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FLOTATION PROCESS

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This invention relates to the flotation of ores and in particular it relates to a flotation process involving the use of an oil as a flotation aid together with a frothing agent.

One object of the invention relates to a flotation process for ores involving the pre-emulsification of an oil in water followed by treatment of the ore with the said emulsion whereby to float the desired components of the ore. A further object of the invention pertains to the combined use of an oil and a sulfate ester salt of a normal straight-chain primary alcohol having from 8 to 18 carbon atoms. A still further object of the invention comprises the process of floating ores by means of a preformed emulsion of oil in water containing an alkyl sulfate ester of the character described. Another object of the invention comprises a practical method for floating manganese ores by means of an oil flotation aid. Other objects of the invention will appear hereinafter.

The use of oils for the flotation of mineral ores has been known for many years. However, oil flotation methods at the present time are limited in number as far as commercial practice is concerned for various practical reasons, among which may be mentioned the failure of oil to satisfactorily float certain types of mineral ore, the low yield of high grade concentrate as compared with other flotation processes and the consequent high cost and low economy. In accordance with the present invention it has been found that mineral ores can be very efficiently and satisfactorily floated if the oil which is to serve as the flotation aid is thoroughly emulsified in water prior to the treatment of the ore, the oil in water emulsion then being introduced into the ore pulp to be treated together with a suitable flotation agent. The general function of the oil is to act as a collector, the flotation agent serving to generate a foam or froth, and the oil assisting in the flotation by concentrating the ore in the froth.

It has also been found that mineral ores can be satisfactorily floated by the combined use of an oil and a sulfate ester salt of a normal straight-chain primary alcohol having from 8 to 18 carbon atoms. The scope of the invention includes the combined use of the oil and sulfate ester salt without prior emulsification of the oil in water, but in the preferred form of the invention, the oil is first thoroughly emulsified in water by the use of sulfate ester salt which serves as an excellent emulsifying agent, the emulsion then being introduced into the ore pulp wherein the alkyl ester salt also serves as a frothing agent.

The following examples illustrate the preferred form of the invention which however, are not to be construed as limiting the real scope of the invention:

Example 1

An emulsion was prepared having the following formula:

Mixed sodium alkyl sulfate esters-----	0.125	gms.	
Sulfonated abietene-----	0.10	gms.	
Crude Mexican petroleum (Panuco) 10		gms.	10
Pine tar creosote-----	2.3	gms.	
10% sodium hydroxide solution----	5	cc.	
Water-----	20	gms.	

The above emulsion was prepared by dissolving the sodium alkyl sulfate esters and the sulfonated abietene in water, dissolving the creosote in the crude petroleum, adding the petroleum mixture to the water solution, and emulsifying in a high speed (e. g., 10,000 R. P. M.) mixer. Complete emulsification required less than one minute. The emulsification was stable and easily extended with water.

The mixed sodium alkyl sulfate ester salts comprised about 50% sodium n-cetyl sulfate, 40% sodium n-oleyl sulfate and 10% sodium n-stearyl sulfate. The sulfonated abietene was prepared according to conventional methods by reacting abietene with a strong sulfonating agent.

The emulsion prepared as above was extended with 300 cc. of water making a total of 335 cc. of liquid. Approximately 500 gms. of Cuban manganese ore containing about 17% Mn was deslimed by placing in a bucket and adding approximately five liters of water, and agitating. Then the pulp was allowed to settle for ten minutes and the supernatant liquid siphoned off. The amount of slime so removed made about 100 grams and analyzed 10% Mn. Then the balance of the ore was placed in a five liter flotation cell of the Callow type in which air is introduced under pressure from the bottom of the cell. Three thousand cc. of water was added to the cell, and the water-extended emulsion inserted into the cell in lots during the operation of the cell until 225 cc. had been added, the pH being maintained at approximately 7.4 during the run by adding small quantities of dilute sulphuric acid to neutralize the alkali in the emulsion. The froth contained both the manganese content of the ore and also a certain amount of slime. The concentrate contained over forty percent Mn calculated as the element manganese. The tailings analyzed less than 3% of manganese.

Example 2

An emulsion was prepared according to the manner described in Example 1 and had the following formula:

5	Mixed sodium alkyl sulfate esters identical with the mixture described in Example 1	.125	gram
	Oleyl alcohol	.125	gram
10	Mexican crude oil (Panuco)	10	grams
	Pine tar creosote	2	grams
	10% sodium hydroxide solution	5	cc.

The emulsion was extended with 300 cc. of water, making a total of 335 cc. 225 cc. of the emulsion prepared as above was used for floating manganese ore of the same character and amount as was treated in accordance with the process of Example 1, and in the manner of Example 1, the emulsion being added in 75 cc. lots.

20 The concentrate contained over 44% Mn, the middlings about 30% and the tailings contained less than 3% Mn.

While in these examples previous desliming of the ore was carried out in both cases, it was proven by successful runs that previous desliming of the ore was not necessary.

Example 3

30 500 gms. of ore were treated in the flotation cell without desliming, and 300 cc. of a similar emulsion were added. The slime went with the concentrate from which it was later removed by dewatering.

The above examples indicate the rate of efficiency of the applicants' process as applied to the treatment of manganese ore. The invention, however, is applicable to the treatment of many other ores, for example, it may be applied to the floating of bauxite, phosphate rocks, iron ores, particularly of the earthy or surface types, zinc carbonate, and the like. The process is of greatest utility in treating the earthy type of ore wherein there is a substantial content of humus and humic acids as well as of slimy material. It is furthermore of greatest effectiveness with the non-sulfide bearing ores and ores containing metallic compounds which are not in the definitely crystallized form.

The alkyl sulfate ester salts which may be used in accordance with the present invention are the water-soluble salts, for example, salts of the following metals: sodium, potassium, ammonium, lithium, magnesium, etc. The alkyl radical of the sulfate ester salts must contain at least 8 carbon atoms and preferably from 12 to 18 carbon atoms. The alkyl sulfate esters, salts of which are used in accordance with this invention may be prepared by treating normal straight-chain primary alcohols such as lauryl, myristyl, cetyl, oleyl, stearyl and ricinoleyl alcohols (or any of the alcohols which may be obtained by the catalytic hydrogenation of fatty acids, their alkyl esters, or their naturally occurring glycerides at a temperature of for example 200° to 400° C.) with strong normally sulfonating agents such as 100% sulfuric acid, fuming sulfuric acid or chlorosulfonic acid, at a temperature of 0° to 30° C. This reaction results in the formation of true alkyl sulfuric acids, which may be neutralized by an oxide or hydroxide of a metal, the salt of which is desired. The preceding compounds may be represented by the following general formula:



wherein R represents the residue of a normal primary alcohol containing from 8 to 18 carbon atoms and Y represents the residue of a salt forming compound. The proportion of alkyl sulfate ester salt used may range within wide limits, e. g., 0.0005% up to 1% but preferably from 0.001% up to 0.05% of the water present during the floating of the ore. Where the alkyl sulfate ester salt is used both as an emulsifying agent and as a frothing agent, all of the ester salt may be introduced into the emulsion or the amount of ester salt used in the emulsion may be supplemented by an added amount of ester salt. Either the single alkyl ester salts or mixtures of the salts may be used.

In forming an emulsion usually an elevated temperature of for example 50° to 130° C. may be used altho this temperature is subject to wide variation according to the conditions of emulsification. During the floating of the ore, it is preferred that ordinary temperature be used, altho the floating temperature is not critical. The flotation of the ore and particularly where alkyl sulfate ester salts are used may take place under either acid or alkaline conditions, e. g., from a range of pH 5 to pH 12. It is preferable however, in floating manganese ore, to use a pH of approximately 7. For other ores, the conditions would preferably be alkaline, altho in some cases it may be desirable to have the flotation solution slightly acid.

It has been found that Mexican crude petroleum is particularly useful in floating manganese ore properly. Other oils may be used either for manganese or other ores which may be floated in the manner described. Oils other than Mexican crude petroleum which may be used are: crude petroleum obtainable from Venezuela, Russia, or from various sections of the United States, the crude oil obtainable from Trinidad asphalt by distillation, self-emulsifying oils such as the sulfonated residue obtained in the manufacture of lubricating oil or other oils by treating petroleum fractions with strong sulfuric acid (in such cases an emulsion of the oil in water may be formed without the addition of a further emulsifying agent), pine oil, and the other oils already known to the art for the flotation of mineral ores.

The use of creosote as illustrated in the above examples during the emulsification of the oil tends to aid ready emulsification and to stabilize the emulsion.

Various emulsifying agents which may be used in preparing the oil in water emulsion either with or without the alkyl sulfate ester salts are: sulfonated oleic or ricinoleic acid, Twitchell's reagent, the naphthalene sulfonic acids, triethanolamines and their derivatives such as soaps of the triethanolamines with fatty acids, e. g., oleic, palmitic, and stearic acid, substituted ethylene diamines as the hydrochlorides, resinsates, sulfonated rosin, sulfonated abietene (the hydrocarbon obtained by the thermal decomposition of abietic acid with the splitting off of CO₂), abietic acid and its salts, condensation products of abietene or abietene with epichlorhydrin which are sulfonated, sulfonated olefines, the branched chain higher alcohols obtainable from the catalytic reduction of carbon monoxide with hydrogen, and the derivatives of these alcohols obtainable by treatment of the alcohols with strong sulfonating agents, naphthenic acids, their salts and their sulfonation products, and other well-known emulsifying agents.

The oil in water emulsions which are formed prior to the flotation of the ore and with the aid of emulsifying agents other than the alkyl sulfate ester salts, can be used in accordance with the procedure described in the examples, i. e., they can be added directly to the flotation cell with or without the addition of further flotation agent.

The pH of the emulsion may be regulated by adding a suitable amount of neutralizing agent, e. g., where it is desired to raise the pH value, sodium hydroxide may be added during the emulsification process and where it is desired to lower the pH value sulfuric acid may be added during the emulsification process or for that matter to the water used as the floating medium.

It has been found also that frequently higher normal straight-chain primary alcohols having at least 8 carbon atoms and preferably from 12 to 18 carbon atoms may be used in combination with the emulsifying agent and particularly in combination with the higher alkyl sulfate ester salts.

The function of the oil present during flotation is as a collector, as has been stated above. Other collectors may be used in addition to the oil, e. g., alkyl xanthates and their salts or esters, mercaptans, thioureas, azo and diazo compounds, thiophenols, thiouramdisulfides, dithiophosphates, amines such as alkylamines and triethanolamine and those agents having emulsifying properties and having also frothing or foaming properties.

The invention in its broader scope may be applied to the floating of one or other components of an ore. Thus, by way of example, with a quartz-feldspar ore it is ordinarily desirable to float the feldspar from the quartz. The reverse, however, may in some cases be desired. All that is necessary is to choose a flotation agent which floats one component of the ore from the remainder, the flotation agent being chosen according to the component which it is desired to remove.

The above description and examples are given by way of illustration only. Any variation therefrom which conforms to the spirit of the invention is intended to be included within the scope of the claims.

We claim:

1. In the process for the oil froth flotation of mineral ores, the step which comprises floating a desired component of the ore in an aqueous medium containing oil and a water-soluble sulfate ester salt of a normal straight-chain primary alcohol having at least 8 carbon atoms.

2. In the process for the oil froth flotation of mineral ores, the step which comprises floating a desired component of the ore in an aqueous medium containing oil and a water-soluble sulfate ester salt of a normal straight-chain primary alcohol having from 12 to 18 carbon atoms.

3. In the process for the oil froth flotation of mineral ores, the step which comprises floating a desired component of the ore in an aqueous medium containing oil and the sodium sulfate ester salt of a normal straight-chain primary alcohol having from 12 to 18 carbon atoms.

4. The process of claim 1 characterized in that the oil is first emulsified in water prior to introducing the oil into the ore to be treated.

5. The process of claim 1 characterized in that the oil is first emulsified in water prior to introducing the oil into the ore to be treated, the oil in water emulsion being formed in the presence of a water-soluble sulfate ester salt of a

normal straight-chain primary alcohol having at least 8 carbon atoms.

6. The process of claim 1 characterized in that the oil is first emulsified in water prior to introducing the oil into the ore to be treated, the oil in water emulsion being formed in the presence of a water-soluble sulfate ester salt of a normal straight-chain primary alcohol having from 12 to 18 carbon atoms.

7. A process of floating Cuban manganese ore that comprises dissolving in water a water-soluble sulfate ester salt of a normal straight-chain primary alcohol having from 12 to 18 carbon atoms, adding the water solution to a mineral oil, rapidly stirring the mixture until emulsification takes place, introducing the emulsion into a flotation cell containing water and ore, agitating and aerating, and withdrawing the froth containing the desired component of the ore.

8. In the froth flotation of non-sulfide ores wherein an aqueous suspension of ore is agitated and aerated in the presence of a pre-emulsified mineral oil flotation agent the step which comprises conducting said operation in the presence of a water-soluble compound having the following general formula:



wherein R represents the residue of a normal primary alcohol containing from 8 to 18 carbon atoms, and Y represents the residue of a salt-forming compound.

9. In the froth flotation of manganese ores wherein an aqueous suspension of manganese ore is agitated and aerated in the presence of a pre-emulsified mineral oil flotation agent the step which comprises conducting said operation in the presence of a water-soluble compound having the following general formula:



wherein R represents the residue of a normal primary alcohol containing from 8 to 18 carbon atoms, and Y represents the residue of a salt-forming compound.

10. In the froth flotation of manganese ore wherein an aqueous suspension of manganese ore is agitated and aerated in the presence of a mineral oil flotation agent which has been pre-emulsified with a sodium sulfate ester salt of a normal primary alcohol containing from 12 to 18 carbon atoms, the step which comprises conducting said operation in the presence of a water-soluble compound having the following general formula:



wherein R represents the residue of a normal primary alcohol containing from 12 to 18 carbon atoms.

11. In the froth flotation of non-sulfide ores wherein an aqueous suspension of ore is agitated and aerated in the presence of a mineral oil flotation agent the step which comprises conducting said operation in the presence of a water-soluble compound having the following general formula:



wherein R represents the residue of a normal primary alcohol containing from 8 to 18 carbon atoms, and Y represents the residue of a salt-forming compound.

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