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CONCENTRATION OF NONSULFIDE, NONSILICATE ORES WITH NITRIC ACID TREATED FATTY ACIDS

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14 Claims. (Cl. 209—166)

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This invention relates to the concentration of ores. Particularly, it relates to separating the components with a view to recovering the valuable constituents of a wide variety of non-sulfide ores and minerals. More particularly, it relates to those ores in which non-sulfide, non-silicate minerals are mixed with silicious gangue, or in which silicate minerals are admixed with quartz. Among such ores and minerals to the beneficiation of which the invention is particularly adapted are phosphate, iron ore, barite, calcite, feldspar, fluorspar, manganese ores, kyanite, industrial sands, ilmenite, rutile, and zircon.

The invention utilizes my discovery of new collector reagents of the anionic type, hereinafter described, which are particularly effective in beneficiating non-sulfide ores and minerals. One advantage of these new collector reagents is that they are generally effective in ore pulps which may have a wide range of pH involving acid, neutral and alkaline conditions. A particular advantage of these new reagents is that they require the use of less pH adjusting reagents (alkalis and acids) than other types of anionic reagents known to the art. Another advantage of these reagents is that they are generally self-frothing reagents and frequently do not require the addition of frothers. Still another advantage of these new reagents is their efficiency as collectors, since they produce concentrates of high grade with high recovery by the use of only very small amounts of the reagent.

In general the new collector reagents utilized in the present invention comprise the reaction products resulting from the interaction of strong nitric acid and fatty acid, the hydrocarbon chain of which contains seven or more carbon atoms. These reaction products will be hereinafter called nitric acid treated fatty acid materials. The fatty acids from which the said collector reagents are produced by the action thereon of strong nitric acid, may be unsaturated fatty acids and mixtures of saturated and unsaturated fatty acids. These collector reagents may be produced by the action of nitric acid on animal or vegetable fatty acids, such as red oil (oleic acid), fish-oil fatty acids, cod-liver oil fatty acids, cotton-seed oil fatty acids, castor-oil fatty acids, and mixtures of fatty and resin acids such as tall oil, which is a product obtained from the waste liquor of the

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paper pulp industry sold under various names. I have found the reaction products of concentrated nitric acid with oleic acid, tall oil fatty and resin acids, and fish-oil fatty acids to be particularly effective as collectors.

The new collector reagents can be readily prepared by reacting the fatty acid material with concentrated nitric acid. The mixture of fatty acid material and nitric acid is heated with agitation until a definite reaction takes place. This reaction is fairly violent and can be readily observed. After the completion of the first reaction, the material is again heated to a somewhat higher temperature, at which a second reaction takes place. As soon as this second reaction occurs the heat is removed, and there will be a further rise in temperature to a certain extent. The product of the reaction is then allowed to cool and is ready for use as a flotation collector reagent. When red oil (oleic acid) is employed in making the nitric acid treated fatty acid, the reaction product is soluble in hydrocarbon oils and is preferably used in solution in such oils. When tall oil fatty and resin acids are reacted with nitric acid to produce the collectors of this invention the resulting product may be completely or only partially soluble in hydrocarbon oils. When fish-oil fatty acid is employed, the reaction product, being insoluble in hydrocarbon oil, may be used as a flotation collector in solution in other organic solvents such as, for instance dioxan. While it is generally preferable to use the flotation collectors of this invention dissolved in either hydrocarbon oils, or other organic solvents, they may be added directly to the pulp when in a liquid condition, or solid collectors of this invention may be melted and added directly to the ore pulp.

The proportions of nitric acid to fatty acid material will vary according to the strength of the nitric acid and the particular fatty acid material used, and should preferably amount to 5 or more parts of nitric acid to 100 parts of fatty acid material, by weight, although I have found no advantage in adding more than 15 to 20 parts of nitric acid. I have found that about 10 to 15 parts of concentrated nitric acid to 100 parts of fatty acid material, by weight, generally produces the best collector reagent. Any commercial nitric acid of sufficient strength to react with the fatty

acid material can be utilized. What is known commercially as "concentrated nitric acid" was used in the making of the collector reagents employed in the tests hereinafter described. Agua regia (a mixture of 3 parts hydrochloric acid to 1 part nitric acid) may be used instead of concentrated nitric acid, and probably acts by virtue of its nitric acid content. The above described methods of preparing the nitric acid treated fatty acid materials may of course be modified without departing from the spirit of the invention.

Concentrating processes of known types in which the collector reagents herein described are useful, include froth-flotation concentration by the use of flotation cells, and agglomeration with separation by the use of shaking tables, underwater screens, moving belts, pneumatic launders, revolving perforated cylinders, etc. Other reagents may be used in conjunction with the said collector reagents, appropriate to the particular ores being treated and to the processes used, such as frothers, conditioners and modifiers. Water-insoluble, non-frothing hydrocarbon oils such as fuel oil, kerosene, mineral oil, etc. are particularly useful in conjunction with these collector reagents. The mineral oils which have been purified for medicinal use make good laboratory standard inert hydrocarbon oils generally equivalent to other such oils as mentioned above. Alkalis and acids or other pH adjusters may also be employed with these collector reagents; and they may advantageously be used in step concentration procedures.

The following examples illustrate processes of ore concentration utilizing as collector reagents the nitric acid treated fatty acid materials hereinbefore described. Examples 1 to 9 illustrate the effectiveness of these collector reagents in the concentration of phosphate from phosphate ores. In the tests reported as Examples 10 to 15, a variety of ores and minerals were concentrated or purified using typical nitric acid treated fatty acid materials, thereby illustrating the general applicability of said reagents to ores of the classes referred to above. In all of the examples, the amounts of reagents used are given in pounds per ton of solids in the feed.

Example 1

This test was carried out on a phosphate ore which was plant flotation feed customarily subjected to a froth-flotation treatment. This feed was conditioned in an aqueous pulp, at about 69% solids for 2 minutes, with 2.5 lbs. mineral oil and 2.0 lbs. of nitric acid treated red oil resulting from reaction between only 5 parts of concentrated nitric acid and 100 parts of red oil. After froth-flotation treatment, the results were as follows:

Products	Per cent wt.	Per cent B. P. L.	Per cent insol.	Per cent rec.
Feed	100.0	36.1		100.0
Conc	30.9	78.3	3.9	67.0
Mid	7.8	44.0		9.5
Tail	61.3	13.8		23.5

It will be obvious that the results of this test were poor from the standpoint of recovery, doubtless due to the small proportion of nitric acid used in making the nitric acid treated red oil.

Example 2

In this test, conditions were the same as in Example 1 except that 10 parts of nitric acid (double the amount in Example 1) to 100 parts of red oil were used in making the reaction product. After froth-flotation treatment the results of this test were as follows:

Products	Per cent wt.	Per cent B. P. L.	Per cent insol.	Per cent rec.
Feed	100.0	35.6		100.0
Conc	40.5	77.6	4.4	88.4
Mid-1	2.2	52.5	34.7	3.3
Mid-2	6.6	16.7		3.0
Tail	50.7	3.7		5.3

It will be observed that the results of this test were much better than those of Example 1 so far as recovery is concerned, doubtless due to the larger amount of nitric acid employed in making the nitric acid treated red oil.

Example 3

In this test, all conditions were the same as in Examples 1 and 2, except that 15 parts of nitric acid (three times the amount in Example 1) to 100 parts of red oil were used in making the nitric acid treated red oil, and except that the amount of the latter was only 1.5 libs. per ton of feed. After the froth-flotation treatment, the results of this test were as follows:

Products	Per cent wt.	Per cent B. P. L.	Per cent insol.	Per cent rec.
Feed	100.0	35.9		100.0
Conc	43.0	76.9	4.7	92.1
Mid-2	2.4	37.2	52.3	2.5
Mid-1	8.8	8.1		2.0
Tail	46.8	2.6		3.4

It will be apparent that the results of this test were even better than the results in Example 2 from the standpoint of recovery, and that the grade of the concentrate was satisfactory though not quite as high as in Examples 1 and 2.

Example 4

In this test, all conditions were the same as in Examples 1, 2 and 3 except that 20 parts of nitric acid (four times the amount in Example 1) to 100 parts of red oil were used in making the nitric acid treated red oil, and except that the amount of the latter was only 1.5 lbs. per ton of feed. After the froth-flotation treatment, the results of this test were as follows:

Products	Per cent wt.	Per cent B. P. L.	Per cent insol.	Per cent rec.
Feed	100.0	35.7		100.0
Conc	43.6	76.4	4.9	93.3
Mid-2	2.3	33.4	55.8	2.2
Mid-1	8.4	7.9		1.8
Tail	45.7	2.1		2.7

It will be noted that the results of this test are about the same as the results of Example 3, which seems to prove that 15 to 100 is about the best proportion of nitric acid to red oil for the making of nitric acid treated red oil for use as a collector in the concentration of phosphate.

Example 5

This example is to be compared with Example 3. Its purpose is to show the effect of the use of an alkali, such as caustic soda, along with the mineral oil and nitric acid treated red oil. In this test, the phosphate feed was the same as before, and was conditioned at about 69% solids for 2 minutes with 0.4 lb. caustic soda, 2.5 lbs. mineral

oil and only 0.8 lb. of the reaction product from 15 parts of concentrated nitric acid to 100 parts of red oil. After the froth-flotation treatment, the results of this test were as follows:

Products	Per cent wt.	Per cent B. P. L.	Per cent insol.	Per cent rec.
Feed	100.0	35.8		100.0
Conc	43.2	78.6	3.3	94.9
Mid	2.3	31.3		2.0
Tail	54.5	2.0		3.1

Comparison of the results of this test with the results in Example 3, shows a substantial increase both in the grade of the phosphate concentrate and in recovery. It will be noted that the amount of nitric acid treated red oil used in this example was about half the amount used in Example 3. The excellent results of this test seem to indicate that in the concentration of phosphate ore it is worth while to use an alkali along with the mineral oil and the nitric acid treated red oil employed as the collector reagent.

Example 6

This test illustrates the concentration of phosphate by agglomeration tabling methods. In this test, the feed was deslimed phosphatic sands from which the minus 35 mesh particles had been eliminated. This feed was conditioned at approximately 70% solids for 2 minutes with 0.3 lb. caustic soda, 4.2 lbs. mineral oil and 1.7 lbs. of collector reagent produced by the reaction of concentrated nitric acid and red oil in the proportions of 15 to 100. The thus conditioned feed was subjected to concentration on a shaking table, with the following results:

Products	Percent wt.	Percent B. P. L.	Percent insol.	Percent rec.
Feed	100.0	47.9		100.0
Conc	56.8	76.3	3.2	90.5
Mid	5.6	55.0		6.4
Tail	37.6	3.9		3.1

It will be observed that these results were satisfactory from the standpoints of both grade and recovery.

Example 7

This test illustrates the use of the reaction product of nitric acid and tall oil fatty and resin acids, in the concentration of phosphate ore. In this test, the phosphate feed was the same as in Example 1, and was conditioned at about 69% solids for 2 minutes with 0.4 lb. caustic soda, 2.5 lbs. mineral oil and only 0.8 lb of the product of the reaction of nitric acid with tall oil fatty and resin acids in the proportions of 10 to 100. The thus-conditioned feed was submitted to froth-flotation treatment with the following results:

Products	Per cent wt.	Per cent B. P. L.	Per cent rec.
Feed	100.0	36.3	100.0
Conc	43.1	78.8	93.6
Mid-2	1.2	36.9	1.2
Mid-1	3.9	18.8	2.0
Tail	51.8	2.2	3.2

It will be noted that the phosphate concentrate thus produced was highly satisfactory as to both grade and recovery.

Example 8

This test illustrates the use of the reaction product of nitric acid and fish oil fattly acids in the concentration of phosphate ore. In this test, the phosphate feed was the same as in Example 1, and was conditioned at about 70% solids for 2 minutes with 2.5 lbs. mineral oil and 2.0 lbs. of the product of the reaction of nitric acid with fish oil fatty acids, in the proportion of 5 to 100, as a 10% solution in dioxan. The thus-conditioned feed was submitted to froth-flotation treatment with the following results:

Products	Per cent wt.	Per cent B. P. L.	Per cent insol.	Per cent rec.
Feed	100.0	36.0		100.0
Conc	42.6	77.4	5.3	91.5
Mid-2	1.2	39.6		1.3
Mid-1	5.3	14.1		2.1
Tail	50.9	3.6		5.1

It is evident that the phosphate concentrate thus produced was satisfactory as to both grade and recovery.

Example 9

In this test, all conditions were the same as in Example 8, except that 0.4 lb. caustic soda was used along with the nitric acid treated fatty acids of which only 0.8 lb. was employed, the amount of mineral oil being 2.5 lbs. as in Example 8. The results of this test were as follows:

Products	Per cent wt.	Per cent B. P. L.	Per cent insol.	Per cent rec.
Feed	100.0	35.4		100.0
Conc	38.5	79.6	2.7	86.5
Mid	2.4	47.1		3.2
Tail	59.1	6.2		10.3

This test, as compared with Example 8, indicates that the use of caustic soda permits reduction in the amount of nitric acid treated fish oil fatty acids employed, and results in a substantially higher grade of phosphate concentrate, although recovery was somewhat lower.

Example 10

This example illustrates the use of nitric acid treated red oil in the concentration of low grade oxidized iron ore. The ore was conditioned at about 73% solids for 4 minutes with 9.1 lbs. mineral oil and 2.4 lbs. of the product of the reaction of nitric acid with red oil in the proportions of 10 to 100. The results were as follows:

Products	Per cent wt.	Per cent Fe	Per cent insol.	Per cent rec.
Feed	100.0	20.3		100.0
Conc	20.3	60.7	7.5	60.6
Mid-3	2.6	42.1	34.5	5.4
Mid-2	5.6	21.7		5.9
Mid-1	15.2	10.1		7.4
Tail	56.2	7.4		20.7
Conc.-Mid-3	22.9	58.5	10.5	66.0

It will be noted that the iron concentrate was of commercial grade, although the recovery was rather low.

Example 11

This test illustrates the usefulness of nitric acid treated red oil in the concentration of barite ore. The feed was a ground barite ore containing ore particles less than 35 mesh, which had been deslimed. This feed was conditioned

at about 72% solids for 2 minutes with 4.7 lbs. mineral oil and 1.0 lb. of the product of the reaction of nitric acid with red oil in the proportions of 15 to 100. The results of this test were as follows:

Products	Per cent wt.	Per cent $BaSO_4$	Per cent SiO_2	Per cent rec.
Feed	100.0	67.7	----------	100.0
Conc	56.0	95.0	2.6	78.6
Mid-3	7.7	88.5	7.7	10.0
Mid-2	5.0	74.5	19.4	5.5
Mid-1	4.9	38.9	----------	2.8
Tail	26.4	8.0	----------	3.1
Conc.-Mid-3-Mid-2	68.7	92.7	4.5	94.1

It will be seen that the barite concentrate was highly satisfactory as to both grade and recovery.

Example 12

In this test, conditions were the same as in Example 11, except that 0.2 lb. caustic soda was employed along with the mineral oil and nitric acid treated red oil. The results of this test were as follows:

Products	Per cent wt.	Per cent $BaSO_4$	Per cent SiO_2	Per cent rec.
Feed	100.0	69.0	----------	100.0
Conc	54.2	95.9	1.4	75.4
Mid-3	7.5	93.1	2.9	10.2
Mid-2	6.2	85.5	7.4	7.7
Mid-1	5.3	56.4	----------	4.3
Tail	26.8	6.3	----------	2.4
Conc.-Mid-3-Mid-2	67.9	94.7	2.2	93.3

It will be noted that the use of caustic soda, along with the other reagents, resulted in a considerably higher grade of concentrate and only a slightly reduced recovery.

Example 13

This test illustrates the usefulness of nitric acid treated red oil in the froth-flotation of ferruginous impurities away from an industrial sand, to produce a purified sand useful for glass-making. The feed was an industrial sand which had been washed. This feed was conditionad at about 68% solids for 2 minutes with 0.2 lb. caustic soda and 1.0 lb. nitric acid treated red oil produced by the reaction of nitric acid and red oil in the proportions of 15 to 100. The thus-conditioned feed was subjected to froth-flotation treatment with the following results:

Products	Percent wt.	Percent Fe_2O_3	Fe_2O_3 distribution
Feed	100.0	0.161	100.0
Froth Product	6.0	2.0	74.5
Machine Discharge	94.0	0.044	25.5

It will be noted that this treatment resulted in reduction of the ferruginous impurities to only 0.044%, and that the final product was 94% of the feed. Obviously, these are highly satisfactory results.

Example 14

This test illustrates the remarkable usefulness of the reagents of this invention in separating heavy minerals from quartz sand, producing in the same operation a high grade and recovery of heavy mineral as a floating concentrate and a very high quality and recovery of glass sand as a machine discharge. Raw sands used for this test were Florida beach sands containing about 22% of heavy minerals composed of ilmenite, rutile, kyanite and zircon. The beach sands were conditioned at about 70% solids for 2 minutes with only 1.0 lb. nitric acid treated red oil produced by the reaction of nitric acid and red oil in the proportions of 15 to 100. The thus-conditioned beach sands were then subjected to froth-flotation treatment with the following results:

Products	Per cent wt.	Per-cent sink	Per-cent float	Per cent total Fe	Per cent distribution	
					Sink	Float
Feed	100.0	21.7	78.3	2.5	100.0	100.0
Conc	21.8	97.4	2.6	----------	98.0	0.7
Mid-2	1.8	21.0	79.0	----------	1.8	1.8
Mid-1	0.6	4.0	96.0	----------	0.1	0.7
Tail	75.8	0.05	99.95	0.012	0.1	96.8

The results of this test are remarkable, since they show a 98.0% removal of the iron and other heavy minerals with a grade of 97.4%; and a glass sand product containing only .012% Fe and representing about 96.8% recovery of sand.

Example 15

This test illustrates the usefulness of nitric acid treated red oil as a flotation reagent for the concentration of kyanite from an ore consisting largely of kyanite and quartz. A kyanite ore from Virginia was comminuted to —35 mesh and largely deslimed. This ore was then conditioned at about 67% solids for two minutes with .5 lb. sodium silicate and 1.2 lbs. nitric acid treated red oil in the proportions of 15:100. The thus conditioned ore was then subjected to froth-flotation treatment with the following results:

Products	Per-cent wt.	Per-cent sink	Per-cent float	Per cent total Fe	Per cent distribution sink
Feed	100.0	31.2	62.1	----------	100.0
Conc	23.7	92.3	1.0	5.2	70.2
Mid-2	4.0	70.0	8.3	----------	9.0
Mid-1	3.5	54.6	26.3	----------	6.1
Tail	68.8	6.7	88.2	----------	14.7

The results of this test show a high grade kyanite concentrate representing 70.2% recovery, and illustrates the concentration of a silicate mineral from quartz.

What is claimed is:

1. The process of separating the components of an ore of the class consisting of non-sulfide, non-silicate minerals mixed with silicious gangue and silicate minerals admixed with quartz, which comprises subjecting an aqueous pulp of the ore in a suitably divided state to a concentrating operation in the presence of the reaction product resulting from heating a mixture in which the principal ingredient is unsaturated fatty acid material containing hydrocarbon chains of 7 or more carbon atoms and the minor ingredient is nitric acid.

2. The process of separating the components of an ore of the class consisting of non-sulfide, non-silicate minerals mixed with silicious gangue and silicate minerals admixed with quartz, which comprises conditioning an aqueous pulp of the ore in a suitably divided state with a mineral oil and the reaction product resulting from heating a mixture in which the principal ingredient is unsaturated fatty acid material containing hydrocarbon chains of 7 or more carbon

atoms and the minor ingredient is nitric acid, and subjecting the thus conditioned ore pulp to a concentrating operation to separate the ore constituents.

3. The process of separating the components of an ore of the class consisting of non-sulfide, non-silicate minerals mixed with silicious gangue and silicate minerals admixed with quartz, which comprises conditioning an aqueous pulp of the ore in a suitably divided state with a mineral oil, an alkali and the reaction product resulting from heating a mixture in which the principal ingredient is unsaturated fatty acid material containing hydrocarbon chains of 7 or more carbon atoms and the minor ingredient is nitric acid, and subjecting the thus conditioned ore pulp to a concentrating operation to separate the ore constituents.

4. The process of claim 1 employing oleic acid as the unsaturated fatty acid material.

5. The process of claim 1 employing a mixture of fatty and resin acids as the unsaturated fatty acid material.

6. The process of claim 1 employing fish oil fatty acids as the unsaturated fatty acid material material.

7. The process of concentrating phosphate from a phosphate ore which comprises conditioning an aqueous pulp of the ore in a suitably divided state with a mineral oil and the reaction product resulting from heating a mixture in which the principal ingredient is unsaturated fatty acid material containing hydrocarbon chains of 7 or more carbon atoms and the minor ingredient is nitric acid, and subjecting the thus conditioned ore pulp to a concentrating operation to produce a phosphate concentrate.

8. The process of claim 7 employing an alkali along with the mineral oil and said reaction product.

9. The process of concentrating barite from a barite ore which comprises conditioning an aqueous pulp of the ore in a suitably divided state

with a mineral oil and the reaction product resulting from heating a mixture in which the principal ingredient is unsaturated fatty acid material containing hydrocarbon chains of 7 or more carbon atoms and the minor ingredient is nitric acid, and subjecting the thus conditioned ore pulp to a concentrating operation to produce a barite concentrate.

10. The process of claim 9 employing an alkali along with the mineral oil and said reaction product.

11. The process of claim 1 applied to a glass sand to reduce the ferruginous impurities therein and make said sand suitable for glass-making.

12. The process of claim 1 applied to a sand containing heavy minerals to concentrate therefrom the heavy mineral constituents.

13. The process of claim 1 applied to a sand composed largely of quartz and heavy minerals, to concentrate therefrom a high grade heavy mineral as a floating concentrate and a high quality, low iron glass sand product as a non-floating residue.

14. The process of claim 1 in which the reaction product results from heating a mixture of 100 parts unsaturated fatty acid material containing hydrocarbon chains of 7 or more carbon atoms, and not more than about 20 parts of nitric acid.

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