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PROCESS OF CONCENTRATING ORES

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This invention relates to processes of concentrating ores, and it comprises processes of concentrating ores by flotation methods, such as froth flotation, wherein an aqueous pulp of the ore is separated into a concentrate high in mineral values in the presence of mixtures of alkali metal salts of straight-chain saturated and unsaturated aliphatic carboxylic acids containing at least three and not more than ten carbon atoms and a mixture of straight-chain saturated and unsaturated aliphatic hydrocarbons having from five to fourteen carbon atoms.

In our co-pending application Serial No. 141,874 filed May 10, 1937, we have described flotation agents comprising mixtures of saturated and unsaturated aliphatic carboxylic acids containing from three to ten carbon atoms and saturated and unsaturated aliphatic straight-chain hydrocarbons of low molecular weight containing from about five to fourteen carbon atoms. Said mixtures, when added to an aqueous ore pulp, will float the following minerals: Pyrolusite, malachite, chalcopyrite, chalcocite, galena, rutile, franklinite, apatite, ilmenite, zincite, magnetite, and pyrite when the amount of flotation agent is about 300 parts per million of aqueous ore pulp.

We have now discovered that even better results are obtained when such flotation agent, namely a mixture of saturated and unsaturated carboxylic acids and hydrocarbons, is added to the ore pulp and the aliphatic carboxylic acids therein converted to alkali metal salts prior to subjecting the ore pulp to froth flotation. Consequently, in accordance with the present invention, the mineral values in the ore are separated from the gangue in the presence of straight-chain saturated and unsaturated hydrocarbons having from five to fourteen carbon atoms and alkali metal salts of saturated and unsaturated aliphatic carboxylic acids having from three to ten carbon atoms. Although the flotation agents of the aforesaid application are entirely suitable for most purposes, we find that in many cases better results are obtained when the carboxylic acids of said flotation agents are converted to alkali metal salts. Thus, for example, in addition to the ores given above we can float, by processes of the present invention, sphalerite, collophanite and magnetite. This means that by the processes of the present invention we can concentrate phosphate minerals such as collophanite. Hitherto relatively few flotation agents have been found suitable for the flotation of the phosphate ores.

The flotation agents which we use in the present invention are best prepared by hydrolyzing mixtures of nitriles and hydrocarbons obtained as a condensate when higher fatty acid nitriles, such as stearonitrile and lard fatty acid nitriles, are subjected to pyrolytic decomposition. The nitriles in such a mixture will contain from three to ten carbon atoms and, when hydrolyzed with caustic soda or potassium hydroxide, these nitriles are converted to alkali metal salts of the corresponding fatty acids. Proprionitrile yields, on hydrolysis with caustic soda, the sodium salt of propionic acid and the other nitriles in the mixture are likewise converted to sodium or potassium salts of their carboxylic acid equivalents.

In order that our invention may be clearly understood we shall first briefly outline the preparation of such nitrile-hydrocarbon mixtures. Methods of obtaining these are described and claimed in the Ralston, Pool and Harwood Patents 2,033,536 and 2,033,537. These methods in general consist in subjecting high molecular weight nitriles, for example, stearonitrile, palmitonitrile, or large fatty acid nitriles to pyrolytic conditions resulting in the formation of a condensate containing lower molecular weight nitriles and aliphatic straight-chain hydrocarbons. The high molecular weight nitriles can be "cracked" in liquid phase or in vapor phase in the presence of a catalyst. When, for example, stearonitrile is subjected to liquid phase cracking the condensed reaction product obtained is a pale yellow liquid comprising a mixture of saturated and unsaturated nitriles, together with saturated and unsaturated straight-chain hydrocarbons. This nitrile mixture can contain nitriles having from three to ten carbon atoms and hydrocarbons, both saturated and unsaturated, having from five to ten carbon atoms.

The entire mixture obtained as a condensate can then be directly hydrolyzed by admixing it with caustic soda or caustic potash of about twenty percent concentration and heating the mixture in an autoclave or bomb until all the nitriles therein have been converted to sodium or potassium salts of the corresponding aliphatic acids. The hydrolyzate consists of an aqueous solution of the said salts admixed with the hydrocarbons. To the aqueous mixture we then add a mineral acid, such as sulfuric or hydrochloric, to decompose the aliphatic carboxylic acid salts thus liberating the corresponding free fatty acids which at once dissolve in the hydrocarbon portions of the mixture. The hydrocarbon solution of free carboxylic acids is then sep-

arated from the aqueous layer by simple stratification.

This hydrocarbon solution will on the average contain about fifty percent saturated and unsaturated carboxylic acids, the remainder being saturated and unsaturated hydrocarbons having from five to fourteen carbon atoms. The hydrocarbons, however, are straight-chain hydrocarbons and about equal amounts of pentane, pentene, hexane, hexene, heptane, heptene, octane, octene, nonane, nonene, decane and decene will be present. The position of the double bond has not been established but we have evidence indicating that it is terminal. About equal amounts of saturated and unsaturated aliphatic carboxylic acids having three, four, five, six, seven, eight, nine and ten carbon atoms are present. In other words, these acids extend from propionic to capric.

This mixture of carboxylic acids and hydrocarbons is then added to an aqueous pulp of the mineral to be concentrated in proportions of about 150 to 300 parts of the mixture to about one million parts of water. The carboxylic acids are next converted to their corresponding alkali metal salts, more usually the sodium salts, but we can convert them to potassium salts, by adding just enough caustic soda or caustic potash to neutralize the acids. We then subject the ore pulp to froth flotation in the usual way and in accordance with accepted practise, finally skimming off a concentrate of the desired mineral value as a froth.

When hydrolyzing the mixture of nitriles and hydrocarbons we can use varying amounts of caustic soda or caustic potash solution of from ten to twenty percent strength. Generally we admix about equal quantities of the nitrile-hydrocarbon mixture and caustic soda of the said strength and heat the mixture in a bomb or autoclave to a temperature of about 200° C. to insure that all of the nitriles are hydrolyzed to carboxylic acid salts.

The above description will indicate the general methods we employ for converting the nitrile-hydrocarbon mixtures to hydrocarbon solutions of aliphatic carboxylic acids. There are numerous variations in the ultimate composition of the hydrocarbon solution of carboxylic acids possible. The entire condensate obtained when the higher nitriles are cracked will contain saturated and unsaturated nitriles containing from three to ten carbon atoms. By prolonging the cracking, however, nitriles having from eight to ten carbon atoms are further decomposed into hydrocarbons and nitriles having less than eight carbon atoms. Consequently, the composition of the hydrocarbon solution of aliphatic carboxylic acids which we add to the ore pulp and then neutralize with alkali can be varied by variations in the extent to which the higher nitriles are cracked.

Or we can first condense a cracked condensate containing nitriles having three to ten carbon atoms and then fractionally distil such a mixture to obtain fractions in which nitriles of three, four and five carbon atoms predominate, or fractions in which four, five and six carbon atom nitriles predominate. For example, that fraction of nitriles and hydrocarbons boiling from 40° C. to 110° C. will consist mostly of capronitrile and its unsaturated analogues and low boiling hydrocarbons. We can subject such a distillate to hydrolysis, recover a hydrocarbon solution of the free aliphatic carboxylic acids, namely mostly pentanoic and pentenoic acids and hydrocarbons consisting mostly of pentane, pentene, hexane, hexene and heptane and heptene. When we add such a hydrocarbon solution to an aqueous pulp or slurry of any of the above-listed ores, neutralize the carboxylic acids with caustic soda, and then aerate, we are subjecting such an ore to froth flotation in the presence of sodium salts of hexanoic and hexenoic acids and low boiling saturated and unsaturated straight-chain hydrocarbons.

Or we can hydrolyze another fraction having a boiling point range of about 110° C. to 175° C. Such a nitrile-hydrocarbon fraction will consist mostly of capronitrile and oenanthonitrile and their unsaturated analogues, together with saturated and unsaturated hydrocarbons. When this mixture is hydrolyzed we ultimately recover a hydrocarbon solution of hexanoic, hexenoic, heptanoic, and heptenoic acids, together with straight-chain saturated and unsaturated hydrocarbons, such as octane, octene, nonane, nonene and small amounts of decane and decene. That solution, when added to an ore pulp and neutralized with caustic soda, gives us a mixture of ore pulp containing sodium salts of hexanoic, hexenoic, heptanoic and heptenoic acids, and the above-stated hydrocarbons.

In similar ways we can prepare hydrocarbon solutions containing any aliphatic acid, or any quantity thereof in which the aliphatic acid contains from three to ten carbon atoms.

In broad aspects then, our process comprises subjecting the mineral values in ores to concentration by flotation in the presence of small amounts of alkali metal salts of at least one unsaturated aliphatic carboxylic acid having from three to ten carbon atoms and aliphatic saturated and unsaturated straight-chain hydrocarbons having from five to fourteen carbon atoms. We believe that hydrocarbons which we add to the ore pulp have some specific action on the mineral values to be floated so that the surfaces of the mineral values become more readily wetted by water. The aliphatic carboxylic acid salts, in the presence of the hydrocarbons, appear to function as good frothing agents, although, in the absence of the hydrocarbons the frothing qualities are not so pronounced. In any event, we have noted as an observed fact that the above-listed minerals can all be separated by froth flotation processes in the presence of our mixtures of alkali metal salts of aliphatic carboxylic acids and hydrocarbons.

Instead of making our flotation agents from distillates obtained in the cracking of high molecular weight nitriles we can, of course, prepare hydrocarbon solutions of saturated and unsaturated aliphatic carboxylic acids prepared in other ways, add such a solution to the aqueous ore pulp, neutralize with caustic soda, and subject to froth flotation. Even number carbon atom chain carboxylic acids are not abundant in nature and those containing an odd number of carbon atoms, with the exception of valeric acid, are extremely rare. Those containing one double bond do not occur naturally. The synthesis of this mixture would be very costly and difficult and, consequently, the cheapest source thereof is the product obtained from cracking higher molecular weight nitriles. We can, for example, separate the nitriles from the nitrile-hydrocarbon distillates obtained, fractionally distil the nitriles to obtain individual nitriles, and then convert these to the corresponding aliphatic carboxylic acid. Having isolated the separate acids

we can then make up mixtures of straight-chain hydrocarbons of the class described and mixtures of one or more of the aliphatic carboxylic acids.

But for commercial purposes we find it best to directly hydrolyze a nitrile-hydrocarbon distillate containing nitriles corresponding to the carboxylic acids we wish to add to the ore pulp and convert to alkali metal salts.

Having thus described our invention, what we claim is:

1. The method of froth concentrating ores which comprises admixing with an aqueous ore pulp a small amount of a mixture of straight-chain saturated and unsaturated aliphatic hydrocarbons containing from five to fourteen carbon atoms and at least one unsaturated aliphatic carboxylic acid having from three to ten carbon atoms, adding an alkali solution to the pulp to convert said carboxylic acid to an alkali metal salt thereof, and then separating a concentrate rich in the desired mineral values.

2. The process of separating ores by froth flotation which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a mixture of saturated and unsaturated aliphatic straight-chain hydrocarbons having from five to fourteen carbon atoms and at least one alkali metal salt of an unsaturated aliphatic carboxylic acid having from three to ten carbon atoms.

3. The process of froth concentrating ores which comprises adding to an aqueous pulp of the ore a mixture composed of saturated and unsaturated aliphatic straight-chain hydrocarbons containing from five to fourteen carbon atoms and at least one unsaturated aliphatic carboxylic acid having from three to ten carbon atoms, converting said aliphatic carboxylic acid to an alkali metal salt thereof, and then aerating the solution.

4. The process as in claim 1 wherein the alkali metal salt is a sodium salt.

5. The process as in claim 2 wherein the alkali metal salt is a sodium salt.

6. The process as in claim 3 wherein the alkali metal salt is a sodium salt.

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