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# FLOTATION SEPARATION OF PARTICULATE MATERIALS IN NON-AQUEOUS MEDIA

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The present invention relates to a novel method of separation of particulate materials by flotation. More particularly, it relates to separation by flotation of particulate materials suspended in suitable organic liquids using as flotation reagents those chemicals which are capable of reacting or sorbing on certain classes of particles so as to make those particles organophobic.

Conventional flotation has been primarily limited to the minerals industry. Since most minerals have an affinity for aqueous media, i.e. are hydrophilic, conventional flotation has been principally concerned with imparting a hydrophobic or aerophilic coating on certain classes of mineral particles by reacting the mineral surfaces with xanthates, aliphatic acids and amines and other chemicals which will, in effect, give an oily or hydrophobic coating to the selected mineral particles. Conventional flotation reagents generally impart an organophilic as well as aerophilic nature to the chosen particles. Thus separations are limited to systems of aqueous media and gaseous media and systems of aqueous media and organic media. Examples of such media are water, saturated salt solutions and emulsions or mixtures of oil and water in which water is the continuous phase.

Not all particulate materials can be separated by flotation in aqueous media. Thus salts which form many hydrates cannot be floated out of ordinary aqueous systems since the aqueous system does not become saturated and undissolved, floatable particles do not exist. And in some instances, high purity materials cannot be obtained. For example, in the flotation of graphite from sand in aqueous media, only graphite of medium purity can ordinarily be obtained in high yield.

Accordingly, it is a primary object of this invention to provide a new method of flotation separation.

It is still another object of this invention to overcome the shortcomings and disadvantages of the processes heretofore in use.

These and other objects of the invention will be obvious to those skilled in the art from a study of the method hereinafter outlined in detail.

It has now been found that flotation separation of particulate materials can be carried out in organic media-gaseous systems using fluorinated organic compounds having functional groups, as flotation agents. The primary distinguishing characteristics of this invention are the use of an organic liquid as the liquid medium and the use of organophobic or potentially organophobic reagents as collectors in the flotation process. The mechanism of the process is not completely understood. However, it is believed that the fluorinated organic compound reacts chemically with the particle surface, thus rendering said surface organophobic. Ionization is not believed to play a great part in the process due to the use of the non-aqueous media.

Any organic solvent toward which one of the substances to be separated would be naturally organophobic or could be made organophobic would be suitable. Preferred solvents, because of their low cost, are alipathic and aromatic hydrocarbons, such as kerosene, benzene and toluene. Mixtures of such solvents can be used. Also miscible solvent-water mixtures would be usable, especially where the reagent used for imparting flotability gives a hydrophobic and organophobic nature to one of the substances to be separated. Conceivably two immiscible



solvents and gas could be used, separating three substances in a single operation—one into each phase.

The collectors or flotation agents of the present invention are fluorinated organic compounds which impart organophobicity to the particulate materials to be separated. Representative of such compounds are fluorinated aliphatic acids, amines, alcohols and aldehydes. Said organic compounds may be either fully or partially fluorinated. Preferred compounds are the perfluorinated aliphatic carboxylic acids of 1 to 8 carbon atoms. Especially preferred are perfluorobutyric acid and perfluorooctanoic acid. The above described collectors or flotation agents are used in an amount sufficient to float the particulate material. The amount needed for any specific system depends, therefore, on the organic medium, the particulate material to be separated, the gaseous phase and the precise flotation agent.

The gas used in the present flotation method is preferably air. However, other gases can be used.

Frothers, depressors and activators, when needed, can also be added. In this respect, conventional flotation reagents (xanthates, aliphatic acids and amines, for example) which do not react with the fluorinated collectors would function as depressants in the present organic media - gaseous systems since said reagents ordinarily impart a hydrophobic-organophilic nature to the particle surfaces. This would be especially true if they are added prior to the addition of the organophobic collector.

Flotation separation according to the present invention can be carried out in a number of ways. Thus the particulate material may be added to the organic media, followed by addition of the flotation agent. Or the particulate material may be added after the flotation agent and organic media have been mixed. Air, or other suitable gas, is then bubbled through the above mixtures. The temperature at which the process is carried out is not critical. However, ambient temperatures are preferred.

The novel process of this invention, as described herein above, can be used to separate a wide variety of particulate materials as will be evident from the following examples and description of uses. It is to be understood that the examples, given for illustrative purposes only, do not limit the scope of the invention in any way.

A small flotation cell (about 600 cc.) was used in all of the examples. Each test was carried out by bubbling air through the organic media in said cell.

*Example 1*

A mixture of copper powder, iron powder, zinc shavings, sand and guar particles were suspended in kerosene in a small flotation cell. A small amount (several drops) of perfluorobutyric acid was added and nothing of consequence floated. Several more drops of perfluorobutyric acid were added with a medicine dropper and material floated which appeared to be silica and guar. Addition of still more of the acid caused the iron and copper powders to float. Finally everything floated except large zinc shavings which were apparently too heavy.

*Example 2*

A mixture of sand and phosphate ore was added to a small flotation cell and then suspended in kerosene. Air addition caused nothing to float. Nothing floated with addition of small amounts of perfluorobutyric acid. After addition of several dropperfuls of perfluorobutyric acid, both sand and phosphate floated.

*Example 3*

Kerosene containing perfluorobutyric acid was placed in a 600 cc. flotation cell. Successive portions of solid $CaCl_2+2H_2O$, NaCl, $NH_4Cl$, boric acid, and sodium borate were added to the cell and successively and easily

floated. When the same materials were suspended in kerosene without perfluorobutyric acid nothing floated when air was applied.

*Example 4*

Flake graphite was added to kerosene containing a small amount of perfluorobutyric acid in a small flotation cell. Air addition did not float the graphite. Sand was added to the cell, air was bubbled through and very small amounts of sand floated. More perfluorobutyric acid was added and mixed into the suspension of sand and graphite in kerosene, air was bubbled into the cell, and the sand floated, leaving the graphite still suspended in the cell. This example demonstrates that the process of the present invention can be used to separate sand from graphite, the latter being in a relatively pure state.

*Example 5*

One percent by weight of perfluorooctanoic acid was added to about 600 ml. of kerosene. The acid did not completely dissolve and formed a small bottom phase. The upper phase, containing some of the acid, was then taken up and transferred to a small flotation cell. Fifty grams of sand were added. Air was bubbled into the cell and the sand floated.

*Example 6*

Fifty grams of sand were added to 600 cc. of benzene in a small flotation cell. One gram of perfluorooctanoic acid floated the sand when air was bubbled through the cell.

The process of the present invention can be used to separate inorganic salts which form many hydrates and thus can't be floated from a brine; to separate inorganics or minerals from insoluble organics, such as the separation of sand from graphite or shale from coal fines; to separate catalysts (platinum, etc.) and inorganic salts from the products of organic reactions suspended or dissolved in organic media; to separate expensive minerals; and to separate one type of insoluble organic particle from another type of organic particle.

It is to be understood that the invention is not to be limited to the exact details of operation or the compositions and methods shown and described, as obvious modifications will be apparent to those skilled in the art and the invention is to be limited only by the scope of the appended claims.

Having thus described my invention, what I claim as novel and desire to protect by Letters Patent is as follows:

1. The method which comprises: adding a fluorinated organic compound selected from the group consisting of fluorinated aliphatic acids, amines, alcohols and aldehydes to a miscible non-fluorinated liquid organic medium containing particulate materials, the amount of said fluorinated organic compound being sufficient to render the particulate materials organophobic; floating said particulate materials by bubbling a gas through the organic medium; and separating the particulate materials from the organic medium.



2. The method of claim 1 wherein the liquid organic medium is an aliphatic hydrocarbon.

3. The method of claim 1 wherein the liquid organic medium is kerosene.

4. The method of claim 1 wherein the liquid organic medium is an aromatic hydrocarbon.

5. The method of claim 4 wherein the aromatic hydrocarbon is benzene.

6. The method of claim 1 wherein the fluorinated organic compound is a fluorinated aliphatic carboxylic acid of from 1 to 8 carbon atoms.

7. The method of claim 6 wherein the fluorinated carboxylic acid is perfluorinated.

8. The method of claim 7 wherein the perfluorinated aliphatic carboxylic acid is perfluorobutyric acid.

9. The method of claim 7 wherein the perfluorinated aliphatic carboxylic acid is perfluorooctanoic acid.

10. The method which comprises: adding a fluorinated organic compound selected from the group consisting of fluorinated aliphatic acids, amines, alcohols and aldehydes to a miscible non-fluorinated liquid organic medium containing particulate materials, the amount of said fluorinated organic compound being sufficient to render at least one of said particulate materials organophobic; floating said particulate material by bubbling a gas through the organic medium; and separating the particulate material from the organic medium.

11. The method of claim 10 wherein the liquid organic medium is kerosene and the fluorinated organic compound is perfluorobutyric acid.

12. The method of claim 10 wherein the liquid organic medium is benzene and the fluorinated organic compound is perfluorooctanoic acid.


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