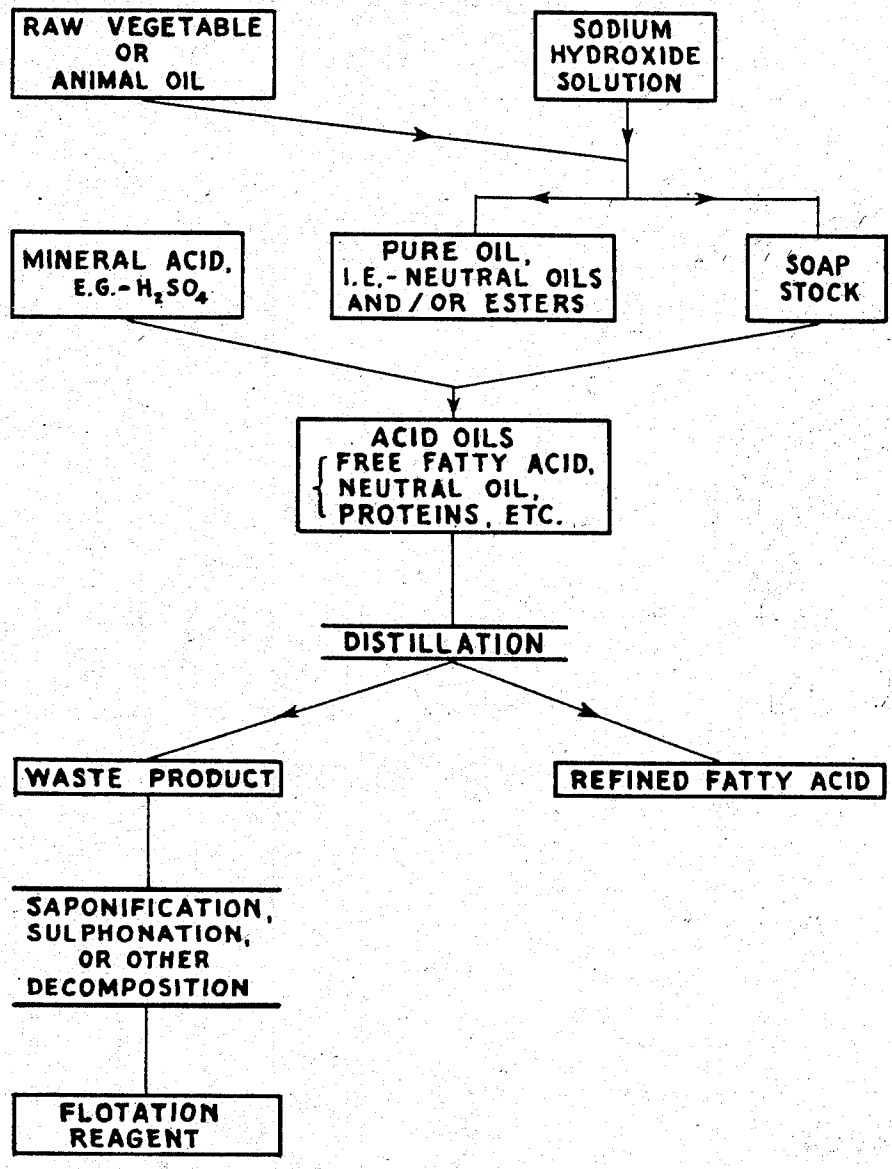
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FROTH FLOTATION REAGENT

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FROTH FLOTATION REAGENT

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This invention relates to froth flotation reagents and more particularly to a flotation reagent for oxide ore minerals and to a method of producing the reagent from the waste products resulting from the refining of vegetable and animal oils and fats.

It is of general utility in the flotation of oxide ore minerals, especially oxides of the alkaline earth metals and particularly calcite. The reagent has excellent and in some cases superior collecting capacity together with sufficient frothing characteristics to limit or make the use of separate frothing agents unnecessary in many cases. It is accordingly among the principal purposes of the invention to provide a reagent of low cost, readily dispersed in cold ore mineral pulps and capable of high dilution in aqueous solutions or emulsions to permit accurate control of the quantities introduced in stage-oiling circuits. The invention will be more fully described hereinafter by reference to examples of its application to the concentration of calcite in the beneficiation of Portland cement raw materials, or the lime-bearing components thereof, but it will be understood that the invention is not limited in utility to the concentration of this mineral.

The raw oils and fats from which the present reagent may be derived are those of the class animal oils and fats and fixed vegetable oils and fats, as distinguished from the volatile or essential oils. Those expressed from soya beans, copra, cotton seed, peanuts and palm seed are typical examples of those of vegetable origin. The animal oils and fats useful for the present purposes comprise the general class more commonly those now used as sources of fatty acids for soap making and froth flotation collectors, and include whale oil and the fish oils.

The accompanying drawing illustrates diagrammatically the sequence of both the common and novel steps in the refining of the raw oils, the production of the reagent, and serves to identify the source of the "waste products" from which the reagent is derived.

The oils and fats, described above are commonly refined, as for production of edible oils and fats, or food ingredients, the first step being carried out by treatment with a cold solution of sodium hydroxide, the neutral oils or esters are thus recovered and separated from the "soap stock" or "foots." The soap stock is a mixture comprising varying proportions of sodium soaps of the free fatty and/or resin acids present in the raw oil, the proteins, which are emulsified in the soap stock, together with other impurities, usually including small amounts of neutral oils. Some of the soap stock have been used heretofore as flotation collectors for oxide ore minerals, usually for bulk oiling of coarse mineral pulps. Their cost, high viscosity, and sometimes excessive frothing characteristics are disadvantages which limit their utility in flotation, by comparison with the present reagent, soap stock being referred to herein as an intermediate source of the ultimate product.

The soap stock is acidified by the addition of a mineral acid, usually sulphuric acid, to produce a product comprising usually a mixture of one or more free fatty and/or resin acids, the proteins, some neutral oils and other impurities. This product is generally called "acid oil" or fatty acid, and the phrase "acid oil" will be used herein to describe this product only. Several of the acid oils have been used heretofore as collectors of oxide ore minerals. Some of them are of such high titre that saponification or emulsification is necessary to promote satisfactory dispersion in flotation pulps, especially in stage-oiling circuits.

To produce the present reagent, the acid oils are further refined, preferably by distillation, to separate the refined fatty acids, as the distillation product, from the other constituents, these constituents being referred to herein as the "waste products" of refining the oils and fats described above. The terms "waste products" appearing throughout the specification and claims are to be construed as defining and limited to these constituents.

The refined fatty acids are generally useful, with some exceptions, particularly some of the vegetable acids, as collecting reagents for oxide ore minerals. However, they are rather expensive for practical use in the recovery of minerals of low value, such as calcite and other alkaline earth metal oxides.

The waste products usually comprise a small residue of free acid, depending upon the degree of distillation, the remainder being largely neutral oils and fats, i. e. fatty acid glycerol esters, the products being generally dark colored, heretofore of no commercial value, usually being burned as fuel in boiler furnaces. They have little, if any, capacity to collect or film oxide ore mineral grains, because upon suspension or emulsification in water they fail to disassociate in sufficient degree, at least, to release surface active ions.

I have discovered, however, that these waste products can be converted to water soluble compounds, or at least that they can be modified to

release surface active ions, and thereby made useful for the flotation of oxide ore minerals, especially the oxides of the alkaline earth metals. The waste products are converted into compounds, which in aqueous solution give surface active ions by either saponification, sulphonation or decomposition by Twitchell's process, hydrochloric acid, or the like, as by breaking down esters to produce substances which in solution give surface active ions capable of reacting with or otherwise filming oxide ore mineral grains.

Conversion of the waste products into such compounds by saponification is preferred because the resulting reagent is less costly and has a wide range of utility, the sulphonated (sulphated esters) products, in some cases, producing excessive frothing effects. Saponification is carried out in the usual way with sodium hydroxide solution, although other soap forming reagents such as soda ash and potassium hydroxide are satisfactory. The saponified reagent is, of course, readily diluted, preferably to 1 to 3% solution, for accuracy in feeding and control, especially in cold weather, and the sulphonated product is preferably used in the form of an aqueous emulsion, as it can thus be added to the flotation pulp in highly dilute form.

The fatty acids derived from the vegetable oils are ordinarily inferior collecting reagents for oxide ore minerals, but the present reagent derived from the waste products of the refining of cocoanut oil or soya bean oil, for example, has unexpected efficiency, comparing favorably with oleic acid and sodium oleate; ordinarily the quantities required per ton of ore are considerably less, and as the present reagent can be produced usually at less than half the cost of oleic acid, its advantages, especially its economy in the flotation of alkaline earth metal oxides will be apparent.

It is to be understood that the waste products, as defined above, of the refining of soya bean oil are quite different from and are not to be confused with the products called phosphatides, soya mud or soya slime, which are the residual substances which precipitate from soya oil before the oil is refined with sodium hydroxide.

The uses and advantages of the present reagent can best be explained by reference to comparative test results in the flotation of calcite for the beneficiation of cement raw materials, or the lime-bearing components thereof. These flotation pulps are especially satisfactory for purposes of illustration, because the flotation of calcite from the usual pulps is a differential separation; the pulps are usually cold and dispersion is difficult, and the mineral particles are usually of extreme fineness, requiring dilute pulps and treatment in stage-oiling circuits. Rapid and complete reagent dispersion in cold water and adaptability to accurate control of quantities introduced to the several stages are essential characteristics of successful reagents for these purposes. It should be understood that the calcite content of raw material mixtures for the production of all types of Portland cement is in the neighborhood of 76%, and, accordingly, that high weight recoveries are ordinarily the objective, rather than high grades of concentrates, provided the grade of the latter is at or above the minimum referred to above.

In the conduct of the following tests, cresylic acid was used as the frother, the saponified and sulphonated forms of the reagent requiring little or no addition of frother.

First example

The raw material used for these tests and demonstrations was a low grade, hard, crystalline limestone containing about 50% calcite, the principal remaining constituents being biotite, wallastonite, quartz and feldspar. The limestone was ground to 85% passing the 200 mesh sieve. The flotation pulp was not deslimed. The following reagents were used:

A. Oleic acid (unmodified).

B. Saponified oleic acid (sodium oleate).

C. Saponified waste product of cocoanut oil refining.

D. Saponified waste product of soya bean refining.

Reagent	Amount in lbs./ton	Percent $CaCO_3$			Weight recovery
		Head sample	Concentrate	Reject	
A	0.8	49.4	93.8	37.5	21.2
B	0.8	49.4	90.2	15.4	45.5
C	0.8	49.4	87.6	18.2	45.0
D	0.8	49.4	85.0	22.0	43.5

It will be seen that reagents B, C, and D, i. e., the saponified oils, produced a concentrate of somewhat lower grade than oleic acid, but commercially satisfactory weight recoveries. The low recovery with oleic acid may be at least partly attributable to the quantity used which was the same as that of the saponified reagents, for purposes of comparison. Reagents C and D were almost as efficient as sodium oleate.

Second example

The material of this test was a finely divided marl of about 72% calcite, the remaining constituents being various types of finely divided clay minerals. The marl was ground to 80% passing the 200 mesh sieve, the ground products were separated at plus and minus 60 microns. The fraction minus 60 microns was used as the flotation pulp (head sample) without desliming. The reagents used were the same as in the first example, but except for the first test, made to illustrate the economies in quantity that are effected with the present reagents, i. e., the fourth and fifth tests, the reagent quantities were those necessary to complete flotation.

Reagent	Amount in lbs./ton	Percent $CaCO_3$			Weight recovery
		Head sample	Concentrate	Reject	
A	2.5	72.6	78.0	69.4	37.2
A	4.7	72.6	77.8	62.0	67.1
B	3.8	72.6	78.7	40.6	78.8
C	2.5	72.6	78.3	34.0	87.1
D	2.5	72.6	80.0	55.0	70.4

It will be seen that, with this material, the concentrates produced with the necessary quantity of oleic acid to complete flotation are of slightly lower grade than those produced by any of the saponified reagents. The quantity of oleic acid required to complete flotation to produce a reasonable weight recovery was considerably larger. Saponified oleic acid produced results generally similar to the present reagent but the quantity required was about 50% greater, and as the cost of this reagent is at least twice that of the present reagent, it will be evident that the latter offers substantial savings. The composition of the material used in this example is such

that satisfactory correction can be made by adding high grade limestone to produce a cement raw material mixture, and this practice would be more economical, although less complete, than correction by flotation with sodium oleate, in view of the cost of that reagent and the quantity required.

Third example

A further series of tests was made to give a comparison between various modifications of the present reagent, derived from the waste products of the refining of cocoanut oil. The following forms of the reagent were used in the tests:

C_1. The waste product saponified with sodium hydroxide.

C_2. The waste product decomposed according to the Twitchell-process to give a fatty acid, which was emulsified in water.

C_3. The above described fatty acid used not as an emulsion but saponified with sodium hydroxide.

C_4. The waste product constituents of which were converted to sulphate esters by sulphonation, the sulphonated product was used as an emulsion in water.

The material used for the tests was a low grade limestone containing about 70% calcite, the principal remaining constituents being wallastonite, quartz and feldspar. The material was ground to 85% passing the 200 mesh sieve and used as the flotation pulp, without desliming.

Reagent	Amount in lbs./ton	Percent $CaCO_3$			Weight recovery
		Head sample	Concentrate	Reject	
C_1	0.84	70.0	91.5	16.4	71.2
C_2	1.00	70.0	89.4	17.4	73.0
C_3	0.84	70.0	93.1	14.0	70.7
C_4	0.84	70.0	91.0	19.6	70.6

The various modifications of the reagent, C_1 to C_4 inclusive, produced by various methods of decomposition, produced generally equivalent flotation results on the material used as the head sample. The modification C_3, the saponified product produced the highest grade concentrate and the lowest reject.

The reagent, as derived from animal oils and fats, is generally more efficient than the derivatives of the vegetable oils and fats, but usually considerably more expensive. For example, the saponified waste product of the refining of whale oil is especially efficient. In a test on a material from the same deposit as that used for the third example, but having a head sample analysis of 80% $CaCO_3$, a concentrate of about 99.0% $CaCO_3$ was produced and with a reject of 15% $CaCO_3$, in a rougher operation, i. e., without cleaning the concentrate.

I claim:

1. A reagent, for the froth flotation of oxide ore minerals, which in water gives surface active ions, comprising the product resulting from the reaction of the waste products remaining after the distillation of impure fatty acid oils produced in the refining of a member from the group consisting of animal and fixed vegetable oils and fats for the recovery of refined fatty acid, with a positive-ion containing substance from the class consisting of strong alkalies and strong acids.

2. A reagent for the froth flotation of oxide ore minerals, which in water gives surface active ions, comprising the product resulting from the reaction of the waste products remaining after the distillation of impure fatty acid oils produced in the refining of a member from the group consisting of animal and fixed vegetable oils and fats for the recovery of refined fatty acid, with a strong alkali.

3. A reagent, for the froth flotation of oxide ore minerals, which in water gives surface active ions, comprising the compounds resulting from the reaction of a strong mineral acid with the waste products remaining after the distillation of impure fatty acid oils produced from the group consisting of animal and fixed vegetable oils and fats for the recovery of refined fatty acid.

4. A reagent, for the froth flotation of oxide ore minerals, which in water gives surface active ions, comprising the compounds resulting from the reaction of Twitchell's reagent with the waste products remaining after the distillation of impure fatty acid oils produced from the group consisting of animal and fixed vegetable oils and fats for the recovery of refined fatty acid.

5. A reagent, for the froth flotation of oxide ore minerals, which in water gives surface active ions, comprising the product resulting from the reaction of the waste products remaining after the distillation of impure fatty acid oils produced in the refining of cocoanut oil for the recovery of refined fatty acid, with a positive-ion containing substance from the class consisting of strong alkalies and strong acids.

6. A reagent for the froth flotation of oxide ore minerals, which in water gives surface active ions, comprising the product resulting from the reaction of the waste products remaining after the distillation of impure fatty acid oils produced in the refining of cocoanut oil for the recovery of refined fatty acid with a strong alkali.

7. A reagent, for the froth flotation of oxide ore minerals, which in water gives surface active ions, comprising the product resulting from the reaction of the waste products remaining after the distillation of impure fatty acid oils produced in the refining of soya bean oil for the recovery of refined fatty acid, with a positive ion containing substance from the class consisting of strong alkalies and strong acids.

8. A reagent for the froth flotation of oxide ore minerals, which in water gives surface active ions, comprising the product resulting from the reaction of the waste products remaining after the distillation of impure fatty acid oils produced in the refining of soya bean oil for the recovery of refined fatty acid, with a strong alkali.

9. The method of producing a reagent for the froth flotation of oxide ore minerals which comprises reacting the waste products, remaining after the distillation of impure fatty acid oils produced in the refining of a member from the group consisting of animal and fixed vegetable oils and fats for the recovery of refined fatty acid, with a positive-ion containing substance selected from the class consisting of strong alkalies and strong acids to produce products giving surface active ions in water.

10. The method of producing a reagent for the froth flotation of oxide ore minerals which comprises subjecting the waste products, remaining after the distillation of impure fatty acid oils produced in the refining of a member from the group consisting of animal and fixed vegetable oils and fats for the recovery of refined fatty acid, to reaction with a soap forming reagent to convert constituents of the said waste products to compounds giving surface active ions in water.

11. The method of producing a reagent for the

froth flotation of oxide ore minerals which comprises subjecting the waste products, remaining after the distillation of impure fatty acid oils produced in the refining of a member from the group consisting of animal and fixed vegetable oils and fats for the recovery of refined fatty acid, to reaction with sulphuric acid to convert at least one of the constituents of said waste products to compounds giving surface active ions in water.

12. The method of producing a reagent for the froth flotation of oxide ore minerals which comprises subjecting the waste products, remaining after the distillation of impure fatty acid oils produced in the refining of a member from the group consisting of animal and fixed vegetable oils and fats for the recovery of refined fatty acid, to reaction with Twitchell's reagent to convert at least one of the constituents of said waste products to compounds giving surface active ions in water.

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