discharged. The supply of pulp to both cells is so regulated that nothing overflows the lips of the cells; and when two cells are used in this way, the surface of the pulp in the first cell is covered by a froth containing a considerable amount of phosphate, and the pulp in the second cell is covered by what may more properly be described as a foam (rather than as a froth) which does not carry nearly the amount of phosphate that is carried by the froth in the first cell. After acid-treatment of the rougher phosphate concentrate in the manner just described, the reagents and acid are substantially removed from it by dewatering and



preferably rinsing in a rake classifier or in any other suitable apparatus. As substantially no phosphate particles float on the surface of the pulp during the rinsing operation in the rake classifier, the assumption seems justified that the acid-treatment of the rougher concentrate, under conditions of aeration as well as agitation and without removing the froth or foam, is particularly effective for removing the reagents which were used in the production of the rougher phosphate concentrate. This assumption is confirmed by the fact that when such an acid-treated rougher phosphate concentrate is subjected in an aqueous pulp to a concentrating operation according to the last step of the method of the Crago patent, the collected material there removed and sent to waste is very largely composed of silicious gangue containing only a very small amount of phosphate. Thus the described improvement in the method of the Crago patent results in the production of a concentrate of high grade with a recovery of a high percentage of the phosphate in the original ore.

In practicing the method of the Crago patent, it is customary in some cases to subject the rougher phosphate concentrate produced by the first step to a cleaning operation before subjecting it to the acid treatment. It is to be understood that such a cleaning operation may be used in the present method without departing from the spirit of the invention, and that in the following claims the expression "rougher concentrate of the mineral values admixed with entrained silicious gangue" is intended to refer to the product resulting from the first step of the method, whether or not that product is subjected to a cleaning operation prior to the acid treatment of it.

What is claimed is:

1. The method of substantially eliminating from a rougher concentrate of a phosphate ore the effect of the negative-ion agents used in the production of said concentrate, which comprises passing said rougher concentrate in an aqueous pulp containing a mineral acid through a tank in which said pulp is agitated and aerated and from which said pulp is removed without removing any froth which forms on the surface of the pulp thereby permitting said froth to remain there until the effect of the negative-ion agents is eliminated from the phosphate particles in said froth and they sink into the body of said pulp.

2. The method of claim 1 followed by rinsing said acid-treated rougher concentrate with water.

ERNEST W. GREENE.
JAMES B. DUKE.

## REFERENCES CITED

The following references are of record in the file of this patent:


UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 2,195,724 | Gaudin | Apr. 2, 1940 |
| 2,231,265 | Gaudin | Feb. 11, 1941 |
| 2,293,640 | Crago | Aug. 18, 1942 |

OTHER REFERENCES

Denver Equipment Index 1936, pages 17, 18, 114, 115.