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PROCESS OF CONCENTRATING ORES AND
FLOTATION AGENTS THEREFORAnderson W. Ralston and William O. Pool, Chi-
cago, Ill., assignors to Armour and Company,
Chicago, Ill., a corporation of IllinoisNo Drawing. Application May 10, 1937, Serial No.
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6 Claims. (Cl. 209—166)

This invention relates to processes of concen-
trating ores and flotation agents thereof, and it
comprises processes wherein an aqueous pulp of
the ore, the mineral values of which are to be
5 separated from the gangue, are subjected to flota-
tion processes in the presence of a flotation agent
comprising mixtures of saturated and unsatu-
rated aliphatic carboxylic acids containing from
about five to ten carbon atoms associated with
10 low molecular weight straight-chain saturated
and unsaturated aliphatic hydrocarbons, said
flotation agent advantageously being prepared by
subjecting mixtures of aliphatic nitriles and such
hydrocarbons to hydrolysis and the recovery of
15 mixtures of such aliphatic carboxylic acids dis-
solved in said hydrocarbons.

Flotation agents are used in great quantities in
the concentration of ores by flotation methods.
These agents modify the surface of the desired
20 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
25 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. Flota-
tion methods require that the surface of the ore
values to be floated should be modified with re-
35 spect to its interfacial tension towards water so
that the surface is "preferentially" wetted by
water. When froth flotation is employed a froth-
ing agent must also be present to assist in the for-
mation of a relatively stable froth during the
40 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
45 substances which appear to have a selective ac-
tion on the values in the ore it is desired to float
so that they modify the interfacial tension there-
of with respect to water. The frothing substance
is commonly a soap. Frequently the flotation
50 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
55 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
5 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
10 to concentration.

In the Ralston, Pool and Harwood Patents
2,033,536 and 2,033,537 there are described meth-
ods of pyrolytically decomposing high molecular
weight nitriles, such as stearo-nitrile, palmito-
15 nitrile, lard fatty acid nitriles and the like, where-
by distillates containing mixtures of lower molec-
ular weight nitriles and hydrocarbons are ob-
tained. Thus, for example, from stearonitrile
there can be obtained a condensate boiling from
20 40° C. to about 275° C. which can be fractionated
to give distillates having any desired boiling point
range within the above upper and lower limits,
and by fractionation of the said condensate frac-
tions or cuts containing two or more nitriles hav-
25 ing from three to ten carbon atoms can be readily
obtained.

For example, when stearonitrile is heated at a
cracking temperature under pressure the con-
densate is a pale yellow liquid containing a mix-
30 ture of saturated and unsaturated nitriles associ-
ated with liquid hydrocarbons. This condensate,
when fractionated, yields the following fractions,
assuming the starting mixture is 100 parts of con-
densate.

25 parts fraction	1 boiling range	40° C.—110° C.	
25 parts fraction	2 boiling range	110° C.—175° C.	
25 parts fraction	3 boiling range	175° C.—220° C.	
20 parts fraction	4 boiling range	220° C.—275° C.	40
5 parts residue	boiling range	above 275° C.	

Fraction 1 is mostly capronitrile and low boll-
ing hydrocarbons. Fraction 2 is mostly enantho-
nitrile and capronitrile together with saturated
and unsaturated hydrocarbons. Fraction 3 is
45 mostly pelargonitrile, caprylonitrile, enantho-
nitrile, saturated and unsaturated hydrocarbons.
Fraction 4 is mostly lauronitrile, undecylonitrile,
caprinitrile, pelargonitrile, saturated and unsatu-
rated hydrocarbons. Each fraction contains an
50 amount of unsaturated nitriles equivalent to the
saturated nitriles present and an amount of un-
saturated hydrocarbons equivalent to the satu-
rated. In other words, they contain approxi-
mately fifty percent unsaturated compounds. 55

There may also be present small amounts of propionitrile, butyronitrile and valeronitrile.

When the starting material is an unsaturated nitrile the condensate will be higher in unsaturated nitriles and hydrocarbons than when the starting material is a saturated nitrile.

We have now discovered that when mixtures containing aliphatic nitriles of from three to ten carbon atoms, together with aliphatic hydrocarbons are subjected to hydrolysis, and the hydrolyzate is treated with a mineral acid we can obtain a hydrocarbon solution of aliphatic carboxylic acids corresponding to the nitriles in the starting mixture, and that such mixture of acids and hydrocarbons is a markedly suitable flotation agent for concentrating many ores.

Thus, for example, when we wish to make our flotation agent from the mixture of nitriles and hydrocarbons we prepare a mixture of caustic soda solution, about 20 percent strength, and the hydrocarbon solution of nitriles and subject the entire mixture to an elevated temperature in an autoclave or bomb. Thus we first isolate a nitrile-hydrocarbon mixture having a boiling point range of 100° C. to 200° C. 2,500 parts by weight of this nitrile-hydrocarbon mixture is mixed with 2,000 parts by weight of a 20 percent solution of sodium hydroxide. The mixture is heated at about 200° C. in a closed vessel, such as autoclave or bomb, until all of the nitriles therein are converted to sodium salts of aliphatic acids corresponding to the nitriles present. Thus, for example, valeronitrile is converted to sodium pentanoate. Caprylonitrile is converted to sodium octanoate. The reaction mixture withdrawn from the autoclave is, therefore, a mixture of the hydrocarbons in the original nitrile starting mixture and an aqueous solution of sodium salts of aliphatic carboxylic acids. To this reaction mixture we add a mineral acid, such as sulfuric or hydrochloric acid, to liberate free aliphatic carboxylic acids from their sodium salts. These aliphatic carboxylic acids are highly soluble in the hydrocarbons present in the mixture and readily dissolve therein. In a sense the hydrocarbons present can be looked upon as an extraction agent for the aliphatic carboxylic acids. We then shake or otherwise agitate the mixture of aliphatic acids, water solution, and hydrocarbons so that solution of the aliphatic acids in the hydrocarbon layer is facilitated, and thereafter we allow the hydrocarbon layer to stratify and decant a hydrocarbon solution of aliphatic carboxylic acids. It is this product which we use as a flotation agent in our process.

The composition of the carboxylic acid-hydrocarbon mixture can vary over wide limits depending largely upon the boiling point range of the nitrile-hydrocarbon mixture subjected to hydrolysis. By appropriate fractionation of the reaction products obtained from cracking higher aliphatic nitriles, namely those containing eighteen carbon atoms on the average, it will be apparent that we can obtain mixtures of nitriles and hydrocarbons wherein the predominating nitriles contain from three to ten carbon atoms, and the hydrocarbons contain from five to ten carbon atoms. Approximately fifty percent of the nitriles and hydrocarbons present will contain one double bond and we believe that the double bond is in a terminal position.

Thus, by condensing various fractions of nitrile-hydrocarbon mixtures and subjecting these to hydrolysis we are able to obtain final reaction products consisting of at least one aliphatic car-

boxylic acid having from three to ten carbon atoms dissolved in an aliphatic straight-chain hydrocarbon containing from five to fourteen carbon atoms. Our flotation agents will contain two or more saturated or unsaturated aliphatic carboxylic acids dissolved in a mixture of hydrocarbons. This is because the nitrile mixtures which we hydrolyze will almost always contain at least two nitriles because it is very difficult to separate, by distillation, a saturated nitrile from an unsaturated nitrile containing the same number of carbon atoms.

Thus, in broad aspects, our flotation agents comprise hydrocarbon solutions of at least two aliphatic carboxylic acids containing from three to ten carbon atoms, at least one of said acids being unsaturated.

The flotation agents of the present invention can be used to concentrate by froth flotation methods any of the following minerals from ores containing the same.

Pyrolusite	Franklinite
Malachite	Apatite
Chalcopyrite	Ilmenite
Chalcocite	Zincite
Galena	Magnetite
Rutile	Pyrite

When using our flotation agents we proceed in the accepted ways of this art. Namely, we first prepare a ground-up mixture of the ore, avoiding the presence of large quantities of slime. Ordinarily the ore is ground to a mesh of about 40 to 100 and then admixed with water to form a pulp in the usual way. To this pulp we add our flotation agents in proportions of about 150 to 300 parts by weight of flotation agent to one million parts by weight of the water. The mixture is then subjected to froth flotation in the usual way and a mineral concentrate skimmed off as a froth.

Thus, for example, we prepare our flotation agent by hydrolyzing a nitrile hydrocarbon mixture having a boiling point range of from 100° C. to 200° C., acidify the hydrolyzate, and separate off a hydrocarbon solution containing saturated and unsaturated aliphatic carboxylic acids having three to eight carbon atoms. As a general rule, about equal quantities of aliphatic acids containing three, four, five, six, seven and eight carbon atoms and their unsaturated analogues will be present. In other words, these acids will contain about equal quantities of propionic acid and other acids in the series up to and including caprylic (octanoic). The hydrocarbons present will have five to ten carbon atoms. We add about 300 parts per million of such a mixture to the ground aqueous pulp of pyrolusite, aerate the pulp in the usual way and skim off the froth of concentrated pyrolusite.

So far as we are aware we are the first to describe mixtures of saturated and unsaturated aliphatic carboxylic acids having from three to ten carbon atoms dissolved in straight-chain saturated and unsaturated hydrocarbons, and we broadly claim our invention with respect thereto. This mixture is superior for the flotation of both metallic and non-metallic ores because of the presence of both saturated and unsaturated straight-chain acids. In the presence of the olefins and paraffins the mixture performs the double function of preferentially wetting minerals to be floated whereby its surface tension with respect to water is so changed that the mineral will float, together with imparting frothing

characteristics to the pulp. Consequently, we need not add any additional frothing agent, but our invention is not to be construed so narrowly as to exclude the addition of further floating agents and frothing agents should such be desired.

Having thus described our invention, what we claim is:

1. The process of concentrating ores which comprises subjecting the ore to froth flotation separation in the presence of a mixture of saturated and unsaturated aliphatic carboxylic acids having from three to ten carbon atoms and saturated and unsaturated aliphatic straight-chain hydrocarbons.

2. The process of concentrating ores, which comprises subjecting the ore to froth flotation separation in the presence of a mixture of saturated and unsaturated aliphatic carboxylic acids having from three to ten carbon atoms and saturated and unsaturated aliphatic straight-chain hydrocarbons, said mixture being derived from a mixture of aliphatic nitriles and hydrocarbons resulting from the pyrolytic decomposition of aliphatic nitriles having eighteen carbon atoms.

3. In the froth flotation of ores the step comprising subjecting an aqueous pulp of the ore to froth flotation in the presence of a flotation agent comprising an admixture of at least one unsaturated aliphatic carboxylic acid having from three to ten carbon atoms and saturated and unsaturated straight-chain aliphatic hydrocarbons having from five to fourteen carbon atoms.

4. In the froth flotation of ores the step which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a flotation agent comprising the product of hydrolyzing a mixture of aliphatic nitriles containing from three to ten carbon atoms and straight-chain aliphatic hydrocarbons.

5. A flotation agent comprising an aliphatic hydrocarbon solution of saturated and unsaturated aliphatic carboxylic acids having from three to ten carbon atoms.

6. A flotation agent comprising an aliphatic hydrocarbon solution of at least one unsaturated aliphatic carboxylic acid having from three to ten carbon atoms.

ANDERSON W. RALSTON.
WILLIAM O. POOL.