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PROCESS OF MINERAL CONCENTRATION

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The present invention relates to a novel process of concentrating minerals from their ores and is herein described both in connection with metalliferous ores and in connection with ores of so-called non-metallic minerals, the latter group of ores including materials containing such minerals as phosphate, calcite, barite, fluorspar, etc.

In accordance with the invention, minerals are concentrated from their ores by the use of an insoluble and unsaponifiable oil, together with a sulpho-fatty-acid compound produced by the action of a sulphonating agent on a free unsaturated fatty acid containing at least twelve carbon atoms. Such compounds may, for example, be produced by reaction of sulphuric acid with such fatty acids as oleic acid, linoleic acid, ricinoleic acid, erucic acid, and other fatty acids of commerce. The function of the sulpho-fatty-acid compound in the process of the present invention is that of a collecting agent. That is, the sulpho-fatty-acid compound effects collection of the mineral values in cooperation with the insoluble and unsaponifiable oil, which oil promotes the efficiency of the concentration, as well as reduces the quantity of sulpho-fatty-acid compound required. Any one of various hydrocarbon oils can be used as the insoluble and unsaponifiable oil, but fuel oil, on account of its low cost, is usually preferred commercially.

The aforementioned two agents, namely, the insoluble and unsaponifiable oil and the sulpho-fatty-acid compound, are both essential to the process of the present invention. The insoluble and unsaponifiable oil, when used without the sulpho-fatty-acid compound, is utterly incapable of achieving concentration. And in the absence of the insoluble and unsaponifiable oil, the sulpho-fatty-acid compound, while being capable of operating as a collector, possesses much less selectivity, commercial results being in many cases impossible by means of the sulpho-fatty-acid compound alone.

If desired, alkali may also be included among the reagents of the invention, although in some cases better results are obtained without alkali.

The use in mineral concentration of sulphuric-acid-reacted organic compounds as cooperating collecting agents with hydrocarbon oil is not new in itself. Sulphuric-acid-reacted fatty acid glycerides have been used in that manner. And it has also come to my knowledge that minerals can be concentrated by the combination with hydrocarbon oil of sulphuric acid esters of aliphatic alcohols. However, in so far as I am aware, no process has heretofore been known employing hydrocarbon oil in conjunction with compounds produced by the action of sulphuric acid on the aforementioned free fatty acids themselves. As I have discovered, this particular combination of sulphuric-acid-reacted compound with hydrocarbon oil is much more effective in mineral concentration than those combinations employing reaction products of sulphuric acid with either fatty acid glycerides or with aliphatic alcohols, better recoveries being obtained with much smaller reagent quantities.

For certain separations the process of the present invention is also superior to the heretofore known processes employing hydrocarbon oil in conjunction with non-reacted fatty acids or the soaps of these acids. Moreover, the additional use of alkali is usually required in these prior processes to insure the effectiveness of such fatty acids or fatty acid soaps.

It is understood that the sulpho-fatty-acid compound employed in the process of the present invention should be used in the proper amount relative to that of the insoluble and unsaponifiable oil to cause collection to be conjointly effected by these two agents. In each of the examples hereinafter given, substantially no effect would be obtained from the sulpho-fatty-acid compound, in so far as collection is concerned, if employed under the particular conditions described in amount substantially smaller than that indicated. In practice, of course, simple experimental tests are necessary to determine the reagent amounts in each individual case, it being a well-known fact that each set of conditions, including the ore treated, presents its own problem as to the exact quantities of reagents to be used.

The sulpho-fatty-acid compounds of the present invention may be used in the form of the crude reaction mixtures obtained by adding, with stirring, concentrated sulphuric acid (of a specific gravity of about 66° Bé.) in various proportions to the corresponding unsaturated fatty acids selected. The ensuing reaction causes a rise in temperature, the resultant product being more viscous than the original free fatty acid. This material is allowed to cool to room temperature, stirring the while. In this state it is ready for use as a collector without further treatment. If desired, however, it may first be neutralized by a substance having an alkaline reaction in water, such as sodium hydroxide, pyridine, etc. This neutralization may be either partial, as indicated by methyl orange, or complete, as indicated by phenolphthalein, the alkaline substance in either

case being added in the presence of the indicating substance until completion of the desired reaction is shown by the color change. Partial neutralization, as indicated by methyl orange, probably results in neutralizing the sulphur-containing acid radical only, whereas complete neutralization, as indicated by phenolphthalein, may result in neutralizing both the sulphur-containing acid radical and the carboxyl group.

The invention is, of course, not limited to any specific method of preparing the sulpho-fatty-acid compound required for use in its process. Any appropriate sulphonating agent which is the equivalent of sulphuric acid can be used instead of that acid for producing the sulphur-containing acid radical, it being understood that the term "sulphonating" is used herein without reference to the character of that radical.

In preparing the ore for treatment by the process of the invention, it is in general desirable that it be comminuted to a particle size most suitable for efficient operation and that it be largely deslimed, its desliming greatly minimizing the consumption of the reagents. Ordinarily, the crude ore is first subjected to a preliminary grinding operation and thereafter screened or classified to remove all particles other than those desired. The undersize may then be deslimed, and the oversize reground, deslimed, and added to the deslimed undersize; or the oversize may be reground, added to the undeslimed undersize, and the whole then deslimed.

Subsequent to mixing the ore with the reagents, the actual step of separating the mineral values may be effected by any desired form of physical concentration, such as froth flotation, tabling, hydraulic classification, etc. In froth flotation, any suitable frother may be added to the ore along with the other reagents.

The following examples described certain tests which have been made in carrying the invention into effect, the reagent proportions in each being figured on the basis of the dry weight tonnage (2,000 lbs.) of the material treated.

Example 1

To a commercial brand of oleic acid, known as "red oil," was added, with stirring, 5% of its weight of concentrated sulphuric acid. The temperature of the mixture was observed to rise, stirring being continued until the original temperature was restored. This reaction mixture containing sulpho-oleic-acid was used in the following test:

Deslimed phosphate feed to plant No. 4 of the Phosphate Recovery Corporation in Florida, consisting mainly of so-called bone phosphate of lime (tri-calcium phosphate) and silica, and of a particle size to pass 28-mesh, was made up with water into a thick pulp of about 70% solids. To this pulp were added, during agitation in an impeller-type mixer, 0.5 lb. per ton of caustic soda, 2.78 lbs. per ton of fuel oil, 1.28 lbs. per ton of the sulphuric-acid-reacted oleic acid product prepared as above described, and 0.14 lb. per ton of a frothing agent consisting of 3 parts of crude rosin residue dissolved in 1 part of kerosene. This addition of reagents required one minute, subsequent to which agitation was continued in the mixer for two more minutes. The pulp thus conditioned was transferred to a laboratory sub-aeration flotation machine where in a diluted state it was agitated for one minute, during which a rougher concentrate was floated and collected. Upon removal of the tailing, the rougher concentrate was returned to the flotation machine where, without further addition of reagents, it was again treated for another period of one minute, a final concentrate being thus obtained. The tailing of this cleaning upon separate analysis was found to constitute a middling, which in commercial operation would be returned to the flotation cells for further extraction of values.

The results of the test were as follows:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	40.71		100.0
Conc	49.6	76.66	5.96	93.4
Midd	4.0	20.47		2.0
Tail	46.4	4.03		4.6

Comparative test 1

The same feed was taken and the same procedures were followed as in Example 1, but the sulphuric-acid-reacted oleic acid product was omitted and, instead, Turkey-red oil (a partly neutralized reaction product of castor oil with sulphuric acid) was employed. As much as 4 lbs. per ton of this material was required, along with the same amounts of caustic soda, fuel oil, and kerosene-rosin frothing agent, to achieve the concentration indicated in the following table:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	40.99		100.0
Conc	42.6	71.94	12.05	74.8
Midd	5.1	32.72		4.1
Tail	52.3	16.60		21.1

Comparative test 2

Here, sodium lauryl sulphate, in the amount of 5 lbs. per ton, was employed instead of the sulphuric-acid-reacted oleic acid product of Example 1. The conditions of the test were otherwise the same as in that example, including the feed and the amounts of caustic soda, fuel oil, and kerosene-rosin frothing agent, the results being as follows:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	39.70		100.0
Conc	19.2	79.57	2.93	38.5
Midd	10.7	72.14		19.4
Tail	70.1	23.82		42.1

Example 2

For the purpose of this example, no alkali was employed. A thick pulp of the same feed as before was conditioned with 2.78 lbs. of fuel oil, 1.28 lbs. of sulphuric-acid-reacted oleic acid material, and 0.14 lb. of kerosene-rosin frothing agent, all per ton of dry feed. The procedures were otherwise identical to those of Example 1, the sulphuric-acid-reacted oleic acid material and kerosene-rosin frothing agent being ob-

tained in the same way. The results of the test were as follows:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	40.94		100.0
Conc	46.5	76.26	6.34	86.6
Midd	3.1	25.69		2.0
Tail	50.4	9.28		11.4

Comparative test 3

With 4 lbs. per ton of Turkey-red oil replacing the sulphuric-acid-reacted oleic acid material in Example 2, all other conditions being the same, including the feed and the amounts of fuel oil and kerosene-rosin frothing agent, the following results were obtained:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	41.09		100.0
Conc	44.4	70.94	12.56	76.7
Midd	7.3	31.61		5.6
Tail	48.3	15.07		17.7

Comparative test 4

A thick pulp of the same feed as before was agitated in the mixer with 5 lbs. per ton of sodium lauryl sulphate, together with the same amounts of fuel oil and kerosene-rosin frothing agent as in Example 2. Subsequently treating the pulp in the flotation machine, no flotation whatever could be effected.

EXAMPLE 3

A material containing sulpho-oleic-acid was here prepared by treating red oil with 10% of its weight of concentrated sulphuric acid, the mixture being stirred until cool. This material was then partly neutralized with caustic soda, employing methyl orange as an indicator, the resulting product being used in the following test:

With a thick pulp of the same feed as before were thoroughly admixed 0.5 lb. per ton of caustic soda, 2.78 lbs. per ton of fuel oil, and 1.2 lbs. per ton of the above partly neutralized sulphuric-acid-reacted oileic acid product. In the usual manner the pulp was thereafter diluted and agitated in the flotation machine to yield a rougher concentrate, which upon removal of the tailing was retreated without further addition of reagents, yielding a final concentrate and a middling.

The results of the test were as follows:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	40.57		100.0
Conc	46.3	77.85	5.03	88.8
Midd	3.9	33.67		3.2
Tail	49.8	6.47		8.0

EXAMPLE 4

Employing the same feed as before, the procedures of Example 3 were repeated, but with the omission of caustic soda in the flotation test. Also, the sulphuric-acid-reacted oleic acid product was in this instance employed in a state of complete neutralization, the neutralizing medium being caustic soda, which was added to the material resulting from the initial reaction with sulphuric acid in the presence of phenolphthalein as an indicator. The final concentrate assayed 77.55% B. P. L., the B. P. L. recovery therein being 88.3%.

EXAMPLE 5

Here, red oil was treated with sulphuric acid in the same manner as in Example 3, but the resulting material was thereafter partly neutralized with pyridine, employing methyl orange as an indicator. In the subsequent test 2 lbs. per ton of this product, together with 0.5 lb. per ton of caustic soda and 2.78 lbs. per ton of fuel oil, were employed, the procedures being otherwise the same as before, the same feed being taken. The B. P. L. assay of the concentrate was 75.56% and the B. P. L. recovery therein 90.5%.

EXAMPLE 6

The conditions of this test were identical in every respect to those of Example 5, except that no caustic soda was used. A concentrate was obtained assaying 74.76% B. P. L., 95% B. P. L. being recovered therein.

As can be readily seen from the preceding examples and comparative tests, the sulphuric-acid-reacted oleic acid of this invention, with or without prior treatment with alkali and in spite of the much smaller quantities used, gives far superior results than either the Turkey red oil or the sodium lauryl sulphate used in other processes with which I am familiar.

EXAMPLE 7

In this instance sulphuric-acid-reacted oleic acid was used without prior treatment with alkali and with no other agents than fuel oil. A thick pulp of the same feed as before was agitated in the mixer with 3 lbs. per ton of fuel oil and 2.1 lbs. per ton of sulphuric-acid-reacted oleic acid product prepared as in Example 1. Thereafter, the pulp was treated in the flotation machine for the production of a rougher concentrate which, upon removal of the tailing, was retreated without further addition of reagents, yielding a final concentrate and a middling. The results of this test were as follows:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	34.13		100.0
Conc	40.3	69.94	13.00	82.6
Midd	10.8	14.74		4.7
Tail	48.9	8.90		12.7

Comparative test 5

Employing the same feed as before, the procedures of Example 7 were repeated omitting the use of fuel oil, the sulphuric-acid-reacted oleic acid product being used alone and in the same amount, namely, 2.1 lbs. per ton. A final concentrate was obtained assaying 65.42% B. P. L., the B. P. L. recovered therein being only 65.4%.

Comparative test 6

The conditions of this test were identical to those of comparative test 5, except that the sulphuric-acid-reacted oleic acid product was used in the increased amount of 5.05 lbs. per ton. A B. P. L. recovery of 94.6% was effected in the final concentrate, but the B. P. L. grade of that concentrate was only 50.07%.

Comparative test 7

A thick pulp of the same feed as before was agitated in the mixer with no other agent than fuel oil, which was used in the same amount as in Example 7, namely, 3 lbs. per ton. Subsequently treating the pulp in the flotation machine, no flotation whatever could be effected.

Comparative test 8

Under the same conditions as in comparative test 7, but with the amount of fuel oil increased to as much as 50 lbs. per ton, still no flotation could be effected in the flotation machine.

Comparative test 9

Here sulphuric-acid-reacted oleic acid and fuel oil both were used, but with the sulphuric-acid-reacted oleic acid in too small relative amount to enable it to function as a collector. A thick pulp of the same feed as before was agitated in the mixer with 3 lbs. of fuel oil and 0.45 lb. of sulphuric-acid-reacted oleic acid product prepared as in Example 1, both per ton of feed. Subsequently treating the pulp in the flotation machine, a froth was collected carrying a negligible amount of solids, no concentration being possible.

EXAMPLE 8

For the purpose of this example a different phosphate feed was taken, namely, that to the Florida plant of Swift and Company, also largely deslimed, but of a much lower grade of phosphate. A thick pulp of this feed was agitated with 2 lbs. of fuel oil and 2 lbs. of sulphuric-acid-reacted oleic acid material, both per ton of dry feed. Here, the sulphuric-acid-reacted oleic acid material was obtained by treatment of red oil with 25% of its weight of concentrated sulphuric acid. Subsequent to the conditioning indicated, the pulp was processed in the flotation machine in the same manner as before, the following results being obtained:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	27.45	-------	100.0
Conc	27.8	75.06	7.13	76.0
Midd	7.3	36.87	-------	9.8
Tail	64.9	5.99	-------	14.2

EXAMPLE 9

The same feed as in Example 8 was taken and the same procedures as before were followed, but in this instance conditioning was carried out with 0.4 lb. per ton of caustic soda, together with the 2 lbs. per ton of fuel oil and 2 lbs. per ton of sulphuric-acid-reacted oleic acid material, the latter agent being prepared in the same manner as in that example. The final concentrate assayed 71.84% B. P. L., the B. P. L. recovery therein being 70.5%.

Comparative test 10

This test was carried out for comparison with Examples 8 and 9. Employing the same feed as in those examples, with a thick pulp thereof were admixed 1.5 lbs. of caustic soda, 5.5 lbs. of fuel oil, 1.5 lbs. of free fatty acid from fish oil, and 0.14 lb. of the kerosene-frothing agent previously described, all per ton of dry feed. The subsequent flotation procedures were the same as before and yielded the results shown in the table below, it being especially noted that the B. P. L. recovery in the final concentrate was much lower than in either of Examples 8 and 9:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	28.67	-------	100.0
Conc	25.6	71.74	11.27	64.1
Midd	8.0	25.52	-------	7.1
Tail	66.4	12.44	-------	28.8

EXAMPLE 10

Linoleic acid was treated with 10% of its weight of concentrated sulphuric acid, the mixture being stirred until cool. A thick pulp of the same feed as in Example 1 was conditioned with 0.27 lb. per ton of this product, together with 0.4 lb. per ton of caustic soda, 4 lbs. per ton of fuel oil, and 0.14 lb. per ton of the kerosene-rosin frothing agent previously described, the subsequent flotation procedures being the same as before and yielding the following results:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	40.29	-------	100.0
Conc	42.1	80.18	2.86	83.8
Midd	3.9	59.28	-------	5.6
Tail	54.0	7.88	-------	10.6

EXAMPLE 11

Ricinoleic acid was treated with 5% of its weight of concentrated sulphuric acid, the mixture being stirred until cool. In the subsequent test 1.33 lbs. per ton of this product were employed, together with 0.6 lb. per ton of caustic soda, 2.66 lbs. per ton of fuel oil, and 0.14 lb. per ton of the kerosene-frothing agent previously described, the test being carried out on the same feed as in Example 1. All other conditions were the same as before, the results being as follows:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	39.33	-------	100.0
Conc	41.7	77.67	4.78	82.4
Midd	8.4	45.01	-------	9.6
Tail	49.9	6.29	-------	8.0

EXAMPLE 12

The same feed as in Example 1 was taken and the same procedures as in Example 11 were followed, but the caustic soda was omitted and the amount of sulphuric-acid-reacted ricinoleic acid product was increased to 3.5 lbs. per ton, the following results being obtained:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	40.13	-------	100.0
Conc	47.4	75.16	7.59	88.8
Midd	5.8	26.13	-------	3.7
Tail	46.8	6.43	-------	7.5

EXAMPLE 13

Erucic acid, a solid at normal temperatures, was melted and thereafter treated with 5% of its weight of concentrated sulphuric acid, stirring of the mixture being carried out until cool. The resulting product was then dissolved in an equal

part by weight of fuel oil, which solution was used as follows:

A thick pulp of the same feed as in Example 1 was agitated in the mixer with 0.6 lb. per ton of caustic soda, an amount of the above fuel oil solution corresponding to 1.27 lbs. per ton of the sulphuric-acid-treated material dissolved therein, an additional amount of fuel oil to bring its total up to 2.71 lbs. per ton, and 0.14 lb. per ton of the kerosene-rosin frothing agent previously described. Subsequently, the pulp was processed in the flotation machine in the same manner as before.

The results of this test were as follows:

Product	Percent weight	Percent assay		Percent recovery
		B. P. L.	Ins.	B. P. L.
Feed	100.0	39.29		100.0
Conc	48.2	77.17	4.98	94.7
Midd	3.8	21.80		2.1
Tail	48.0	2.61		3.2

EXAMPLE 14

A synthetic limestone ore containing about 30% calcium carbonate to 70% quartz, all finer than 28-mesh, was made up with water into a pulp of 70% solids, which pulp was agitated in the mixer with 0.5 lb. of caustic soda, 2.66 lbs. of fuel oil, 2.4 lbs. of sulphuric-acid-reacted oleic acid material, and 0.14 lb. of the kerosene-rosin frothing agent previously described, all per ton of dry feed, the sulphuric-acid-reacted oleic acid material being obtained as in Example 3. As before, the reagents were added during agitation, which addition required one minute, the total period of agitation being three minutes. Subsequent to the conditioning indicated, the pulp was diluted and agitated in the flotation machine for the production of a rougher concentrate which, upon removal of the tailing, was again subjected to treatment in the machine, yielding a final concentrate and a middling. As before, the frothing period in each of the two operations was one minute, the cleaning operation being carried out without further addition of reagents. The results of this test were as follows:

Product	Percent weight	Percent assay $CaCO_3$	Percent recovery $CaCO_3$
Feed	100.0	29.45	100.0
Conc	29.8	92.48	93.6
Midd	3.0	37.68	3.8
Tail	67.2	1.13	2.6

EXAMPLE 15

Valley Forge Cement Company's "Classifier Sands" were made up with water into a pulp of 70% solids, which was agitated in the mixer with 0.4 lb. of caustic soda, 2.23 lbs. of fuel oil, and 1.32 lbs. of sulphuric-acid-reacted oleic acid product prepared as in Example 1, all per ton of dry feed. Subsequently, the pulp in a diluted state was agitated in the flotation machine for one minute, yielding at once a finished concentrate, the following results being obtained:

Product	Percent weight	Percent assay $CaCO_3$	Percent recovery $CaCO_3$
Feed	100.0	76.68	100.0
Conc	83.3	89.36	97.1
Tail	16.7	13.43	2.9

Comparative test 11

The same classifier sands as in Example 15 were processed employing as reagents 0.4 lb. per ton of caustic soda, 2.66 lbs. per ton of fuel oil, and 6 lbs. per ton of sodium lauryl sulphate, all other conditions being the same as in that example. The results were as follows:

Product	Percent weight	Percent assay $CaCO_3$	Percent recovery $CaCO_3$
Feed	100.0	76.51	100.0
Conc	85.2	82.11	91.4
Tail	14.8	44.29	8.6

EXAMPLE 16

Barite ore obtained from the Paga Mining Company of Cartersville, Georgia, and known as "Jig Hutch" product, was sized on a 28-mesh screen. The oversize was ground to pass through the same screen, the total sample being then deslimed and formed into a pulp of 70% solids. This pulp was agitated in the mixer with 0.3 lb. per ton of caustic soda, 3 lbs. per ton of fuel oil, 1.2 lbs. per ton of sulphuric-acid-reacted oleic acid product prepared as in Example 3, and 0.14 lb. per ton of the kerosene-rosin frothing agent previously described, the total period of agitation being three minutes including the time for addition of the reagents, which was one minute. Subsequent to the conditioning indicated, the pulp was treated in the flotation machine as before for one minute, during which a rougher concentrate was separated. Here, upon removal of the tailing, the rougher concentrate was three times retreated in the machine, yielding a final concentrate and three middlings. For each of these cleaning operations the frothing period was one minute, no further addition of reagents being made. The results of this test are indicated in the following table, wherein middling 1 is the tailing of the first cleaning operation, middling 2 is the tailing of the second cleaning operation, and middling 3 is the tailing of the third cleaning operation:

Product	Percent weight	Percent assay		Percent distribution	
		$BaSO_4$	SiO_2	$BaSO_4$	SiO_2
Feed	100.0	88.82	6.84	100.0	100.0
Conc	70.0	96.28	1.22	75.9	12.5
Midd. 3	6.7	89.82	5.62	6.8	5.5
Midd. 2	7.1	80.40	12.47	6.4	12.9
Midd. 1	6.5	76.19	12.51	5.6	11.9
Tail	9.7	48.85	40.30	5.3	57.2

EXAMPLE 17

Barite ore from Sweetwater, Tennessee, was put through a 35-mesh screen, deslimed, and formed into a pulp of 70% solids. To this pulp were added, during agitation in the mixer, 0.8 lb. of caustic soda, 2.66 lbs. of fuel oil, 1.6 lbs. of sulphuric-acid-reacted oleic acid product prepared as in Example 1, and 0.14 lb. of the kerosene-rosin frothing agent previously described, all per ton of dry feed. The addition period was one minute, subsequent to which agitation was continued for two more minutes. The pulp thus conditioned was diluted and agitated in the flotation machine for one minute, a rougher concentrate being obtained which, upon removal of the tailing, was twice retreated in the machine, without further addition of reagents, yielding a final

concentrate and two middlings, each retreatment requiring about one minute. The results of the test are shown in the following table, middling 1 being the tailing of the first retreatment and middling 2 being the tailing of the second retreatment:

Product	Percent weight	Percent assay $BaSO_4$	Percent recovery $BaSO_4$
Feed	100.0	92.34	100.0
Conc	79.3	96.31	82.7
Midd. 2	11.1	89.81	10.8
Midd. 1	5.7	75.09	4.6
Tail	3.9	43.98	1.9

Comparative test 12

The procedures of Example 17 were repeated on the same barite ore with the sulphuric-acid-reacted oleic acid product omitted, 1.6 lbs. per ton of Turkey-red oil being used instead, along with the same amounts of caustic soda, fuel oil, and kerosene-rosin frothing agent. The results in this instance were as follows:

Product	Percent weight	Percent assay $BaSO_4$	Percent recovery $BaSO_4$
Feed	100.0	92.33	100 0
Conc	58.0	96.47	60.7
Midd. 2	14.2	94.60	14.5
Midd. 1	15.0	90.70	14.7
Tail	12.8	72.96	10.1

EXAMPLE 18

A thick pulp of fluorspar ore from the slime pond tailing of the Rosiclare plants of the Hillside Fluorspar Company, Illinois, containing as gangue constituents both silica and calcite, was agitated in the mixer with 0.26 lb. of sulphuric acid-reacted oleic acid product prepared as in Example 3, 0.44 lb. of fuel oil, and 0.14 lb. of the kerosene-rosin frothing agent previously described, all per ton of dry feed, the total period of agitation being three minutes including the time for adding the reagents, which was one minute. Subsequently, the pulp was diluted and agitated in the flotation machine for one minute, a rougher concentrate being separated which, upon removal of the tailing, was three times retreated in the machine, without further addition of reagents, yielding a final concentrate and three middlings, the frothing period for each of the retreatments being about one minute. The results are shown in the following table, wherein middling 1 is the tailing of the first retreatment, middling 2 is the tailing of the second retreatment, and middling 3 is the tailing of the third retreatment:

Product	Percent weight	Percent assay			Percent recovery CaF_2
		CaF_2	$CaCO_3$	SiO_2	
Feed	100.0	46.11	34.65	16.98	100.0
Conc	48.7	82.82	16.35	0.26	85.6
Midd. 3	4.7	19.52	78.69	0.57	2.0
Midd. 2	7.3	15.72	82.73	0.51	2.4
Midd. 1	9.4	19.34	75.34	3.88	3.9
Tail	29.9	9.64	32.98	54.92	6.1

EXAMPLE 19

Low grade copper sulphide ore from Utah was ground to minus 65-mesh, the ground ore being made up with water into a pulp of 70% solids, without desliming. To this pulp were added, during agitation in the mixer, 0.5 lb. of caustic soda, 1 lb. of fuel oil, 2 lbs. of sulphuric-acid-reacted oleic acid product prepared as in Example 3, and 0.14 lb. of the kerosene-rosin frothing agent previously described, all per ton of dry feed. This addition required one minute, subsequent to which agitation was continued for two more minutes. The pulp thus conditioned was diluted and agitated in the flotation machine for ten minutes, a rougher concentrate being separated which, upon removal of the tailing, was again treated in the machine for ten minutes, without further addition of reagents, yielding a final concentrate and a middling. The results of the test were as follows:

Product	Percent weight	Percent assay		Percent recovery Cu
		Cu	Fe_2O_3	
Feed	100.0	1.05	4.33	100.0
Conc	4.7	12.15	47.70	54.3
Midd	1.5	8.14	21.90	11.4
Tail	93.8	0.38	1.88	34.3

EXAMPLE 20

Oxidized copper ore from the Utah Copper Company, containing azurite and malachite, was ground to minus 65-mesh, the ground ore being first deslimed and thereafter formed into a pulp of 70% solids. This pulp was agitated in the mixer with 0.5 lb. per ton of caustic soda, 1 lb. per ton of fuel oil, 1.67 lbs. per ton of sulphuric-acid-reacted oleic acid product prepared as in Example 3, and 0.14 lb. per ton of the kerosene-rosin frothing agent previously described, the total period of agitation being three minutes including the time for adding the reagents, which was one minute. Subsequently, the pulp was diluted and agitated in the flotation machine for one and one-half minutes, yielding a rougher concentrate which, upon removal of the tailing, was three times retreated in the machine, on each occasion for one and one-half minutes, without further addition of reagents, a final concentrate and three middlings being obtained by these cleaning operations. The results are indicated in the following table, wherein middling 1 is the tailing of the first cleaning operation, middling 2 is the tailing of the second cleaning operation, and middling 3 is the tailing of the third cleaning operation:

Product	Percent weight	Percent assay Cu	Percent recovery Cu
Feed	100.0	2.05	100.0
Conc	5.9	28.44	82.0
Midd. 3	1.9	6.95	6.3
Midd. 2	3.9	2.27	4.4
Midd. 1	10.6	0.47	2.4
Tail	77.7	0.13	4.9

EXAMPLE 21

The identical procedures of Example 20 were repeated on the same oxidized copper ore, except that no alkali was employed and the rougher concentrate was only twice retreated in the flotation machine, the fuel oil, sulphuric-acid-reacted oleic acid product, and kerosene-rosin frothing agent being employed in the same amounts, namely, 1 lb. per ton, 1.67 lbs. per ton, and 0.14 lb. per ton, respectively. The results are shown in the following table, middling 1 being the tailing

of the first cleaning operation and middling 2 being the tailing of the second cleaning operation:

Product	Percent weight	Percent assay Cu	Percent recovery Cu
Feed	100.0	2.06	100.0
Conc	3.3	36.89	59.2
Midd. 2	2.1	12.79	13.1
Midd. 1	8.6	2.40	10.2
Tail	86.0	0.42	17.5

It has also been found that the aluminum silicate mineral known as kyanite may be floated by the process of the present invention.

The applicability of the process of the invention to tabling is shown by the following example.

EXAMPLE 22

The same deslimed phosphate feed as in Example 1 was taken, a sample of this feed being made up with water into a pulp of 70% solids. To this pulp were added, during agitation in the mixer, 0.8 lbs. per ton of caustic soda, 6.66 lbs. per ton of fuel oil, and 8.42 lbs. per ton of sulphuric-acid-reacted oleic acid product prepared as in Example 1. The addition period was one minute, subsequent to which agitation was continued for two minutes more. Thereafter, the pulp was fed to a laboratory-size Wilfley table over a period of one minute, with the following results:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	36.66	-------	100.0
Conc	42.4	70.12	12.12	81.1
Tail	57.6	12.03	-------	18.9

Comparative test 13

Employing the same phosphate feed, the procedures of Example 22 were repeated with the sulphuric-acid-reacted oleic acid product omitted, 9 lbs. per ton of Turkey-red oil being used instead, along with the same amounts of caustic soda and fuel oil of that example. The tabling results in this instance were as follows:

Product	Percent weight	Percent assay		Percent recovery B. P. L.
		B. P. L.	Ins.	
Feed	100.0	36.94	-------	100.0
Conc	43.7	67.71	15.42	80.1
Tail	56.3	13.06	-------	19.9

None of the detailed procedures described herein should be interpreted as limiting the invention, these procedures being capable of being modified in many ways without departing from its spirit.

What is claimed is:

1. A process of concentration comprising admixing an ore with an insoluble and unsaponifiable oil and a sulpho-fatty-acid compound produced by the action of a sulphonating agent on a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the mineral values from the ore, said oil and sulpho-fatty-acid compound being used in relative amounts to cause them to conjointly effect collection of said values.

2. A process of concentration comprising admixing an ore with an insoluble and unsaponifiable oil and a sulpho-fatty-acid compound produced by the action of a sulphonating agent on a free unsaturated fatty acid of at least twelve carbon atoms, said sulpho-fatty-acid compound being at least in part neutralized by a substance having an alkaline reaction in water, and separating in an aqueous pulp the mineral values from the ore, said oil and sulpho-fatty-acid compound being used in relative amounts to cause them to conjointly effect collection of said values.

3. A process of concentration comprising admixing an ore with an insoluble and unsaponifiable oil and the reaction mixture obtained by reacting a sulphonating agent with a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the mineral values from the ore, said oil and reaction mixture being used in relative amounts to cause them to conjointly effect collection of said values.

4. A process of concentration comprising admixing an ore with an insoluble and unsaponifiable oil and the reaction mixture obtained by reacting a sulphonating agent with a free unsaturated fatty acid of at least twelve carbon atoms, said reaction mixture being used in a state of at least partial neutralization by a substance having an alkaline reaction in water, and separating in an aqueous pulp the mineral values from the ore, said oil and reaction mixture being used in relative amounts to cause them to conjointly effect collection of said values.

5. A process of concentration comprising admixing an ore with an insoluble and unsaponifiable oil and a sulpho-fatty-acid compound produced by the action of sulphuric acid on a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the mineral values from the ore, said oil and sulpho-fatty-acid compound being used in relative amounts to cause them to conjointly effect collection of said values.

6. A process of concentration comprising admixing an ore with an insoluble and unsaponifiable oil and the reaction mixture obtained by reacting sulphuric acid with a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the mineral values from the ore, said oil and reaction mixture being used in relative amounts to cause them to conjointly effect collection of said values.

7. A process of concentration comprising admixing an ore with an insoluble and unsaponifiable oil, a sulpho-fatty-acid compound produced by the action of a sulphonating agent on a free unsaturated fatty acid of at least twelve carbon atoms, and an alkali, and separating in an aqueous pulp the mineral values from the ore, said oil and sulpho-fatty-acid compound being used in relative amounts to cause them to conjointly effect collection of said values.

8. A process of concentration comprising admixing an ore with an insoluble and unsaponifiable oil, the reaction mixture obtained by reacting sulphuric acid with a free unsaturated fatty acid of at least twelve carbon atoms, and an alkali, and separating in an aqueous pulp the mineral values from the ore, said oil and reaction mixture being used in relative amounts to cause them to conjointly effect collection of said values.

9. A process of concentration comprising agitating an aqueous pulp of suitably divided particles of an ore with an insoluble and unsaponifi-

able oil and a sulpho-fatty-acid compound produced by the action of a sulphonating agent on a free unsaturated fatty acid of at least twelve carbon atoms, and concentrating the mineral values from the pulp by froth flotation, said oil and sulpho-fatty-acid compound being used in relative amounts to cause them to conjointly effect collection of said values.

10. A process of concentration comprising agitating an aqueous pulp of suitably divided particles of an ore with an insoluble and unsaponifiable oil and the reaction mixture obtained by reacting sulphuric acid with a free unsaturated fatty acid of at least twelve carbon atoms, and concentrating the mineral values from the pulp by froth flotation, said oil and reaction mixture being used in relative amounts to cause them to conjointly effect collection of said values.

11. A process of concentration comprising admixing an ore containing a non-metallic mineral with an insoluble and unsaponifiable oil and a sulpho-fatty-acid compound produced by the action of a sulphonating agent on a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the non-metallic mineral values from the ore, said oil and sulpho-fatty-acid compound being used in relative amounts to cause them to conjointly effect collection of said values.

12. A process of concentration comprising admixing an ore containing a non-metallic mineral with an insoluble and unsaponifiable oil and the reaction mixture obtained by reacting sulphuric acid with a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the non-metallic mineral values from the ore, said oil and reaction mixture being used in relative amounts to cause them to conjointly effect collection of said values.

13. A process of concentration comprising admixing an ore containing phosphate with an insoluble and unsaponifiable oil and a sulpho-fatty-acid compound produced by the action of a sulphonating agent on a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the phosphate values from the ore, said oil and sulpho-fatty-acid compound being used in relative amounts to cause them to conjointly effect collection of said values.

14. A process of concentration comprising admixing an ore containing phosphate with an insoluble and unsaponifiable oil and the reaction mixture obtained by reacting sulphuric acid with a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the phosphate values from the ore, said oil and reaction mixture being used in relative amounts to cause them to conjointly effect collection of said values.

15. A process of concentration comprising admixing an ore containing barite with an insoluble and unsaponifiable oil and a sulpho-fatty-acid compound produced by the action of a sulphonating agent or a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the barite values from the ore, said oil and sulpho-fatty-acid compound being used in relative amounts to cause them to conjointly effect collection of said values.

16. A process of concentration comprising admixing an ore containing barite with an insoluble and unsaponifiable oil and the reaction mixture obtained by reacting sulphuric acid with a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the barite values from the ore, said oil and reaction mixture being used in relative amounts to cause them to conjointly effect collection of said values.

17. A process of concentration comprising admixing an ore containing calcite with an insoluble and unsaponifiable oil and a sulpho-fatty-acid compound produced by the action of a sulphonating agent on a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the calcite values from the ore, said oil and sulpho-fatty-acid compound being used in relative amounts to cause them to conjointly effect collection of said values.

18. A process of concentration comprising admixing an ore containing calcite with an insoluble and unsaponifiable oil and the reaction mixture obtained by reacting sulphuric acid with a free unsaturated fatty acid of at least twelve carbon atoms, and separating in an aqueous pulp the calcite values from the ore, said oil and reaction mixture being used in relative amounts to cause them to conjointly effect collection of said values.

19. A process of concentration comprising admixing an ore with an insoluble and unsaponifiable oil and a sulpho-oleic-acid compound produced by the action of a sulphonating agent on oleic acid and separating in an aqueous pulp the mineral values from the ore, said oil and sulpho-oleic-acid compound being used in relative amounts to cause them to conjointly effect collection of said values.

20. A process of concentration comprising admixing an ore with an insoluble and unsaponifiable oil and the reaction mixture obtained by reacting sulphuric acid with oleic acid, and separating in an aqueous pulp the mineral values from the ore; said oil and reaction mixture being used in relative amounts to cause them to conjointly effect collection of said values.

FRANCIS X. TARTARON.

CERTIFICATE OF CORRECTION.

Patent No. 2,126,292. August 9, 1938.

FRANCIS X. TARTARON.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 17, for "90.5%" read 96.5%; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 20th day of September, A. D. 1938.

Henry Van Arsdale

(Seal) Acting Commissioner of Patents.