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# UNITED STATES PATENT OFFICE

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## CONCENTRATION OF ACIDIC MINERALS

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9 Claims. (Cl. 209—166)

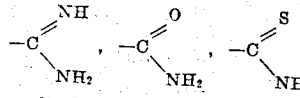
The present invention relates to mineral concentrations and more particularly relates to a new class of reagents for selectively separating acidic minerals from other ore constituents.

Still more particularly, the present invention relates to the use of isothioureas such as S-alkyl pseudo-thioureas, N-substituted S-alkyl pseudo-thioureas, and the salts of said pseudo-thioureas 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 product represented by the following general formula:



in which R' is hydrogen or an alkyl, aryl, aralkyl or alicyclic radical, or a radical such as



and R is an alkyl radical including alkyl radicals containing oxygen, sulfur or nitrogen; preferably R is an alkyl radical having 8 or more carbon atoms and less than 32 carbon atoms.

The compounds which we use in carrying out the process of the present invention may be prepared by several different methods. In a preferred method they are prepared by reacting thiourea or an N-substituted thiourea with an alkyl halide or other alkylating agent, for example, when an alcoholic solution of approximately equimolecular quantities of thiourea and lauryl bromide are refluxed for about 6 hours, a quantitative yield of S-lauryl pseudo-thiourea hydrobromide is obtained. When an N-substituted thiourea is employed instead of thiourea, such as for example N-ethyl thiourea, N-benzyl thiourea, N-phenyl thiourea, or N-cyclohexyl thiourea, guanyl thiourea, thiobiuret, dithiobiuret or the like, for reaction with lauryl bromide under similar conditions, the corresponding N-substituted S-lauryl pseudo-thiourea hydrobromide is obtained. Instead of lauryl bromide we may use other alkylating agents such as actyl iodide, myristyl chloride, cetyl chloracetate, lauroyl-amino ethyl acetate, chlormethyl myristyl ether, β-chlor ethyl palmitate etc.

Our reagents may also be prepared by a process which comprises reacting thiourea hydrochloride or an N-substituted thiourea hydrochloride with an alcohol and in most instances the alcohol employed should be one containing at least 8 carbon atoms and preferably not more than 32 carbon atoms. It is an advantage, however, that relatively crude mixtures of such alcohols produced by catalytic methods from hydrocarbons may be employed. Similarly in the process heretofore, crude mixtures of alkyl halides may be employed.

Still another method for preparing our reagents is one in which cyanamide is reacted with a mercaptan. In this case the mercaptan should be one containing 8 or more carbon atoms.

Representative compounds that may be used in the present invention include the following:

S-octyl pseudo thiourea hydro-iodide
S-lauryl pseudo thiourea hydro-bromide
S-myristyl pseudo thiourea hydro-chloride
S-cetyl pseudo thiourea hydro-bromide
S-lauryl pseudo guanyl thiourea hydro-bromide
S-lauryl mono-pseudo dithiobiuret
S-lauryl aceto pseudo thiourea hydrochloride
S-(N-lauroyl-amino ethyl aceto)-pseudo thiourea hydrochloride
S-lauryl pseudo N-phenyl thiourea hydrobromide
S-lauryl methoxy pseudo thiourea 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 ore concentrating processes provided that satisfactory dispersion and distribution is effected. If desired the free pseudo-thioureas may be treated with an acid other than a hydrohalide acid, such as a nitric acid, to produce the water-soluble nitrate.

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.

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.

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.

A series of flotation tests were made on a sample of phosphate ore from the Old Colony mine near Brewster, Florida. In these tests the procedure was as follows:

A charge of ore containing 600 grams of dry solids was conditioned for two minutes in laboratory size Fagergren flotation machine at 22% solids and then thoroughly deslimed. The deslimed sands were transferred to the flotation machine, diluted with water to give a pulp containing 22% solids and reagents as shown in the individual tests were added. The pulp and reagents were conditioned five seconds by agitating with the air valve closed. Air was then introduced and the resulting concentrate froth removed by skimming two minutes. The results of the various tests are shown in the table.

*Table*

| Test No. | Feed | | Concentrate | | | Tailing | | | Reagents |
|---|---|---|---|---|---|---|---|---|---|
| | Wt. gr. | Per cent insol. | Wt. per cent | Per cent insol. | Per cent dist. insol. | Per cent wt. | Per cent insol. | Per cent dist. insol. | |
| 2 | 603.9 | 54.54 | 60.01 | 85.35 | 93.91 | 39.99 | 8.31 | 6.09 | Octyl pseudo-thiourea hydrobromide 5.00 lbs. per ton, pine oil 0.24 lb./ton. |
| 3 | 609.0 | 54.54 | 66.50 | 81.10 | 98.88 | 33.50 | 1.83 | 1.12 | Lauryl pseudo-thiourea hydrobromide 0.50 lb./ton, pine oil 0.12 lb./ton. |
| 4 | 613.0 | 54.54 | 68.35 | 79.31 | 99.39 | 31.65 | 1.05 | 0.61 | Myristyl pseudo-thiourea hydrobromide 0.50 lb./ton, pine oil 0.12 lb./ton. |
| 7 | 611.7 | 54.54 | 70.46 | 75.40 | 97.41 | 29.54 | 4.76 | 2.59 | Cetyl pseudo-thiourea hydrochloride 0.50 lb./ton, pine oil 0.12 lb./ton. |
| 11 | 606.5 | 54.54 | 60.35 | 87.56 | 96.88 | 39.65 | 4.29 | 3.12 | Lauryl pseudo-guanyl thiourea hydrobromide 0.50 lb./ton, pine oil 0.12 lb./ton. |

In test No. 2 octyl pseudo thiourea hydrobromide and pine oil added by stages. Total flotation time—5 minutes.

An analysis of the metallurgical data in the table shows that in all tests the phosphate product (tails) is of satisfactory marketable grade. In the tests the phosphate product is of an average better grade than currently produced by the flotation of phosphate particles from the silica. In two of the tests, 3 and 4, the percent insol. is less than 2% and this represents a commercially high grade phosphate product.

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.

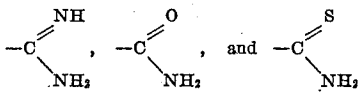
In the treatment of iron ores we have found that our reagents may be employed in flotation processes for removing the silica therefrom and the tailings resulting from such processes are much higher in iron content than concentrates produced by the conventional soap flotation of the iron minerals.

We claim:

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:



in which R' is a member of the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloaliphatic,

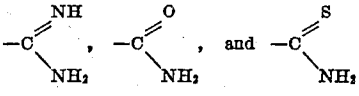


radicals and R represents a member of the group consisting of alkyl, and alkyl groups containing oxygen, sulfur or nitrogen, and the salts of such compounds.

2. In ore concentrating processes utilizing differential surface wettability principles of separating acidic ore materials from non-metallic ore, 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:

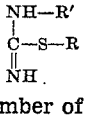


in which R' is a member of the group consisting of alkyl, aryl, aralkyl, cycloaliphatic,

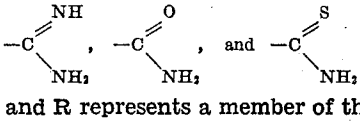


radicals and R represents a member of the group consisting of alkyl, and alkyl groups containing oxygen, sulfur, or nitrogen, and the salts of such compounds.

3. 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:



in which R' is a member of the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloaliphatic,

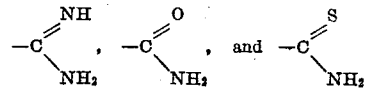


radicals and R represents a member of the group consisting of alkyl, and alkyl groups containing oxygen, sulfur, or nitrogen, and the salts of such compounds.

4. 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:



in which R' is a member of the group consisting of hydrogen, alkyl, aryl, aralkyl, cycloaliphatic,



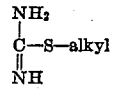
radicals and R represents a member of the group consisting of alkyl, and alkyl groups containing oxygen, sulfur, or nitrogen, and the salts of such compounds.

5. 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:



in which R represents a radical of the group consisting of alkyl and alkyl groups containing oxygen, sulfur, or nitrogen, and the salts of such compounds.

6. 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:



and salts of such compounds.

7. 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 lauryl pseudo-thiourea hydrobromide.

8. 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 cetyl pseudo-thiourea hydrochloride.

9. 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 lauryl pseudo-guanyl thiourea hydrobromide.

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