

## UNITED STATES PATENT OFFICE

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## FROTH FLOTATION OF ACIDIC MINERALS

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The present invention relates to mineral concentration. More particularly it relates to a new class of reagents for selectively separating acidic minerals from ore materials.

This application is in part a continuation of our application Serial No. 326,952, filed March 30, 1940.

In accordance with this invention natural ores or artificial materials comprising mixtures of acidic minerals with other mineral constituents are subjected to a separation or concentration process in the presence of a promoter of the class comprising the condensation products obtained by reacting one molecular equivalent of a polyalkylene polyamine with two molecular equivalents of a fatty acid, or the salts of such products, to effect a separation of the acidic minerals from the other ore constituents. Particularly this invention relates to the use of the diacyl reaction products of polyalkylene polyamines with fatty acids, fatty acid glycerides or other esters, either as the free base or as the substantially water-soluble salts of such products, as promoters or collectors for acidic minerals in froth flotation, film flotation, stratification, agglomeration, tabling, and related mineral separation processes. While the invention is not limited to any particular ore concentrating process or to any particular ore, its most important field of usefulness is in connection with the froth flotation processes of separating silica or silicate minerals, such as mica, from non-metallic ores, such as limestone, bauxite, barytes, ilmenite, calcite and the like, and especially phosphate minerals.

The compounds that have been found to have a selective filming attraction for acidic minerals and useful for carrying out the present invention include broadly the diacyl reaction products of polyalkylene polyamines with fatty acids, fatty acid glycerides or other esters, and salts of these reaction products. These compounds are, in general, surface active and are basic in character. A general method of preparing the above reagents comprises heating two molecular equivalents of a fatty acid, or an amount of fatty acid glyceride sufficient to yield the equivalent of 2 mols. of the fatty acid, with one molecular equivalent of a polyalkylene polyamine at a temperature of about 230–240° C. until the reaction is complete. The compounds produced by the above reaction are the type represented by the general formula when Y and Y' are both long chain hydrocarbon radicals. To produce compounds of the type in which Y is a long chain hydrocar-

bon radical and Y' is a short chain hydrocarbon radical 1 mol. of a polyalkylene is reacted with a mixture comprising 1 mol. of a long chain fatty acid and 1 mol. of a short chain fatty acid. The products are usually homogeneous viscous pastes which are soluble in aliphatic alcohols or other organic solvents. They combine with acids such as formic, acetic, hydrochloric, and the like to yield salts which are soluble in water. These diacyl derivatives of the polyalkylene polyamines are those most probably represented by the following general formula:



wherein A represents the group



or a plurality of such groups serially arranged, R and R<sub>1</sub> represent hydrogen or alkyl radicals, Y represents an aliphatic hydrocarbon radical containing at least 9 carbon atoms which hydrocarbon radical may contain one or more double bonds and may be substituted by hydroxy groups, Y' represents an aliphatic hydrocarbon radical, which hydrocarbon radical may contain one or more double bonds and may be substituted by hydroxy groups, and the salts of such compounds.

Representative polyalkylene polyamines which may be employed in condensing with the fatty acids are diethylene triamine, dipropylene triamine, dibutylene triamine, triethylene tetramine, tetraethylene pentamine, or mixtures of any two or more of such polyamines either as relatively pure compounds or crude mixtures. In general they are polyamines the different amino groups of which are separated from one another by a hydrocarbon radical containing from 2 to 12 carbon atoms. It is an advantage of the present invention that relatively crude mixtures of the various polyamines may be used for reacting with the fatty acids or fatty acid glycerides which results in the production of reagents at a lower cost than possible by using the purified polyamines. For example, when based on the saponification value of cottonseed oil and the average molecular weight of a crude mixture of polyethylene polyamines, a ratio of approximately 20 parts of amine to 100 parts of oil will yield a product consisting essentially of diacyl derivatives. The product so produced is suitable for use as a silica promoter and it is not necessary to remove the glycerin split off by the reaction.

Either the saturated, unsaturated, or hydroxy fatty acids and fatty acid glyceride having at

least 9 carbon atoms, may be employed for reacting with the polyamines. Representative acids and fatty acid glycerides include lauric, palmitic, stearic, oleic, ricinoleic, capric, and cyristic, mixtures of such acids or glycerides and especially mixtures of the fatty acids or glycerides found in the fats and oils of either vegetable or animal sources, such as those in coconut oil, palm oil, palm kernel oil, cottonseed oil, corn oil, linseed oil, olive oil, peanut oil, fish oils, and the like. The fatty acids or glycerides described above may be replaced in part by short chain aliphatic acids; such as, formic, acetic, propionic, butyric, valeric, caproic, heptioic, octoic, lactic, hydroxybutyric, etc., to produce compounds in which Y' is a short chain hydrocarbon radical and Y is a long chain hydrocarbon radical.

The promoter action of the reagents of the present invention will, of course, vary with different acidic ore materials and with the different polyalkylene polyamine fatty acid condensation products or salts used. For example, with the diacyl polyalkylene polyamines produced from fatty acid glycerides in which the average molecular weight of the fatty acids is comparatively low, such as those of coconut oil and palm kernel oil, the best results are obtained when such compounds are used in the form of their water-soluble acid addition salts, for example, the acetates. When the diacyl polyalkylene polyamine is produced from fatty acid glycerides the average molecular weight of the fatty acids of which is relatively high, such as those of cottonseed oil, they give the best results when used in the form of the free base. Therefore, it is not necessary in the present invention to use water-soluble salts, and the compounds in the form of the free base may be used provided satisfactory dispersion and distribution is effected. In the froth flotation operations, dispersion may be effectively obtained by feeding an alcoholic solution of the compound into the flotation circuit or by the use of emulsions containing the reagents dispersed therein.

The reagents of the present invention are effective promoters of collecting agents for acidic ore materials generally and said acidic materials may be either worthless gangue or valuable ore constituents. The most important use, however, is in connection with the froth flotation of silica from non-metallic ores in which the siliceous gangue may represent a much smaller proportion of the ore rather than metallic and sulfide ores in which the gangue usually represents the major proportion of the ore. Representative acidic ore materials are the feldspars, quartz, pyroxenes, the spinels, biotite, muscovite, clays, and the like.

While as stated heretofore, the present invention is not limited to the treatment of any particular ore materials, it has been found to be well suited for froth flotation of silica from phosphate rock, and this is a preferred embodiment of the invention. In the processes of removing silica from phosphate rock the conditions are such that practically complete removal of the silica must be accomplished in order to produce a salable phosphate material. It is therefore an advantage of this invention that our reagents not only effect satisfactory removal of the silica but are economical in amounts used. The quantities required range from 0.1 pound to 2.0 pounds per ton of ore depending upon the particular ore and the particular reagent. The invention is not, however, limited to the use of such quantities.

These reagents have also been successfully used

for the flotation of feldspar from quartz and for the flotation of mica from quartz and calcite.

The reagents of the present invention may be used alone or in mixtures with other promoters. They may likewise be used in conjunction with other cooperating materials such as conditioning reagents, activators, frothing reagents, depressing reagents, dispersing reagents, oily materials such as hydrocarbon oils, fatty acids or fatty acid esters.

These new reagents are also adaptable for use in any of the ordinary concentrating processes such as film flotation, tabling, and particularly in froth flotation operations. The ore concentrating processes employed will depend upon the particular type or kind of ore which is being processed. For example, in connection with phosphate rock, relatively coarse, phosphate bearing material, for example 28 mesh and larger, can be economically concentrated by using these reagents in conjunction with other materials such as fuel oil or pine oil and subjecting to concentration by the use of tables or by film flotation. The -28 mesh phosphate rock material is best concentrated by means of froth flotation employing these improved silica promoters.

When the reagents of the present invention are employed as promoters in the froth flotation of silica from phosphate rock the conditions may be varied in accordance with procedures known to those skilled in the art. The reagent may be employed in the form of aqueous solutions, emulsions, mixtures, or solutions in organic solvents such as alcohol and the like. The reagents may be introduced into the ore pulp in the flotation cell without prior conditioning or they may be conditioned with the ore pulp prior to the actual concentration operation. They may also be stage fed into the flotation circuit.

Other improved phosphate flotation features which are known may be utilized in connection with the present invention such as the very complete removal of the slime prior to flotation which is an aid to better results, as pointed out in the Erickson application Serial No. 325,011, filed March 20, 1940, and the Mead and Maust application Serial No. 320,121, filed February 21, 1940, which describes a process for classifying and desliming phosphate flotation feed by means of a hindered settling classifier and which deslimed feed is well suited for treatment in accordance with this invention.

The invention will be further illustrated by the following specific examples which are illustrations of the preferred embodiments thereof, but it is not intended to limit the invention thereby.

#### EXAMPLE

Flotation tests as follows were made on a sample of Florida phosphate ore from the Old Colony mine near Brewster. This ore material which was essentially -48 +200 mesh material was agitated and "scrubbed" with water to break up the clay balls. The slimes were subsequently removed by decantation and repeated washing until the ore material was substantially free of slimes.

Separate 600 gram samples of deslimed flotation feed were diluted to 22% solids with water and transferred to a laboratory size Fagergren flotation machine. The particular reagent or reagent combination was then added and conditioned with the pulp for 3 seconds. Air was admitted to the machine and the resultant concentrate was skimmed off for 2 minutes. The flotation test products were then filtered, dried,

weighed, and assayed. The metallurgical data obtained in these tests are presented in Table I. The result of the flotation tests employed in the table are the averages of at least two duplicate flotation tests, the results of which check within the limits of reasonable experimental error.

Table I

| Test No. | Reagent: <sup>1</sup> Diacidyl reaction product of polyethylene polyamines and— | Tailing (phosphate product) |                   |
|----------|---------------------------------------------------------------------------------|-----------------------------|-------------------|
|          |                                                                                 | Weight (per cent)           | Insol. (per cent) |
| 1        | Cottonseed oil.....                                                             | 28.43                       | 1.76              |
| 2        | Soya bean oil.....                                                              | 30.71                       | 2.41              |
| 3        | Peanut oil.....                                                                 | 28.52                       | 2.31              |
| 4        | Corn oil.....                                                                   | 29.34                       | 2.10              |
| 5        | Linseed oil.....                                                                | 32.59                       | 2.82              |
| 6        | Menhaden oil.....                                                               | 33.16                       | 2.63              |
| 7        | Lard.....                                                                       | 32.94                       | 2.16              |
| 8        | Oleic acid.....                                                                 | 37.25                       | 3.67              |

<sup>1</sup> All reagents used as the free base and fed as a solution in a mixture of aliphatic alcohols having from 7-10 carbon atoms. (0.8 lb./ton alcohol with 0.6 lb./ton reagent.)

Another series of tests was run on a different sample of phosphate rock from the Old Colony mine. The testing procedure, scrubbing, desliming, and flotation used for this series of tests was the same as that followed in the previous test. The metallurgical data obtained in these tests are found in Table II.

Table II

| Test No. | Diacidyl reaction product of polyethylene polyamines and— | Added as—                                                      | Lb./ton feed |                        | Tailing (phosphate product) |                 |
|----------|-----------------------------------------------------------|----------------------------------------------------------------|--------------|------------------------|-----------------------------|-----------------|
|          |                                                           |                                                                | Promoter     | Higher alcohol frother | Weight (per cent)           | Per cent insol. |
| 1        | Cottonseed oil.....                                       | 43% soln. in a mix. of aliphatic alcohols (7-10 carbon atoms). | 0.9          | 1.2                    | 22.33                       | 1.70            |
| 2        | Cottonseed oil.....                                       | 43% soln. in a mix. of aliphatic alcohols (7-10 carbon atoms). | 0.6          | 0.8                    | 28.43                       | 1.76            |
| 3        | Cottonseed oil.....                                       | 43% soln. in a mix. of aliphatic alcohols (7-10 carbon atoms). | 0.5          | 0.67                   | 29.40                       | 2.16            |
| 4        | Cottonseed oil.....                                       | 43% soln. in a mix. of aliphatic alcohols (7-10 carbon atoms). | 0.4          | 0.53                   | 32.05                       | 2.76            |
| 5        | Cottonseed oil.....                                       | 25% soln. in isopropyl alcohol.....                            | 0.4          | 0.12                   | 37.58                       | 2.73            |

<sup>1</sup> In test 5 the frother used was 0.12 lb. of pine oil per ton, and in addition 1.20 lbs. of isopropyl alcohol per ton were added with the promoter.

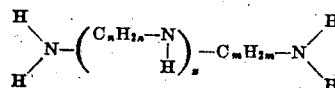
An analysis of the metallurgical data found in Tables I and II shows that in all tests the phosphate product (tailings) is of a satisfactory marketable grade, and that the phosphate product is a better grade than that currently produced by the flotation of phosphate particles from the quartz. In most of the tests the recovery of a satisfactory phosphate product is much higher than would be obtained in the soap flotation of the phosphate ores.

While the above examples relate specifically to the flotation of silica from phosphate rock, the present invention is not limited to such operations and the reagents used are useful in the treatment of various other types of ore materials wherein it is desirable to remove acidic minerals in the froth. For example, the reagents are useful in the treatment of the rake sands from the tailings produced in cement plant operations. In this particular instance the rake sands are treated by flotation to remove part of the alumina which is present in the form of mica and the removal of silica is not desirable. Our reagents have been found to be useful in such flotation operations. The reagent may also be used for the flotation of silica from iron ores containing magnetite, limonite and quartz, and in tests conduct-

ed on this type of ore the rough tailing resulting from the flotation of silica, containing both magnetite and limonite, assayed much higher in iron than concentrates produced by the conventional soap flotation of the iron minerals.

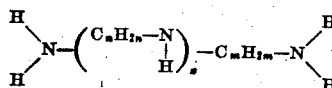
We claim:

1. In the froth flotation process of separating phosphate ore values from acidic siliceous gangue the step which comprises subjecting the ore to froth flotation in the presence of a reagent comprising the diacidyl reaction products of a polyalkylene polyamine represented by the following general formula:



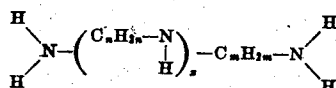
in which  $n$ ,  $m$ , and  $x$  are small whole numbers with cottonseed oil.

2. In the froth flotation process of separating phosphate ore values from acidic siliceous gangue the step which comprises subjecting the ore to froth flotation in the presence of a reagent comprising the diacidyl reaction products of a polyalkylene polyamine represented by the following general formula:



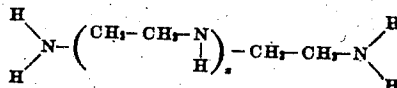
in which  $n$ ,  $m$ , and  $x$  are small whole numbers with peanut oil.

3. In the froth flotation process of separating phosphate ore values from acidic siliceous gangue the step which comprises subjecting the ore to froth flotation in the presence of a reagent comprising the diacidyl reaction products of a polyalkylene polyamine represented by the following general formula:



in which  $n$ ,  $m$ , and  $x$  are small whole numbers with corn oil.

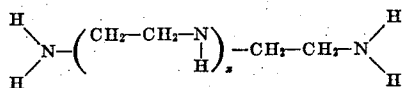
4. In the froth flotation process of separating phosphate ore values from acidic siliceous gangue the step which comprises subjecting the ore to froth flotation in the presence of a reagent produced by reacting cottonseed oil with a mixture of polyethylene polyamines, represented by the following general formula:



in which  $x$  is a small whole number in a propor-

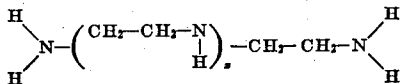
tion such that the diacidyl polyethylene polyamine is produced.

5. In the froth flotation process of separating phosphate ore values from acidic siliceous gangue the step which comprises subjecting the ore to froth flotation in the presence of a reagent produced by reacting peanut oil with a mixture of polyethylene polyamines, represented by the following general formula:



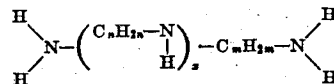
in which  $x$  is a small whole number in a proportion such that the diacidyl polyethylene polyamine derivative is produced.

6. In the froth flotation process of separating phosphate ore values from acidic siliceous gangue the step which comprises subjecting the ore to froth flotation in the presence of a reagent produced by reacting corn oil with a mixture of polyethylene polyamines, represented by the following general formula:



in which  $x$  is a small whole number in a proportion such that the diacidyl polyethylene polyamine derivative is produced.

7. In the froth flotation process of separating non-metallic ore values from acidic siliceous gangue the step which comprises subjecting the ore to froth flotation in the presence of a promoter for the acidic siliceous gangue, said promoter being chosen from the group consisting of the mixture of reaction products obtained by reacting substantially 2 equivalents of a fatty acid glyceride in which the fatty acid radical of said glyceride has at least 10 carbon atoms with substantially one equivalent of a polyalkylene polyamine represented by the following general formula:



in which  $n$ ,  $m$ , and  $x$  are small whole numbers, and salts of such products.

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