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PROCESS OF CONCENTRATING ORES

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This invention relates to flotation agents and processes of concentrating ores therewith, and it comprises as new flotation agents mixtures of aliphatic nitriles in which nitriles of at least three and not more than ten carbon atoms predominate, it further comprises as flotation agents mixtures of such aliphatic nitriles with aliphatic hydrocarbons, it further comprises as flotation agents those mixtures of nitriles and hydrocarbons obtained from the pyrolysis of fatty acid nitriles containing at least twelve and generally eighteen carbon atoms, and it further comprises processes of concentrating ores wherein finely ground ore is mixed with a water solution of said flotation agents and a concentrate rich in certain constituents of said ore is recovered.

Flotation agents are used in great quantities in the concentration of ores by flotation methods. These agents modify the surface of the desired values in the ore in such a way that the values are floated, leaving the gangue behind. Thus, for example, in the froth flotation of ores an aqueous pulp of the ore is first prepared, flotation agents are added thereto, and the mixture is aerated whereby metalliferous values in the ore collect as a froth which can be readily skimmed off and the metal values therein recovered. Similarly, non-metalliferous values, such as phosphate rock, can be separated from the siliceous gangue.

Oleic acid was one of the first flotation agents used in the froth flotation of ore, and many other flotation agents have since been proposed. Flotation methods require that the surface of the ore values to be floated should be modified with respect to its interfacial tension towards water so that the surface is "preferentially" wetted by water. When froth flotation is employed a frothing agent must also be present to assist in the formation of a relatively stable froth during the aeration. The minute bubbles formed adhere to the surface-modified ore value causing them to rise as a froth.

Oleic acid, fuel oil and other hydrocarbon oils are frequently used as "collectors". These are substances which appear to have a selective action on the values in the ore it is desired to float so that they modify the interfacial tension thereof with respect to water. The frothing substance is commonly a soap. Frequently the flotation agents used are mixtures, the constituents of which perform the two functions just stated; and sometimes a single substance will perform both functions.

There have been many different flotation agents proposed, and of late most of these agents are

synthetically-prepared chemicals such as xanthates. Synthetic flotation agents are quite expensive, and the art has desired more efficient flotation agents which could be prepared at little cost and which would function as flotation agents with most of the ores commercially subjected to this type of concentrating process. Many oxide and carbonate ores, for example, are not readily floated by flotation agents hitherto proposed without some special treatment of the ore prior to concentration.

We have now discovered flotation agents which are suitable for concentrating all of the metalliferous ores commonly subjected to flotation processes and, additionally, will float some of the non-metalliferous ores such as apatite. Our flotation agents work well with all the metalliferous ores hereinafter listed, and by using our agents we are able to commercially concentrate these ores and thus separate them from the siliceous gangue with which they occur in nature. The flotation agents of the present invention have been tested with all of the ores given in the following list and have been found to be satisfactory.

Ore	Value floated
Chalcopyrites.....	CuFeS ₂
Pyrite.....	FeS ₂
Galena.....	PbS
Sphalerite.....	ZnS
Zincite.....	ZnO
Apatite.....	Ca ₃ F(PO ₄) ₃
Malachite.....	CuCO ₃ —Cu(OH) ₂
Chalcocite.....	Cu ₂ S
Rutile.....	TiO ₂

Our flotation agents can be broadly characterized as mixtures of aliphatic nitriles in which the predominating nitriles thereof contain from three to ten carbon atoms. We are not dealing herein with the use of any single pure nitrile, but we are dealing with mixtures containing two or more different nitriles, the molecules of which contain at least three carbon atoms and not more than ten carbon atoms. For example, the flotation agents of the present invention will contain two or more of the following nitriles: propionitrile, butyronitrile, valeronitrile, capronitrile, oenanthonitrile, caprylonitrile, pelargononitrile, and caprinitrile and nitriles of the same carbon chain length containing one double bond. Propionitrile contains three carbon atoms including that in the CN group and caprinitrile contains ten carbon atoms including that in the CN group. These nitriles are also known as aliphatic cyanides. We shall give the name of the cyanide as well so that there

can be no misunderstanding as to the substances which we use. The corresponding cyanides are as follows: ethyl cyanide, propyl cyanide, isopropyl cyanide, butyl cyanide, isobutyl cyanide, amyl cyanide, hexyl cyanide, heptyl cyanide, octyl cyanide and nonyl cyanide. In the description which follows, however, we will refer to our flotation agents as nitriles.

Although we can use the nitrile mixtures alone with advantage, and broadly claim our invention with reference to the use of these substances, we generally have present certain amounts of aliphatic hydrocarbons some of which may be unsaturated. The predominating hydrocarbons will contain from seven to fourteen carbon atoms. Most probably the hydrocarbons act as collecting substances and thus modify the wettability of the floated values in the ore. The best way of preparing our flotation agents is by subjecting higher fatty acid nitriles, namely those containing twelve or more carbon atoms in the molecule, and generally eighteen carbon atoms in the molecule to pyrolysis under conditions which result in a cracking of the high molecular weight nitrile to give reaction products containing lower molecular weight saturated and unsaturated nitriles, namely those having from three to ten carbon atoms in the molecule, together with quantities of saturated and unsaturated straight-chain aliphatic hydrocarbons. Methods of cracking high molecular weight nitriles, for example, stearonitrile, are disclosed in the Ralston, Pool and Harwood Patents Nos. 2,033,536 and 2,033,537. These methods, in general, consist in subjecting stearonitrile to heat and pressure in the liquid phase, or if in vapor phase to heat and a catalyst, and condensing a reaction mixture composed of lower molecular weight nitriles and hydrocarbons. The predominating nitriles in such reaction mixtures will contain from three to ten carbon atoms, and the predominating hydrocarbons will contain from about seven to fourteen carbon atoms. Generally the respective quantities of individual nitriles present in the reaction mixture are about the same. Thus, for example, there may be equal quantities of nitriles containing three, four and five carbon atoms, namely equal quantities of propionitrile, butyronitrile and valeronitrile and their unsaturated analogues. It would serve no useful purpose for us to elaborate upon the methods of making such reaction mixtures since such methods are fully disclosed in the aforesaid patents. Unsaturated nitriles as well as unsaturated hydrocarbons will be present in the reaction mixture.

Although we find it advantageous to use mixtures of "cracked" nitriles which contain hydrocarbons as well, we can, however, first separate the nitriles from the hydrocarbons and thus obtain nitrile mixtures consisting predominately of two or more nitriles substantially free of hydrocarbons. All such mixtures, so long as they contain at least two different nitriles each of which contains at least three and not more than ten carbon atoms, are useful in our process.

We shall now describe specific examples of using our flotation agents for the concentration of metalliferous ores.

For example, we first prepare a nitrile hydrocarbon mixture by cracking stearonitrile and condensing a distillate having a boiling point range of about 105° to 150° C. This mixture contains about equal quantities of nitriles having three, four, five and six carbon atoms. In

other words, about equal quantities of propionitrile, butyronitrile, valeronitrile and capronitriles, as well as their unsaturated analogues, are present. The mixture also contains aliphatic hydrocarbons having seven, eight, nine and ten carbon atoms in the molecule. The relative proportions of these hydrocarbons has not been fully ascertained, and some of them are highly unsaturated.

We next grind the ore, such, for example, as pyrites, zincite, rutile, galena or sphalerite under water to a mesh of about 40 to 100. It is better to avoid large quantities of slime which would result if the grinding is prolonged. The water is then decanted from the ground ore and replaced by an equal volume of an aqueous mixture of the flotation agent. This is advantageously composed of about 150 to 200 parts of the nitrile-hydrocarbon mixture incorporated in about one million parts of water. The pulp is then aerated in the usual way and the froth skimmed off. This froth consists predominantly of metalliferous values in the treated ore.

When we increase the quantity of flotation agent to about 400 to 600 parts per million of water we have no difficulty in concentrating pyrite.

In another example we prepare a nitrile-hydrocarbon mixture having a boiling point range of about 140° to 150° C. This mixture consists of about equal quantities of nitriles having five, six and seven carbon atoms, together with straight-chain hydrocarbons having nine, ten, and eleven carbon atoms. Concentrations of our flotation agents in amounts of 150 to 200 parts per million will float pyrites and chalcopyrite. Concentrations of 400 to 500 parts per million will float malachite and chalcocite. Concentrates of 300 to 600 parts per million will separate zincite, rutile, sphalerite and galena from the siliceous gangue.

From the above examples it will be apparent that the quantity of flotation agent present may have to be varied depending upon the ore treated, and it is to be expected that those skilled in the art will preliminarily determine the best quantity of agent before floating large batches of ore. Likewise the concentration of the ore in the pulp for best results can be readily determined by small scale tests as is usual in this art. We do not, of course, have to vary the present process steps used in flotation methods since our invention deals primarily with new flotation agents and not with any variation in the accepted mechanical handling of the materials.

Similar results are obtained when distillates of mixed nitriles free of hydrocarbons are used, for we have observed that the nitrile mixtures act both as collecting agents and as frothing agents. Probably some of the nitriles in the mixture act more as collectors than as frothers, but we are not able to state just which nitriles are predominantly collectors and which are predominantly frothers.

Although our nitrile mixtures contain chiefly those nitriles having at least three and not more than ten carbon atoms, we do not wish to have our invention so narrowly construed as to exclude small amounts of nitriles having more than ten carbon atoms. We try to avoid the presence of these, but when we prepare our nitriles by cracking stearonitrile and similar high molecular weight nitriles, traces of nitriles having more than ten carbon atoms may be present. Consequently, in the appended claims we define our nitrile flotation agents as comprising predomi-

nantly those nitriles of from three to ten carbon atoms.

Other ways of making the nitriles can, of course, be used, and such ways are described in the literature. But for reasons of economy we prefer to make our flotation agents by subjecting high molecular weight nitriles to pyrolysis.

For some reason not fully understood the mixture of nitriles obtained from the cracking of stearonitrile, and having the boiling point range stated, contains about equal quantities of nitriles of from three to ten carbon atoms. We do not wish to be bound, however, to mixtures of this relative composition, since we can use nitrile mixtures in which the predominating nitrile, for example, is valero, for example, amounting to as much as fifty percent of the mixture, together with smaller amounts or butyro and propionitrile.

Having thus described our invention, what we claim is:

1. In the froth flotation of ores the step which comprises subjecting to froth flotation an aqueous pulp of the ore containing a mixture of saturated and unsaturated aliphatic nitriles in which nitriles having at least three and not more than ten carbon atoms predominate.

2. In the froth flotation of ores the step which comprises subjecting to froth flotation an aqueous pulp of the ore containing a mixture of saturated

and unsaturated aliphatic nitriles and hydrocarbons in which nitriles having at least three and not more than ten carbon atoms predominate and in which the predominating hydrocarbons are straight-chain aliphatic hydrocarbons having from about seven to fourteen carbon atoms.

3. The process as in claim 2 wherein the mixture of nitriles and hydrocarbons corresponds substantially to that obtained by subjecting high molecular weight nitriles having from twelve to eighteen carbon atoms to pyrolytic cracking.

4. The process as in claim 2 wherein the mixture of nitriles and hydrocarbons has a boiling point range of about 105° C. to about 150° C.

5. The process as in claim 2 wherein the mixture of nitriles and hydrocarbons has a boiling point range of about 140° C. to about 150° C.

6. In the froth flotation of ores the step comprising concentrating the ore by froth flotation in the presence of a mixture of saturated and unsaturated aliphatic nitriles containing three, four, five and six carbon atoms.

7. In the froth flotation of ores, the step comprising concentrating the ore by froth flotation in the presence of a mixture of saturated and unsaturated aliphatic nitriles containing five, six, seven and eight carbon atoms.

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