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MINERAL CONCENTRATION

David Walker Jayne, Jr., Old Greenwich, Harold Milton Day, Cos Cob, and Stephen Edward Erickson, Glenbrook, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

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6 Claims. (Cl. 209—166)

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

In accordance with the present 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, said promoters being the condensation products obtained by reacting polyalkylene polyamine with naphthenic acids or with mixtures of naphthenic acids or with mixtures of naphthenic acids and fatty acids and salts of such products to effect separation of the acidic minerals from the other ore constituents. Particularly, this invention relates to the use of the reaction products of the polyalkylene polyamines with naphthenic acid either as the free base or as the substantially water soluble salts of such a product as a promoter 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, limonite, calcite, and the like, and especially phosphate minerals.

The compounds that have been found to have a selective filming attraction for acidic ores and which are useful for carrying out this invention include broadly the reaction products of polyalkylene polyamines with naphthenic acid or mixtures of naphthenic acid and fatty acids. The compounds are not limited to those produced by reacting any particular grade or class of naphthenic acids with the polyalkylene polyamine. This is an advantage of the present invention because it permits the use of the crude naphthenic acid mixtures obtained in the refining of petroleum. The term "naphthenic acids" used in the present specification and claims is intended to include any single hydro-aromatic monocarboxylic acid or mixtures of such acids and any crude mixtures of such acids containing a significant proportion of saponifiable material. The naphthenic acids are usually obtained in the refining of petroleum and are frequently associated with appreciable quantities of unsaponifiable oil. Furthermore, the naphthenic acids will vary in composition depending upon the particular type of petroleum from which they are obtained. If desired, these crude naphthenic materials may be purified prior to use in the preparation of our reagents. On the other hand, we have found that the crude naphthenic acid materials obtained from a number of widely different petroleum sources are entirely satisfactory for producing our reagents. The reagents which we use are not limited to those produced by reacting any particular molecular ratio of the polyalkylene polyamines with naphthenic acids, hence when one mole of polyalkylene polyamine is reacted with one mole of naphthenic acid, the mono-acidyl derivative is produced. When one mole of polyalkylene polyamine is reacted with two moles of naphthenic acid a product is produced consisting principally of the di-acidyl derivative. Suitable reagents may also be prepared using an excess of either the naphthenic acid or polyalkylene polyamine.

A satisfactory method of preparing our reagents comprises reacting a polyalkylene polyamine with naphthenic acids at a temperature of from 200 to 240° C. until the reaction is complete. For example, a suitable product is produced by heating a mixture of 25 parts of crude mixed polyethylene polyamine and 60 parts of crude naphthenic acids (acid value 183) to a temperature of about 220° C. and then cooling to room temperature. The product so produced is a dark viscous paste readily and completely soluble in dilute acetic acid, giving a colorless solution. The acetate of this reaction product is prepared by adding four parts of glacial acetic acid to 25 parts of the condensation product. The product obtained is a stiff water-soluble paste.

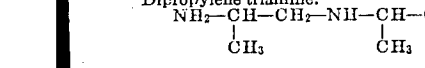
Representative polyalkylene polyamines which may be employed in condensing with naphthenic acids and fatty acids to produce our reagents are the polyalkylene polyamines obtained by heating an alkylene chloride with ammonia under pressure at a temperature of about 80 to 120° C. When ethylene chloride is employed there is obtained a mixture of diethylene triamine, triethylene tetramine, tetraethylene pentamine, and some ethylene diamine. We prefer to use such a mixture of polyalkylene polyamines; however, it is not necessary to use such a mixture and the individual polyalkylene polyamines themselves may be employed. It is, of course, understood that when propylene chloride, butylene chloride, amylene chloride, and the like, are employed instead of ethylene chloride in reacting with ammonia, the corresponding polyalkylene polyamines are obtained. The expression "polyalkylene poly-

amines" employed in the claims, therefore refers to and includes any one of the polyalkylene polyamines referred to above or to a mixture of such polyalkylene polyamines. These polyamines derived from alkylene compounds are chain compounds having an amino group on each end of the chain, or in other words, the amino groups are separated by at least one group such as —alkyl—NH—alkyl—. The formulae for some of the polyalkylene polyamines employed are as follows:

Diethylene triamine:
$NH_2—CH_2—CH_2—NH—CH_2—CH_2—NH_2$

Triethylene tetramine:
$NH_2—CH_2—CH_2—NH—CH_2—CH_2—NH—CH_2—CH_2—NH_2$

Dipropylene triamine:



The reagents actually employed and claimed in the present invention are the acylated polyalkaline polyamines produced by either partially or completely acylating the compounds represented by the above formulae, that is to say, one of the hydrogens on each of the amino groups at the end of the chain is replaced by naphthenyl radicals or the hydrogen on only one of the amino groups is replaced by a naphthenyl radical. The above 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.

The reagents of the present invention are effective promoters or 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.

The promoter action of the reagents of the present invention will, of course, vary with different ore minerals and with the different polyalkylene polyamine-naphthenic acid condensation products or salts used. It is an advantage of the invention, however, that good results are obtained when the polyamines are used in the form of the water-soluble salts, as for example, the acetates, formates, hydrochlorides, etc. However, it is not necessary to use the water soluble salts and the compounds in the form of the free bases may be used provided satisfactory dispersion and distribution are effected. In 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.

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 process of removing silica from phosphate rock, the conditions are such that the 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 silica, but are economical in amounts used. The quantities required range from 0.6 to 2.0 pounds per ton of ore depending upon the particular ore and the particular reagents. 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 or 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 reagents 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 slimes 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 example which is an illustration of the preferred embodiment thereof, but it is not intended to limit the invention thereby.

EXAMPLE 1

Flotation tests as follows were made on a sample of Florida phosphate rock from the Old Colony Mine near Brewster. A fine flotation feed (—35 +200 mesh) was produced by scrubbing, polishing, and desliming until the ore material was substantially free of slimes.

Separate 600-gram samples of the deslimed flotation feed were diluted to 22% solids with water and transferred to a laboratory size Fager-

gren flotation machine. The particular reagent or reagent combination was then added and conditioned with the pulp for 3 seconds. Air was then admitted to the machine and the resulting concentrate froth 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.

Table I

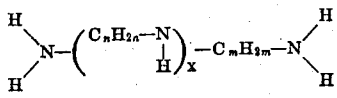
Test No.	Feed, per cent insol.	Concentrate			Tailing			Reagents	Lbs./ton of feed [1]
		Per cent wt.	Per cent insol.	Dist. per cent insol.	Per cent wt.	Per cent insol.	Dist. per cent insol.		
1	60.48	62.59	93.92	97.19	37.41	4.54	2.81	± Pine oil.	0.60 0.12
2	59.63	64.11	91.56	98.44	35.89	2.60	1.56	± Pine oil.	0.90 0.12

[1] The acetate of the reaction product of mixed polyethylene polyamines and naphthenic acid.

While the above example relates specifically to the flotation of silica from phosphate rock, the present invention is not limited to such operations and the reagents 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 conducted on this type of ore the rough tailing resulting from the flotation of silica containing both and limonite, assayed much higher in iron than concentrates produced by the conventional soap flotation of the iron minerals.

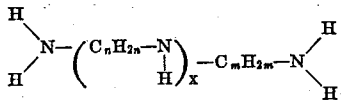
What I claim is:

1. In ore concentrating processes utilizing differential surface wettability principles of separating acidic ore materials from other ore constituents the process which comprises carrying out the concentration operation in the presence of a promoter for the acidic ore material, said promoter comprising the reaction products of polyalkylene polyamines represented by the following general formula:



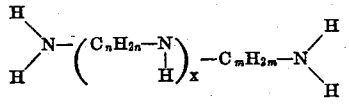
in which n, m, and x are small whole numbers, with naphthenic acids, and salts thereof.

2. In ore concentrating processes utilizing differential surface wettability principles of separating acidic siliceous gangue from non-metallic ore constituents the process which comprises carrying out the concentrating operation in the presence of a collector for the acidic siliceous gangue, said promoter comprising the reaction products of polyalkylene polyamines represented by the following general formula:



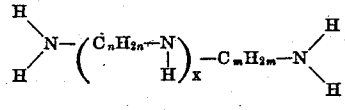
in which n, m, and x are small whole numbers, with naphthenic acid, and salts thereof.

3. In ore concentrating processes utilizing differential surface wettability principles of separating acidic siliceous gangue from phosphate ore values the process which comprises carrying out the concentrating operation in the presence of a collector for the acidic siliceous gangue, said promoter comprising the reaction products of polyalkylene polyamines represented by the following general formula:



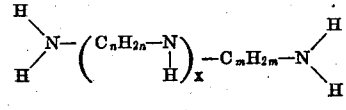
in which n, m, and x are small whole numbers, and naphthenic acid, and salts thereof.

4. 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 reagent comprising the reaction products of polyalkylene polyamines represented by the following general formula:



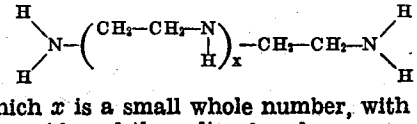
in which n, m, and x are small whole numbers, with naphthenic acid, and salts of such reaction products.

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



in which n, m, and x are small whole numbers, with naphthenic acid, and the salts of such compounds.

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



in which x is a small whole number, with naphthenic acid, and the salts of such compounds.

DAVID WALKER JAYNE, JR.
HAROLD MILTON DAY.
STEPHEN EDWARD ERICKSON.