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CONCENTRATION OF PHOSPHATE ORES

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The present invention relates to a novel process of concentrating phosphate ores.

In accordance with the invention, such ores are concentrated by procedures involving their admixture with a non-frothing organic liquid immiscible with water, such as fuel oil, and a compound included in the class consisting of acids derived from phosphoric acid by replacement of hydrogen with aliphatic hydrocarbon groups containing at least twelve carbon atoms and the salts of said organic-phospho acids with salt-forming bases. Such compounds are simply the acid esters formed by reaction of phosphoric acid with aliphatic alcohols of the carbon content stated and the reaction products of said acid esters with suitable bases. The aliphatic alcohols capable of use in producing these compounds may be normal primary alcohols, but other types of alcohols may also be used. The aliphatic alcohol residues or hydrogen-replacing groups in the compounds thus not only comprise simple alkyl radicals, but may also consist of the residues of unsaturated olefinic alcohols. Examples of organic-substituted compounds of phosphoric acid which may be used in the process of the present invention are the acid esters of that acid with such alcohols as lauryl, cetyl, myristyl, and oleyl alcohols, as well as the alkali-metal and alkaline-earth-metal salts of such acid esters.

Instead of the aforementioned phosphoric acid derivatives, it has also been found possible to employ, with non-frothing water-immiscible organic liquids, derivatives of thiocarbonic acid similarly containing aliphatic alcohol residues of at least twelve carbon atoms, such as the alkali-metal and alkaline-earth-metal salts of xanthic acids containing the alcohol radicals lauryl, cetyl, myristyl, oleyl, etc. However, the claims of this application do not cover the use with non-frothing water-immiscible organic liquids of these thiocarbonic acid derivatives, which subject-matter is separately claimed in our application Serial No. 186,586, filed January 24, 1938, which is a division of the present application.

Many non-frothing organic liquids, substantially insoluble in or immiscible with water in the proportions used, may be employed to carry out the process of the present invention by cooperating with the organic-substituted compounds herein described. Such liquids contain no substantial amounts of free fatty acids. Such widely varying types of non-frothing substantially water-immiscible organic liquids as fuel oil, kerosene, dipentene (a terpene hydrocarbon), crude solvent naphtha (from coal tar, water gas tar, and carbon tetrachloride have proved useful in carrying out the process of the present invention. Fuel oil, however, on account of its low cost, is generally preferred.

The organic-substituted compounds used in the process of the present invention have certain characteristics of soap and are in general capable of operating as frothing agents. However, the principal function of the organic-substituted compounds used in the process of the present invention is to make the non-frothing water-immiscible organic liquids also used effective by causing those liquids to adhere selectively to the phosphate values in the ore.

The organic-substituted compounds used in the process of the present invention need not be pure compounds. For instance, the alcohols employed in making them may be of commercial grades containing substantial amounts of other alcohols of not widely differing molecular weight, which results in the production of mixtures of organic-substituted compounds of varying carbon content in the substituted radical. The process of the present invention may obviously be carried out with such mixtures, provided the organic-substituted compounds having radicals of at least twelve carbon atoms largely predominate.

It is also to be understood that the process of the present invention is not limited to the exclusive use of the organic-substituted compounds herein described with their cooperating non-frothing water-immiscible organic liquids. Other agents known to those skilled in the art may be employed to contribute their own peculiar properties, such as frothing ability, pH control, etc., whereby the best conditions for the exercise of the intended functions of the organic-substituted compounds herein described and their cooperating non-frothing water-immiscible organic liquids may be obtained.

In carrying out the process of the present invention, addition to the ore of the various reagents used may be made with the ore either in a state of dryness or in the form of an aqueous pulp. In either case, of course, the subsequent step of separating the phosphate values is carried out in an aqueous pulp of the ore. For this separation, various physical forms of concentration have been found useful, which include froth flotation, tabling, and hydraulic classification.

In preparing the ore for treatment by the process of the present invention, it is in general desirable that it be largely deslimed, its desliming

greatly minimizing the consumption of the agents used, improving the results obtained, and rendering the process commercially practicable. In most cases, the crude ore is first subjected to a preliminary grinding operation, after which slimes are removed.

Examples will now be given describing tests which have been made in carrying the invention into effect, it being understood that the reagent proportions indicated in each example are expressed in the usual manner as pounds per ton (2000 lbs.) of dry material treated.

Example 1.—A lot of 20-mesh deslimed Florida phosphate ore, consisting mainly of tricalcium phosphate and silica, was mixed dry with 0.5 lb. of potassium cetyl phosphate and 9.5 lbs. of fuel oil, both per ton of ore. Subsequent to this mixing, the material was transferred to a (laboratory-size) subaeration flotation machine, where it was diluted and concentrates collected in the usual manner. After removal of the tailings, these concentrates were retreated in the same machine without further addition of reagents to yield final concentrates, a small middlings product being obtained. The final concentrates assayed 60.2% tricalcium phosphate and the tailings 9.6%. The heads contained 25.3% tricalcium phosphate, the recovery in the final concentrates being 70.9%.

Example 2.—Another lot of the same deslimed phosphate ore was formed into a thick pulp with 1 lb. per ton of crude potassium myristyl phosphate, in the form of a 0.4% aqueous solution, and with 11.5 lbs. per ton of fuel oil. This mixture was then treated in a flotation machine in the same manner as in Example 1, the results in this instance being as follows:

	Percent weight	Percent assay $Ca_3P_2O_8$	Percent recovery $Ca_3P_2O_8$
Heads	100.0	24.9	100.0
Concs	30.8	68.4	84.6
Midds	19.2	9.6	7.4
Tails	50.0	4.0	8.0

Example 3.—With a further lot of the same deslimed phosphate ore, were admixed 0.5 lb. per ton of potassium cetyl phosphate, in the form of an aqueous solution, and 16.8 lbs. per ton of dipentene. Frothing of the material was then carried out in a flotation machine in the usual manner. From heads containing 26.7% tricalcium phosphate, concentrates assaying 74.2% and tailings 14.6% tricalcium phosphate were obtained, the tricalcium phosphate recovery being 56.4%.

Example 4.—Still another lot of the same deslimed phosphate ore was mixed with 1 lb. per ton of potassium cetyl phosphate, in the form of a 0.33% aqueous solution, and with 18 lbs. per ton of kerosene. Subsequent treatment of the material in a flotation machine yielded, from heads containing 28.42% tricalcium phosphate, concentrates assaying 73.0% and tailings 15.8% tricalcium phosphate. The tricalcium phosphate recovery was 56.7%.

While the foregoing examples describe tests carried out with compounds of potassium, the sodium compounds are equally as effective in the process of the present invention. The barium and ammonium compounds are also useful in the process of the present invention, although the sodium and potassium compounds are preferred.

What is claimed is:

1. A process of concentration comprising admixing with a phosphate-bearing ore, in a suitably divided state and relatively free from slimes, a non-frothing organic liquid immiscible with water and a compound included in the class consisting of acids derived from phosphoric acid by replacement of hydrogen with aliphatic hydrocarbon groups of at least twelve carbon atoms and the salts of said organic-phospho acids with salt-forming bases; and separating in an aqueous pulp the phosphate values from the ore.

2. A process of concentration comprising admixing with a phosphate-bearing ore, in a suitably divided state and relatively free from slimes, a non-frothing organic liquid immiscible with water and an alkali-metal salt of an acid ester of phosphoric acid with an aliphatic alcohol of at least twelve carbon atoms; and separating in an aqueous pulp the phosphate values from the ore.

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