

UNITED STATES PATENT OFFICE

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BENEFICIATION OF ACIDIC MINERALS

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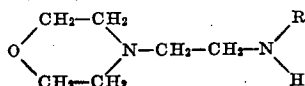
The present invention relates to mineral concentrations and more particularly relates to a new class of reagents for selectively separating acidic minerals from other ore constituents.

Still more particularly, the present invention relates to the use of a higher alkyl and acyl derivatives of N-aminoethyl morpholine and salts of such derivatives as promoters or collectors for acidic minerals in froth flotation, film flotation, stratification, agglomeration, tabling and related mineral separation processes. While the present invention is not limited to any particular ore concentrating process utilizing differential surface wettability principles or to any particular ore, its most important field of usefulness is in connection with froth flotation processes of separating silica or silicate minerals, such as mica, from non-metallic ores including limestone, bauxite, barytes, ilmenite, calcite, and the like, and especially phosphate minerals wherein the silicious gangue is floated away from the phosphate minerals.

In accordance with this invention natural ores or artificial materials comprising a mixture of acidic minerals with other mineral constituents are subjected to a separation or concentration process in the presence of a promoter for the acidic ore minerals, said promoter being a higher alkyl or acyl derivative of N-aminoethyl morpholine.

The reagents of the present invention are effective promoters or collectors for negatively charged or acidic ore materials generally and said acidic material may either be worthless gangue or valuable ore constituents. The most important uses are, however, in connection with the froth flotation of silica from non-metallic ores in which the silicious gangue may represent a minor 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 compounds which we have found to be useful in carrying out the present invention may be represented by the following general formula:



where R is an alkyl radical containing 8 to 30 carbon atoms, an alkylol ester radical, or an acyl radical containing from 8 to about 32 carbon atoms.

The present invention is not particularly concerned with methods for preparing the above compounds and any suitable method may be employed. In general, we have found that the compounds wherein R is a higher alkyl radical can conveniently be prepared by the reaction of an alkyl halide with N-aminoethyl morpholine to produce the hydrohalide salts of the alkylated products. The compounds wherein R is an acyl radical can be conveniently prepared by the reaction of a higher molecular weight carboxylic acid, a higher molecular weight carboxylic acid ester, a higher molecular weight carboxylic acid chloride, or the like, with N-aminoethyl morpholine. The compounds wherein R is an alkylol ester radical can be obtained by reacting an alkylene halide ester of a higher molecular weight carboxylic acid, such as for example the oleic acid ester of ethylene chlorohydrin, with N-aminoethyl morpholine. The following preparations will serve to illustrate methods for the preparation of certain representative compounds.

N-(lauryl aminoethyl) morpholine hydrobromide

A solution of 24.9 grams of lauryl bromide and 13 grams of N-aminoethyl morpholine in 100 cc. of anhydrous ethanol was boiled under reflux for six hours; then the alcohol removed by distillation. The product was a soft tan paste which gave a "soapy" solution.

Instead of lauryl bromide we can use other alkylating agents, such as octyl iodide, myristyl chloride, cetyl chloroacetate, chloroethyl myristyl ether, β -chloroethyl palmitate, etc., it only being required that the alkylating agent employed be one that contained from about 8 to not more than about 30 carbon atoms.

Reaction product of N-aminoethyl morpholine and coconut oil

A mixture of 130 grams of N-aminoethyl morpholine and 220 grams of coconut oil was heated to 230° C. in an open short-neck flask and then cooled to room temperature. The product was a light brown paste completely soluble in dilute acetic acid to give a clear solution which foamed readily.

Instead of the specific acylating agent employed in the above process other higher molecular weight carboxylic acid esters may be employed, it being understood that the higher molecular weight carboxylic acid refers to such acids having preferably at least 8 and usually not more than 32 carbon atoms. It is also understood that the higher molecular weight acylating agents may be acids themselves, other esters thereof, or halogen derivatives thereof. Among the sources of such acylating agents we may mention the following acids which, of course, will also include the esters and halogen derivatives of such acids. These higher molecular weight carboxylic acids may either be saturated, unsaturated, or hydroxyl containing fatty acids, the preferred ones being those having at least 9 carbon atoms, such as for example, lauric, palmitic, stearic, oleic, ricinoleic, capric, myristic, mixtures of such acids, and especially mixtures of the fatty acids obtained from the fats and oils of either vegetable or animal sources or their glycerides, such as those from coconut oil, palm oil, palm kernel oil, cottonseed oil, corn oil, linseed oil, olive oil, peanut oil, fish oils, and the like. Other suitable acids include talloel acids, petroleum acids, such as naphthenic acids and carboxy acids produced by the oxidation of petroleum, and the like.

Representative compounds that can be used in carrying out the present invention include the following: N-(lauryl aminoethyl) morpholine hydrobromide, N-(cetyl aminoethyl) morpholine hydrochloride, N-(lauroyl aminoethyl) morpholine hydrochloride, N-(myristoyl aminoethyl) morpholine acetate, N-(cetyl methoxy aminoethyl) morpholine hydrochloride, N-((lauroyl- β -hydroxyethyl)-aminoethyl) morpholine hydrochloride.

We prefer to use these compounds in the form of their hydrohalide salts since they are either water soluble or readily dispersible in aqueous solutions. On the other hand, it is not necessary that they be used in the form of hydrohalide salts and satisfactory results can be obtained using the free base in our process provided that satisfactory dispersion and distribution are effected. It is, of course, understood that salts other than the hydrohalide salts may be prepared, such as for example, nitrates, acetates, formates, other salts of low molecular weight organic acids and salts of aromatic sulfonic acids, such as for example, benzene-sulfonic acid or p-toluene sulfonic acid salts.

While as stated heretofore the present invention is not limited to the treatment of any particular ore material, it has been found to be well suited for froth flotation of silica from phosphate rock and is the 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 also economical in amounts used. The quantities required range from 0.2 pound per ton of ore depending upon the particular ore and the particular reagent. The invention is not, however, limited to such quantities.

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 condition-

ing reagents, oily or fatty 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 very economically concentrated by using these reagents in conjunction with a material such as fuel oil or pine oil and subjecting to concentration by the use of tables or by film flotation. The -28 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, which is the preferred embodiment thereof, the condition 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 reagent may be introduced into the ore pulp prior to the actual concentration operation. It may also be stage fed into the flotation circuit.

In its most important aspect the present invention is utilized for the treatment of non-metallic ore materials but it is to be understood that our reagents under proper conditions may be used advantageously for the treatment of metallic ore materials.

Other improved phosphate flotation features which are known may be utilized in connection with the present invention such as splitting the phosphate flotation feed into a plurality of size ranges and floating each size separately as described in the U. S. Patent No. 2,156,245, and the very complete removal of the slime prior to flotation which is also 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 feed by means of a hindered settling classifier and which deslimed feed is well suited for treatment in accordance with this invention.

This invention will be further illustrated by the following specific tests which are illustrations of the preferred embodiments thereof, but is not to be strictly limited thereby.

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 Fagergren flotation machine. The particular reagent or reagent combination was then added and conditioned with the pulp for three seconds. Air was then admitted to the machine and the resulting concentrate froth was collected until the froth became barren. The flotation test products were 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
		Per cent weight	Per cent insol.	Dist. per cent insol.	Per cent weight	Per cent insol.	Dist. per cent insol.		
1	54.54	60.11	83.06	91.55	39.89	11.56	8.45	b.----- Pine oil.	10.00 0.12
2	54.54	53.86	90.05	88.93	46.14	13.08	11.07	c.----- Pine oil.	3.00 0.12

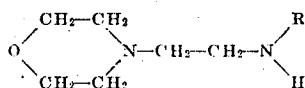
a Acetate of coconut fatty acids amide of N-aminoethyl morpholine.
b Acetate of coconut fatty acids amide of N-aminoethyl morpholine.

When rake classifier sands such as those produced from the tailings at the Valley Forge Cement Company plants are treated by flotation using our reagents, the alumina in the form of mica, is removed in part from the silicious material and a cement product is produced which has greatly improved properties.

In the treatment of iron ores we have found that our reagent may be employed in flotation processes for removing the silica therefrom and the tailings resulting from such processes are much higher in iron content than concentrates produced by the conventional soap flotation of the iron minerals.

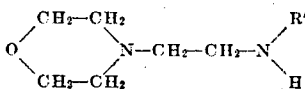
What we claim is:

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 substance of the group consisting of those represented by the following formula:



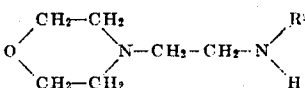
where R is a member of the group consisting of alkylol ester radicals, alkyl radicals containing 8 to 30 carbon atoms and acyl radicals containing from 8 to about 32 carbon atoms and salts of such compounds.

2. 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 substance of the group consisting of those represented by the following formula:



where R' is an alkyl radical containing from 8 to 30 carbon atoms and salts of such compounds.

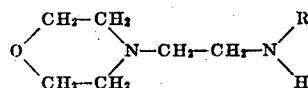
3. In ore concentrating processes utilizing differential surface wettability principles of separating acidic ore materials from other ore constituents, the process which comprises carrying out the concentration operation in the presence of a substance of the group consisting of those represented by the following formula:



where R² is a higher molecular weight acyl radical and salts of such compounds.

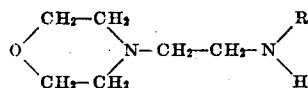
4. In the froth flotation process of separating acid silicious gangue from none-metallic ore values, the step which comprises subjecting the

ore to froth flotation in the presence of a product of the group consisting of those represented by the following formula:



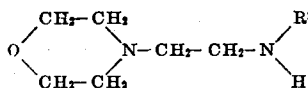
where R is a member of the group consisting of alkyl radicals containing 8 to 30 carbon atoms and acyl radicals containing from 8 to about 32 carbon atoms and salts of such compounds.

5. In the froth flotation process of separating acidic silicious gangue from non-metallic ore values, the step which comprises subjecting the ore to froth flotation in the presence of a product of the group consisting of those represented by the following formula:



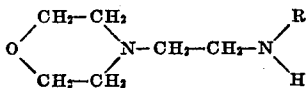
where R' is an alkyl radical containing from 8 to 30 carbon atoms and salts of such compounds.

6. In the froth flotation process of separating acidic silicious gangue from non-metallic ore values, the step which comprises subjecting the ore to froth flotation in the presence of a product of the group consisting of those represented by the following formula:



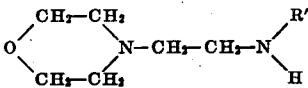
where R² is a higher molecular weight acyl radical and salts of such compounds.

7. In the froth flotation process of separating acidic silicious gangue from phosphate ore values, the step which comprises subjecting the ore to froth flotation in the presence of a product of the group consisting of those represented by the following formula:



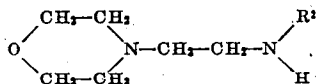
where R is a member of the group consisting of alkyl radicals containing 8 to 30 carbon atoms and acyl radicals containing from 8 to about 32 carbon atoms and salts of such compounds.

8. In the froth flotation process of separating acidic silicious gangue from phosphate ore values the step which comprises subjecting the ore to froth flotation in the presence of a product of the group consisting of those represented by the following formula:



where R' is an alkyl radical containing from 8 to 30 carbon atoms and salts of such compounds.

9. In the froth flotation process of separating acidic silicious gangue from phosphate ore values, the step which comprises subjecting the ore to froth flotation in the presence of a product of the group consisting of those represented by the following formula:



where R² is a higher molecular weight acyl radical and salts of such compounds.

10. In the flotation process of separating acidic silicious gangue from phosphate ore values, the step which comprises subjecting the ore to froth

flotation in the presence of N-((lauroyl-β-hydroxyethyl)-aminoethyl) morpholine hydrochloride.

11. In the flotation process of separating acidic silicious gangue from phosphate ore values, the step which comprises subjecting the ore to froth flotation in the presence of N-(lauryl aminoethyl) morpholine hydrobromide.

12. In the flotation process of separating acidic silicious gangue from phosphate ore values, the step which comprises subjecting the ore to froth flotation in the presence of N-(lauroyl aminoethyl) morpholine acetate.

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