Patented Mar. 7, 1939

2,149,546

UNITED STATES PATENT OFFICE

2,149,546

FLOTATION AGENTS AND PROCESS OF CONCENTRATING ORES THEREWITH

Anderson W. Ralston and William O. Pool, Chicago, Ill., assignors to Armour and Company, Chicago, Ill., a corporation of Illinois

No Drawing. Application May 7, 1937, Serial No. 141,374

6 Claims. (Cl. 209—166)

This invention relates to flotation agents and processes of concentrating ores therewith, and it comprises as new flotation agents mixtures of straight-chain saturated and unsaturated aliphatic carboxylic acids in which the predominating fatty acids therein contain at least five and not more than ten carbon atoms, it further comprises as flotation agents those fatty acid mixtures resulting from the hydrolysis of nitriles obtained by cracking high molecular weight nitriles, such as stearonitrile, and it further comprises processes wherein finely-ground ore is mixed with a water solution of said flotation agents, and a concentrate rich in the desired ore value separated therefrom.

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.

In the Harwood and Pool co-pending application, S. N. 139,611, filed April 28, 1937, there are described flotation agents comprising nitriles having from three to ten carbon atoms such, for example, as propionitrile, butyronitrile, valeronitrile and others. We have now discovered another class of flotation agents which can be made from these nitriles and which are especially advantageous when used to float, as by froth flotation methods, the following minerals: pyrolusite, malachite, chalcopyrite, chalcocite, galena, rutile, franklinite, apatite, and ilmenite.

The flotation agents of the present invention can be broadly characterized as mixtures of saturated and unsaturated straight-chain aliphatic carboxylic acids in which acids having from five to ten carbon atoms predominate. Thus our flotation agents will contain two or more of the following acids: pentanoic, pentenoic, hexanoic, hexenoic, octanoic, octenoic, nonanoic, nonenoic, decanoic and decenoic acids. The double bond in unsaturated acids is usually in the terminal position. We believe that the very effective flotation properties of this mixture of acids are due to the presence of the unsaturated low chain acids when associated with the low chain saturated acids.

These acid mixtures are most conveniently prepared from their corresponding nitriles by subjecting mixtures of nitriles having from five to ten carbon atoms in the molecule thereof to alkaline hydrolysis in ways well known for the preparation of carboxylic acids from the corresponding nitriles. The nitrile starting mixture is best prepared by subjecting high molecular weight fatty acid nitriles, namely those nitriles having from twelve to eighteen carbon atoms, to pyrolytic decomposition or cracking in accordance with processes described in the Ralston, Pool and Harwood Patent Nos. 2,033,536 and 2,033,537. These methods in general consist in subjecting a higher fatty acid nitrile, such as stearonitrile, lard fatty acid nitriles and the like to heat in the liquid phase, or to heat and a catalyst in the vapor phase and condensing a

distillate composed of lower molecular weight nitriles and hydrocarbons. As stated in said patents, the reaction products from such pyrolytic cracking consist of saturated and unsaturated nitriles having from three to ten carbon atoms, together with quantities of saturated and unsaturated straight-chain hydrocarbons.

Having first prepared a mixture of nitriles and hydrocarbons in the manner stated we can then subject the entire mixture to alkaline hydrolysis by mixing with it caustic soda solution having about ten to twenty percent strength and heating the mixture under 50 pounds pressure for about 30 minutes in a suitable autoclave. The alkali converts the nitriles present to sodium salts of acids corresponding to the nitrile. These sodium salts are soluble in water whereas the hydrocarbons in the original starting mixture are not. Consequently, we can readily separate off the upper layer of hydrocarbons. To the lower layer of aqueous sodium salt solution of the aliphatic acids we then add hydrochloric or sulfuric acid to decompose the sodium salts and liberate the free carboxylic acid. The acids which we obtain are but slightly soluble in water and the layer of free acids can readily be removed from the aqueous layer. Although these acids are but slightly soluble in water such small amounts thereof are used in the actual flotation of the ore that these small amounts readily dissolve in the aqueous ore pulp. In the preparation of the acids, however, the amount of water present is insufficient to dissolve material quantities of the acids.

The nitrile starting mixture which we use contains nitriles having from five to ten carbon atoms. This corresponds to a cracked nitrile mixture containing constituents having a boiling point range of about 140° to 240° C. Since valeronitrile boils at 141° and caprinitrile at 236° C. a distillate from this source having this boiling point range will contain nitriles which when hydrolyzed will yield a mixture of saturated and unsaturated carboxylic acids having from five to ten carbon atoms. The percentage of acids containing one double bond will be approximately fifty percent and the amount of acids of different carbon lengths will be approximately equal. In other words, equal quantities of the different aliphatic acids are present therein.

Other mixtures of carboxylic acids can be prepared in like manner. When we wish to prepare a mixture consisting predominantly of C_5 and C_6 acids, that is the pentanoic, pentenoic, hexanoic and hexenoic acids, we first obtain a nitrile distillate having constituents boiling between about 140° and 160° C. since within that range the corresponding nitriles are present. Such a mixture, when subjected to hydrolysis, as stated, will yield a carboxylic acid mixture consisting predominantly of the above-mentioned acids. When we wish to make a flotation agent containing mostly C_5 and C_8 acids, inclusive, we condense a nitrile mixture having constituents boiling at 163° to 199° C. In similar ways we can prepare nitrile mixtures which, upon hydrolysis, will yield carboxylic acid mixtures having any desired acids from five to ten carbon atoms and approximately fifty percent of which will contain one double bond.

Or we can first separate the nitriles from the hydrocarbons in the cracked reaction products obtained from cracking stearonitrile or similar high molecular weight nitriles. Such methods of separating the nitrile from the hydrocarbons are disclosed in the co-pending application of William O. Pool, S. N. 100,763, filed September 14, 1936. That method consists in subjecting the mixture of aliphatic nitriles and hydrocarbons to the action of a solid adsorbent which will preferentially adsorb the nitriles. The nitriles can then be recovered from the adsorbent. Or the nitriles can be extracted from their mixture with the hydrocarbons by means of preferential solvents as described in the co-pending application of Ralston and Pool, S. N. 89,850, filed July 9, 1936.

Thus, for example, we can first condense a distillate containing nitriles having five, six and seven carbon atoms, together with hydrocarbons. We subject this distillate to treatment for the separation of the nitriles therein, and then hydrolyze the separated nitriles to give us a carboxylic acid mixture containing such acids as pentanoic, pentenoic, hexanoic and hexenoic. Or we can condense another cracked nitrile distillate having a boiling point range which will include nitriles of six, seven and eight carbon atoms, separate the nitriles from the hydrocarbons and subject the nitrile mixture to hydrolysis.

From the foregoing it will be apparent that we can prepare mixtures of carboxylic acids having any desired composition by first starting with stearonitrile, lard fatty acid nitriles or other high molecular weight nitriles. Although our invention is broad enough to include making the carboxylic acids in other ways we know of no way which is as simple and as economical as that described. Our flotation agents are unusual in that they are mixtures of saturated and unsaturated straight-chain carboxylic acids containing both odd and even numbered carbon chains. Unsaturated low chain acids and odd carbon atom chain acids are quite rare and with the exception of valeric do not occur in nature.

In broad aspects then, our invention comprises the concentration of ores by flotation methods in which to the ore pulp we add small amounts of a carboxylic acid mixture in which acids having from five to ten carbon atoms predominate and in which approximately fifty percent of the acids present contain one double bond. One such mixture may contain equal parts of pentanoic, pentenoic, hexanoic and hexenoic acids; another may contain equal parts of nonanoic, nonenoic, decanoic and decenoic acids. Still another may contain fifty percent by weight of pentanoic and pentenoic acids, forty percent by weight of hexanoic and hexenoic acids and ten percent by weight of octanoic and octenoic acids. Mixtures can, of course, be made readily by first hydrolyzing a mixture of nitriles containing saturated and unsaturated nitriles from five to ten carbon atoms in length, recovering the mixed free carboxylic acids, fractionally distilling the mixed acids to obtain substantially pure free fatty acids and then preparing flotation agents containing any desired proportion of two or more acid mixtures.

Our flotation agents are used in substantially the same way as other flotation agents are used in the concentration of ores. In accordance with accepted procedure in this art the ground ore, which should not be ground too fine because slimes are objectionable, is admixed with water containing a flotation agent to form a slurry or pulp which is then aerated in ways well known and the froth of mineral concentrate skimmed off.

The amount of flotation agents present can be varied over fairly wide limits. Usually we employ from about 150 to about 300 parts of flota-

tion agent per million parts of water. The amount of water solution with respect to the ore is, of course, sufficient to give a pulp which can be readily aerated, and the requirements as to this are well understood in the art.

Thus, for example, we prepare a ground mixture of galena and gangue, add thereto sufficient water solution containing about 240 parts per million of the flotation agent, and subject the pulp to froth flotation. We are able to obtain concentrates high in galena. All of the other minerals mentioned above are floated in the same general way.

Some minerals will require more than about 240 parts per million of the flotation agent and others may require less. All of the minerals given above can be floated satisfactorily when the amount of flotation agent is 240 parts per million, but other minerals may possibly require variation in this specific amount. It is presumed that those skilled in the art will test small batches of minerals prior to subjecting large quantities to flotation. The flotation agents of the present invention are somewhat specific in their action. When but 240 parts per million of water are used they will not float the following minerals: celestite, cassiterite in pegmatite, corundum, zincite, collophanite, pyrite, magnetite, and sphalerite. Consequently, our flotation agents permit the separation of zincite, for example, from galena should such minerals be present in the same ore.

Although our flotation agents consist primarily of two or more carboxylic acids containing from five to ten carbon atoms we do not wish to have our invention so narrowly construed as to exclude small amounts of carboxylic acids having less than five carbon atoms. We try to avoid the presence of these, but frequently the nitrile mixture subjected to hydrolysis will contain small amounts, perhaps five percent, of nitriles having three carbon atoms and which will yield carboxylic acids having three carbon atoms on hydrolysis. Consequently, in the appended claims we define our flotation agents as comprising predominantly those aliphatic carboxylic acids of from five to ten carbon atoms.

We find that our acid mixtures are extremely more effective as flotation agents than substantially pure acids. They are quite superior, for example, to caprylic or capric acid. We attribute their superior action to the presence of odd carbon chain acids and especially to the presence of unsaturated acids. These unsaturated acids, we find, possess dispersing properties which differ materially from saturated acids of the same chain length. The presence of the double bond in the carbon chain probably modifies the adsorption phenomena. When such acids are associated with saturated acids the mixture possesses quite superior flotation properties. These unusual results are possibly best explained by reference to surface tension phenomena. The combined effect of the mixed saturated and unsaturated acids is much more than merely additive and minerals can be floated by this mixture which cannot be separated by the pure acids themselves or by mixtures of these saturated acids. Thus pentanoic, pentenoic, hexanoic and hexenoic acids will produce better results than either of the saturated acids alone or a mixture of the two saturated acids.

Consequently, our invention is directed to the use of a mixture of saturated and unsaturated acids of between five and ten carbon atom chain lengths.

In the specific examples given above the composition of the flotation agents used is such that about equal quantities of pentanoic, pentenoic, hexanoic, hexenoic, heptanoic, heptenoic, octanoic, octenoic, nonanoic, nonenoic, decanoic and decenoic acids are present. When this mixture is used maximum flotation is obtained.

The cracked nitrile mixtures we hydrolyze yield acid mixtures containing approximately fifty percent of unsaturated acids. We do not, however, want to be limited to these exact proportions. If the acid mixture contains 20 percent or more of unsaturated acids it is effective. For reasons of economy we prefer to use the hydrolyzed nitrile mixtures and these inherently contain about 40 to 60 percent, usually about 50 percent of unsaturated acids.

Although we have more specifically described our invention with reference to the use of our flotation agents as the predominating flotation agent used, we can, of course, add additional agents to the ore pulp to assist in flotation. For example, we can use fuel oil, soaps, and similar agents in addition to the mixed aliphatic acids described.

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 carboxylic acids in which acids having at least five and not more than ten carbon atoms predominate.

2. In the froth flotation of ores, the step comprising subjecting the ore to froth flotation in the presence of a mixture of saturated and unsaturated aliphatic carboxylic acids containing acids having five, six, seven, eight, nine and ten carbon atoms.

3. A flotation agent comprising a mixture of saturated and unsaturated aliphatic carboxylic acids in which acids having from five to ten carbon atoms predominate.

4. A flotation agent comprising a mixture of aliphatic carboxylic acids obtained from the hydrolysis of a mixture of nitriles resulting from the cracking of stearo-nitrile.

5. A flotation agent comprising a mixture of at least two organic acids chosen from the group consisting of pentanoic, pentenoic, hexanoic, hexenoic, heptanoic, heptenoic, octanoic, octenoic, nonanoic, nonenoic, decanoic or decenoic acids, one of which is unsaturated.

6. In the froth flotation of ores, the step comprising subjecting the ore to froth flotation in the presence of at least two organic acids chosen from the group consisting of pentanoic, pentenoic, hexanoic, hexenoic, heptanoic, heptenoic, octanoic, octenoic, nonanoic, nonenoic, decanoic or decenoic acids, one of which is unsaturated.

ANDERSON W. RALSTON.
WILLIAM O. POOL.