

UNITED STATES PATENT OFFICE

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BENEFICIATION OF ACIDIC MINERALS

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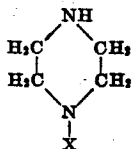
The present invention relates to mineral concentrations and more particularly relates to a new class of reagents for selectively separating acidic minerals from other ore constituents.

Still more particularly, the present invention relates to the use of alkylated piperazines, acylated piperazines and salts thereof, 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 such as limestone, bauxite, barytes, limenite, 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 high molecular weight carboxylic acid derivative of piperazine or a higher alkyl derivative of piperazine.

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 include broadly the products represented by the following general formula:



where X represents a higher alkyl radical, an alkylol ester radical, or an acyl radical of a higher molecular weight carboxylic acid and the salts of such compounds. It is to be understood that the acyl radical is an acyl radical of a higher molecular weight carboxylic acid and that the alkyl radical is a higher alkyl radical, i. e., one containing from 8 to about 32 carbon atoms. The acylated compounds which we use in carrying out the process of the present invention can be very conveniently prepared by the thermal reaction of piperazine with higher molecular weight carboxylic acids or by reacting piperazine hydrohalides with alkali metal salts of higher molecular weight carboxylic acids. Similarly, the products may be prepared by thermally reacting esters of higher molecular weight carboxylic acids with piperazine. The following preparations will serve to illustrate methods for the preparation of certain representative compounds.

Higher monoacyl derivatives of piperazine

A mixture of 21 grams of piperazine hexahydrate and 28 grams of oleic acid was heated in an open beaker with agitation to 200° C., then cooled to room temperature. The product was a brown paste readily and completely soluble in dilute acetic acid to give a clear solution. This reaction product was converted to the acetate by adding to it 6 grams of glacial acetic acid.

Piperazine and coconut oil fatty acid (molar ratio 1:1)

A mixture of 21 grams of piperazine hexahydrate and 21 grams of coconut oil fatty acids was heated in an open beaker with agitation to 220° C. and cooled to room temperature. This product was a soft tan-colored wax readily and completely soluble in dilute acetic acid to give a clear solution. This reaction product was converted to the acetate by adding to it 6 grams of glacial acetic acid.

Instead of the specific acylating agents employed in the above process other higher molecular weight carboxylic acids 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, 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, 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.

The alkylated compounds which we use in carrying out the process of the present invention can be very conveniently prepared by the reaction of piperazine with a higher alkyl alkylating reagent. The following preparation will serve to illustrate a method for preparing a representative compound.

Lauryl piperazine hydrobromide

A solution of .1 mol of lauryl bromide and .1 mol of piperazine in anhydrous ethanol was boiled under reflux for five hours and the alcohol then removed by distillation. The product was a soft paste which dissolved in water to give a soapy solution.

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

The esters of any of the foregoing acids and halogen substituted aliphatic alcohols, such as for example the esters of ethylenechlorhydrin, may be utilized to give alkylol ester derivatives.

Representative compounds that can be used in carrying out the present invention include the following: oleoyl piperazine acetate, lauroyl piperazine hydrochloride, lauryl piperazine hydrochloride, N-cetyl methoxy piperazine hydrochloride, N-(lauroyl- β -hydroxyethyl)-piperazine 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 is 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 conditioning reagents, oily or fat 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. They 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, 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 flotation 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 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			Tailings			Reagents	Lbs./ton of feed
		Per cent wt.	Per cent insol.	Dist. per cent insol.	Per cent wt.	Per cent insol.	Dist. per cent insol.		
1.....	59.55	56.90	93.92	89.74	43.10	14.18	10.26	a.....	0.30
								Pine oil.....	0.12
2.....	59.53	66.70	88.00	98.60	33.30	2.50	1.40	b.....	0.60
								Pine oil.....	0.12
3.....	59.49	60.13	94.34	95.35	39.87	6.94	4.65	c.....	2.00
								Pine oil.....	0.12

a. The acetate of the reaction product of piperazine and oleic acid.

b. The hydrochloride of the reaction product of piperazine and oleic acid.

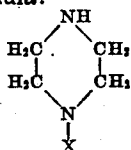
c. The hydrochloride of the reaction product of piperazine and coconut oil fatty acids.

When the 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.

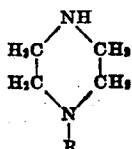
What we claim is:

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 sufficient amount of a substance selected from the group consisting of those represented by the following formula:



where X is a member of the group consisting of higher alkyl radicals, an alkylol ester radical, higher molecular weight carboxylic acyl radicals and salts of such compounds to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

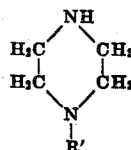
2. In ore concentrating processes utilizing differential surface wettability principles of separating acidic ore materials from other ore constituents, the process which comprises carrying out the concentration operation in the presence of a sufficient amount of a substance selected from the group consisting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



where R represents a higher alkyl radical and salts of such compounds to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

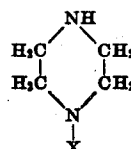
3. In ore concentrating processes utilizing differential surface wettability principles of separating acidic ore materials from other ore constituents, the process which comprises carrying

out the concentration operation in the presence of a sufficient amount of a substance selected from the group consisting of those represented by the following formula:



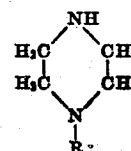
where R' represents a higher molecular weight carboxylic acyl radical and salts of such compounds to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

4. 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 sufficient amount of a product selected from the group consisting of those represented by the following formula:



where X is a member of the group consisting of higher alkyl radicals, an alkylol ester radical, higher molecular weight carboxylic acyl radicals and salts of such compounds to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

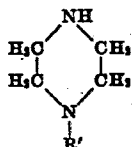
5. In the froth flotation process of separating acidic silicious gangue from non-metallic ore values, the step which comprises subjecting the ore to froth flotation in the presence of a sufficient amount of a product selected from the group consisting of those represented by the following formula:



where R represents a higher alkyl radical and

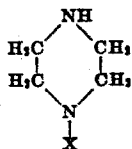
salts of such compounds to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

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 sufficient amount of a product selected from the group consisting of those represented by the following formula:



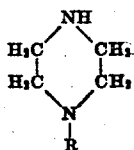
where R' represents a higher molecular weight carboxylic acyl radical and salts of such compounds to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

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 sufficient amount of a product selected from the group consisting of those represented by the following formula:



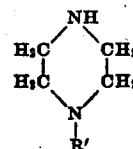
where X is a member of the group consisting of higher alkyl radicals, an alkylol ester radical, higher molecular weight carboxylic acyl radicals and salts of such compounds to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

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 sufficient amount of a product selected from the group consisting of those represented by the following formula:



where R represents a higher alkyl radical and salts of such compounds to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

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 sufficient amount of a product selected from the group consisting of those represented by the following formula:



where R' represents a higher molecular weight carboxylic acyl radical and salts of such compounds to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

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 a sufficient amount of the oleic acid acyl derivative of piperazine to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

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 a sufficient amount of the coconut oil fatty acid acyl derivative of piperazine to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

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 a sufficient amount of lauryl piperazine hydrobromide to be effective in promoting a substantially complete separation of the acidic materials from the remainder of the ore.

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