& ASSORTING SOLIDS
166

Patented Jan. 21, 1947

2,414,714

UNITED STATES PATENT OFFICE

2,414,714

FROTH FLOTATION OF OXIDIZED IRON ORES WITH SULFONATED OILS

Robert B. Booth, Springdale, and Earl C. Herkenhoff, Stamford, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application February 10, 1944, Serial No. 521,868

8 Claims. (Cl. 209—166)

1

This invention relates to a process of beneficiating iron ores. More particularly, the invention relates to those processes of iron ore beneficiation by froth flotation in which sulfonated saponifiable oils are used as promoting reagents.

The beneficiation of iron ore by froth flotation has presented a number of peculiarly difficult practical problems. Naturally-occurring high grade ores have kept the unit value at a low figure. Economic considerations have, therefore, required a beneficiated concentrate to contain a high content of iron and that the recovery be fairly high. While it is a comparatively simple matter to concentrate certain iron ores by froth flotation with a number of different promoters of the anionic-type, such as oleic acid and the like, the results obtained have not been within an economically competitive range.

Rapidly diminishing sources of available high grade ore, particularly in the United States, have recently created increasing interest in beneficiating low grade iron ores by froth flotation. It is therefore a principal object of the present invention to develop such a process which will permit the production of concentrates in a sufficiently high grade and recovery to be advantageously compared with naturally-occurring ores. At the same time it is also desirable that the process be one which is simple in operation, low in cost and makes use of readily available reagents.

In general, according to the present invention, these objects are accomplished by conditioning low grade iron ores with a sulfonated saponifiable oil and an acid having a dissociation constant greater than 10^{-7}. For best results an accessory oiling agent, preferably an unsulfonated oil, is usually helpful. The conditioned ore is then subjected to froth flotation in a conventional procedure.

Throughout the specification and claims the term "sulfonated oils" is used in the ordinary commercial sense to designate the products obtained by treating a saponifiable oil with a sulfonating agent, usually strong sulfuric acid. Consequently, it is quite possible that the products may be either sulfonated or sulfated or both. There is no intention that the term "sulfonated oils" shall be restricted to include only those compounds in which the sulfur is present in the form of sulfonic acid groups.

2

Commercially acceptable results are not ordinarily obtainable without an acid treatment of the ore except possibly in those cases in which the sulfonated oil reagent is very highly sulfonated. Such cases are actually not an exception since such promoters are usually either sufficiently acid in themselves to produce the necessary number of available $H+$ ions or contain sufficient residual acid from the sulfonating operation to furnish the necessary acidity. Apparently the acid treatment produces some change in the nature of the mineral surfaces. The exact nature of this surface change is not wholly understood and it is not meant that the present invention be limited to any particular theory of operation. It does appear to be necessary that the oil be sulfonated and that sufficient acid be used during the ore treatment to produce a pH of less than seven.

It is an advantage of the present invention that the particular acid from which the $H+$ ions are derived does not appear to be critical except that results of practical utility in general are not obtained when using weaker acids than those having a dissociation constant of 10^{-7}. It is, of course, necessary that the acid anion should not have a depressive action on the iron minerals as is the case with tannic acid and the like. Sulfuric acid gives as good results as any and because of its availability and relatively low cost is probably preferable in practical operation. It is, however, not superior to other strong acids in the quality of the results obtained and the choice is based on the dictates of economics and not because of the similarity of the sulfate anion to the sulfonate or sulfate groups on the promoter.

It is also an advantage of the present invention that it is not limited to any particular ore. The froth flotation process of the present invention produces excellent results with the more common iron minerals such as hematite and magnetite. However, other iron minerals such martite, limonite, siderite, goethite and the like which are commonly present in iron ores also may be

successfully floated by the procedure of the present invention. Taconite ores are amenable to treatment by the present process. The present process is not only capable of beneficiating naturally-occurring, low-grade ores which are too low in iron for blast furnace feed and which cannot be beneficiated readily by washing and similar operations, but will also produce commercially acceptable concentrates from tailings rejected in ordinary beneficiating processes in common use.

While commercially acceptable results may be obtained in many cases in the operation of the process of the present invention without the use of an accessory oiling agent, in most cases a definite improvement in both recovery and grade is obtained when one is used. Preferably, therefore, an oiling agent such as an unsulfonated oil is used. These oils may be either unsaponifiable mineral oils or hydrocarbons or saponifiable organic oils. In some cases the sulfonated reagent itself may have sufficiently oily characteristics or may contain a sufficient amount of oil as a diluent therewith so that the use of additional oiling agents may be unnecessary. Such cases, however, are ordinarily the exception rather than the rule, and require higher amounts of promoter. Since in most cases the promoter is more expensive than an oil, such use ordinarily is not to be preferred.

The process of the present invention behaves normally with respect to slimes in the ore. Like many common anionic flotations a small amount of slime can be tolerated but increasing amounts generally produce corresponding decreases in the grade of the concentrate and increases in the amount of reagents required. It is therefore desirable to deslime the feed fairly thoroughly although the extreme degree of desliming essential with many cationic flotations is unnecessary.

The invention will be described in greater detail in connection with the following examples which are meant to be illustratve only and not by way of limitation. All parts are by weight unless otherwise noted. In these examples a similar mechanical procedure was followed throughout. The ore was ground to about minus 28 mesh, if necessary, and then deslimed by hydraulic classification. The deslimed ore was then conditioned with the flotation reagents including the sulfonated oil, the acid and the oiling agent when one is used. Unless otherwise noted, the conditioning step is carried out at high solids, about 60–70%. The conditioned pulp was then diluted to about 20–22% solids and subjected to froth flotation in a Fagergren type flotation machine. Unless otherwise noted, the rougher concentrate was subjected to one cleaner flotation without additional reagents. In the tabulated results which are given, the degree of sulfonation is indicated by listing the parts of sulfonating agent per 100 parts of oil. Unless otherwise noted, any excess acid was not neutralized. In some instances commercially available preparations were used and their source is indicated.

Example 1

A number of samples of a Minnesota iron ore washer plant reject, assaying about 14.5% iron and containing principally hematite and quartz with small amounts of limonite, were tested using different sulfonated oils. The effect of these oils was tested using a sulfonated oil alone, with sulfuric acid, with an accessory oiling agent, an unsulfonated oil, and finally with both the acid and the accessory oil. Illustrative results are shown in Table 1.

Table 1

Promoter used				Reagents used (lbs./ton)		Concentrate		Rougher tailing	
Oil used	Sulfonation		Lbs. per ton	H_2SO_4	Fuel oil	Assay, per cent Fe	Distrib. of Fe per cent	Assay, per cent Fe	pH
	Parts oil	Parts sulfuric acid							
Cottonseed	100	10	5.26	None	None	40.49	79.91	3.57	6.0
	100	10	5.26	None	2.32	36.35	83 79	3.80	------
	100	10	5.26	2.10	None	58.55	49.95	7.71	2.75
	100	10	5.26	2.10	2.32	57.16	55.15	6.90	2.8
Do	100	30	4.20	None	None	47.94	92.00	1.27	4.1
	100	30	4.20	None	3.48	51.65	95.48	0.69	------
	100	30	4.20	2.10	None	54.43	91.07	1.27	------
	100	30	4.20	2.10	3.48	58.02	70.49	4.75	2.6
Do	100	50	3.16	None	None	39.11	86.36	2.07	4.1
	100	50	3.16	None	4.64	46.70	90.51	1.15	------
	100	50	3.16	2.10	None	55.55	87.52	1.38	------
	100	50	3.16	2.10	4.64	58.20	72.13	3.80	2.7
Castor oil—Commercial sulfonated castor oil. Aquasol AR-90 (American Cyanamid Co.)	------	------	2.14	None	None	12.37	83.67	33.31	7.0
			2.14	None	4.48	14.82	95.50	14.03	------
			2.14	2.14	None	45.15	59.89	5.82	------
			2.14	2.14	4.48	52.57	94.73	0.81	2.9

From these results it will be seen that the sulfonated oils when used alone produced a quite satisfactory recovery but that the beneficiation, particularly in the case of the sulfonated castor oil, was not wholly satisfactory. The addition of fuel oil to the circuit caused, in certain cases, an immediate improvement in the grade, but, in general, did appear to exert an appreciable effect on the recovery. The use of the sulfonated oil with acid but no oiling agent, on the other hand, produces an improved grade in all cases. The optimum combination from the practical point of view, was that of sulfonated oil, acid and oiling agent, and this gave a very high grade even though the recovery was ordinarily somewhat less than when the sulfonated oil was used alone. This was because some of the iron in this ore was present as relatively low grade middlings. The variations in the degree of sulfonation show that it is not particularly critical over a very wide range, but that in general less promoter is required when employing a highly sulfonated reagent.

Example 2

In order to show the wide variety of oils which may be sulfonated to produce suitable reagents for use according to the present invention, a number of samples were treated using different sulfonated products. Some of the products were

& ASSOCIATING SOLIDS

sulfonated for use in these tests, others were commercially available preparations. In the first 26 tests, a Minnesota ore washer reject assaying about 25% iron, containing chiefly hematite and some limonite in a silica gangue, was used. In the 40th to 44th tests a composite of washer plant rejects from the treatment of Minnesota ores was used. This composite assayed about 22% iron. In the remaining tests a washer reject similar to that used in Example 1 was treated. The results are shown in Table 2. In all tests the pH of the rougher tailings ranged from 2.5 to 3.0.

stituent of the sulfonated product contains at least one aliphatic group having twelve or more carbon atoms. It is also quite apparent that these need not be pure in the sense that they are free from other constituents, nor need they be used alone since it is quite apparent that the mixed oils, both natural and artificial, produce equally acceptable results. It will be noted that the sulfonated products in neutralized or unneutralized form as well as the salts of the sulfonated products, which are precipitated from aqueous solution or dispersion by the addition of an appropriate metallic salt, are also useful promoters.

Table 2

Sulfonation			Conditioning and flotation, pounds per ton			Iron concentrate	
Oil used		H_2SO_4	Sulfonated product	H_2SO_4	Fuel oil	Assay, per cent Fe	Distribution, per cent Fe
Type							
Linseed	100 pts	30 pts	5.7	2.3	2.3	58.16	83.76
Cottonseed	100 pts	30 pts	5.8	2.3	2.3	58.69	88.51
Refined soy	100 pts	50 pts	1.2	2.3	2.3	60.70	80.62
Recovered soy	100 pts	10 pts	5.7	2.3	2.3	59.50	57.05
Do	100 pts	20 pts	5.8	2.3	2.3	56.68	85.23
Do	100 pts	30 pts	2.4	2.4	4.8	55.88	78.87
Do	100 pts	40 pts	2.3	2.3	9.4	53.47	90.32
Do	100 pts	40 pts	1.2	2.4	4.7	56.68	73.69
Do	100 pts	50 pts	1.2	2.4	4.8	58.56	85.21
Sperm	100 pts	50 pts	1.8	2.4	9.5	56.28	89.70
Linseed (non-drying) (fraction)	100 pts	50 pts	1.8	2.4	4.8	58.96	94.96
Fish	100 pts	50 pts	1.8	2.4	4.8	59.09	92.86
Do	100 pts	50 pts	1.8	2.4	None	31.29	35.98
Corn	100 pts	50 pts	1.8	2.4	4.8	59.90	82.98
Teaseed	100 pts	50 pts	1.7	2.3	4.6	59.23	79.52
Herring	100 pts	50 pts	1.8	2.3	4.7	58.96	91.31
Cod	100 pts	50 pts	1.7	2.3	4.6	57.35	87.34
Peanut	100 pts	50 pts	1.8	2.3	4.7	59.90	80.04
Rapeseed	100 pts	50 pts	1.7	2.3	4.6	59.90	83.19
Rice bran	100 pts	50 pts	1.8	2.3	4.7	59.76	71.18
Neat's-foot	100 pts	50 pts	1.8	2.4	4.7	59.50	69.76
Mixed synthetic glycerides	100 pts	50 pts	1.8	2.3	4.7	59.50	73.56
Soy—sulfonated (neutralized)			2.4	2.4	4.8	59.78	75.19
Peanut—sulfonated (neutralized)			2.2	2.2	4.4	54.99	84.55
Sulfonated mixture (neutralized) (fish oil, 1 part; sperm oil, 1 part; coconut oil, 3 parts.			2.5	2.5	4.9	59.90	67.10
Sulfonated castor oil (Aquasol-AR-90)			2.4	2.4	4.8	56.65	83.09
Glyceryl monolaurate	1 mol	2 mols	5.2	2.1	3.7	56.68	71.84
Glyceryl mono-oleate	1 mol	2 mols	4.3	2.1	3.0	52.53	81.54
Glyceryl ricinoleate	1 mol	2 mols	4.2	2.1	3.4	53.81	77.74
Do	1 mol	4 mols	3.5	2.1	3.3	50.92	77.21
Stearo glyceryl sulfate, concentrated (Onyx Oil and Chem. Co.).			2.1	2.1	6.8	56.51	87.83
Mixed mono- and diglycerides of liquid C_{18} fatty acids.	100 pts	70 pts	2.0	2.0	3.3	54.19	81.43
Ethylene glycol monooleate	1 mol	2 mols	4.3	2.1	4.5	57.32	81.69
Coconut oil	100 pts	35 pts. (SO_3HCl)	2.1	2.1	0.5	57.35	78.64
Methyl ester of talloel	100 pts	50 pts	1.6	2.1	3.2	55.78	87.01
Diethlene glycol monolaurate	1 mol	1 mol	4.2	2.1	4.6	55.48	62.18
Diethylene glycol monooleate	1 mol	1 mol	4.2	2.1	4.1	55.48	70.18
Diethylene glycol monoricinoleate	1 mol	3 mols	3.2	2.1	2.8	53.47	82.52
Propylene glycol monooleate	1 mol	2 mols	4.2	2.1	3.6	50.92	75.68
Propylene glycol monoricinoleate	1 mol	2 mols	4.2	2.1	3.9	54.27	85.66
Mannide mono-oleate	100 pts	50 pts	2.8	1.8	2.0	60.91	85.01
Mannitan mono-laurate	100 pts	50 pts	4.9	1.9	3.9	62.30	73.50
Sorbitan mono-laurate	100 pts	50 pts	5.9	2.0	3.9	61.33	71.24
Sorbitan tri-oleate	100 pts	60 pts	6.0	2.0	2.2	52.66	89.38
Ethyl oleate	100 pts	30 pts	6.2	2.1	1.8	55.09	70.09
Soya oil (neutralized with NH_4OH after sulfonation).	100 pts	50 pts	2.13	2.66	3.98	56.39	82.24
Soya oil (neutralized with mono-ethanolamine after sulfonation).	100 pts	50 pts	2.44	2.10	3.92	56.18	85.01
Castor oil, sulfonated (calcium salt—pptd. with calcium chloride).			2.10	2.63	4.16	54.59	88.51
Soya oil (aluminum salt—pptd. with aluminum sulfate).	100 pts	50 pts	2.09	2.61	4.14	56.71	75.51

It is apparent that the oils which can be sulfonated to produce effective promoting reagents in the acid circuit of the present invention include a wide variety of materials. They appear to have one common characteristic, all are saponifiable oils. It will be seen that the materials include such a wide variety of esters as ethyl oleate, the methyl ester of talloel, fatty acid esters such as the oleate, laurate, and ricinoleate of polyhydroxy alcohols such as the glycols, glycerin, mannitol, sorbitol and the like. In each case, however, it will be noted that the non-polar con-

EXAMPLE 3

In order to illustrate the wide limits of the acids which can be used to provide the necessary H+ ions during the beneficiation operation, various sulfonated oils and a variety of added acid reagents were employed on a number of samples of iron ore. All the ore samples used were low grade, those used in the first 19 tests assaying about 25% Fe, and those in the remaining tests assaying about 14.5% Fe. The results are shown in Table 3.

Table 3

Sulfonation			Conditioning and flotation				Iron concentrate		
Oil used		Parts H_2SO_4	Lbs./ton sulfonated product	Acid		Addition agents		Assay, percent Fe	Distrib., percent Fe	Rougher tailing pH
Type	Parts			Type	Lbs./ton	Type	Lbs./ton			
Cottonseed	100	60	2.1	Sulfuric	5.2	Cottonseed oil	4.1	55.00	82.91	2.3
Do	100	60	2.1	do	5.2	Talloel	4.2	54.86	81.88	2.3
Do	100	60	2.1	do	3.1	Bunker C fuel oil	4.2	52.71	85.01	2.5
Do	100	60	2.1	do	3.1	Oleic acid	4.2	54.46	84.31	
Do	100	60	2.1	do	3.2	Naphthenic acid	4.3	50.95	84.17	
Do	100	60	2.1	do	3.2	Crude oil	4.2	51.63	87.35	
Do	100	60	2.1	do	3.2	Lauryl mercaptan	4.2	55.54	78.99	
Do	100	60	2.1	Nitric	3.2	Talloel methyl ester	4.2	51.22	85.66	2.7
Do	100	60	2.1	Sulfuric	3.2	Fuel oil No. 2	4.2	54.05	81.62	2.6
Do	100	60	2.1	Sulfamic	5.2	do	4.2	55.54	79.18	2.6
Castor	100	67	1.6	Hydrochloric	4.1	Keryl chloride	4.1	56.89	81.73	2.2
Do	100	67	1.5	Acetic	5.1	Fuel oil No. 2	4.1	53.25	83.39	3.9
Do	100	67	1.8	Sulfuric	2.3	Bunker C fuel oil	4.7	51.46	80.92	
Fish	100	50	1.8	do	2.3	Fish oil	4.7	56.82	90.00	2.7
Recovered soy	100	50	1.8	do	2.3	Coconut oil	4.7	59.36	80.87	2.7
Rice bran	100	60	2.1	do	3.2	Fuel oil No. 2	4.2	56.08	82.30	2.6
Do	100	60	2.1	Hydrofluoric	1.6	do	4.2	57.96	85.41	3.2
Do	100	60	2.1	Formic	3.2	do	4.2	56.62	77.72	
Do	100	60	2.1	p-Toluene sulfonic.	8.4	do	4.2	52.10	83.68	2.6
Castor oil (neutralized).			2.1	Sulfuric	2.1	Fuel oil, 22° Bé	4.5	52.57	94.73	2.9
Do			2.1	None		do	4.5	14.82	95.50	6.9
Do			2.1	Sulfurous	6.3	do	4.5	52.69	90.70	2.9
Do			2.1	Hydrofluoric	2.1	do	4.5	55.01	92.08	3.3
Do			2.1	Boric	5.3	do	4.5	14.13	94.01	6.9
Do			2.1	Citric	3.2	do	4.5	55.70	70.21	3.9
Do			2.1	Carbonic saturated.		do	4.5	21.08	85.30	6.2

Form this, and the preceding examples, the importance in obtaining commercially acceptable results by having a sufficient amount of available H+ ions during the operation is clearly apparent. The tests show that the acids used may be varied over a wide range, but that they must have a dissociation constant of at least 10^{-7}. Carbonic acid appears to be just on the border line, being useful in some cases and not in others. However, it is of no practical commercial importance because of its relatively high cost. Boric acid is definitely outside the acceptable range.

Example 4

A series of tests similar to that of Example 3 was made on a number of samples of the same ore (assaying 14.5% Fe) used in the latter part of that example. In each case, 2.1 lbs./ton of an oil sulfonated by treatment with 60% by weight of 95.5% sulfuric acid and 4.2 lbs./ton of fuel oil were used. Instead of adding acid per se, a number of acid salts were used. It was found that substantially any strongly acid salts can be used provided the anion is a constituent of an acid having a dissociation constant greater than 10^{-7} and the salts have no deleterious effect on the flotation of the iron minerals. Illustrative results are shown in Table 4.

Table 4

Sulfonated oil used	Acidic material		Iron concentrate, per cent Fe		Rougher tailing pH
	Type	Lbs./ton	Assay	Distribution	
Cottonseed	Sodium chlorosulfonate.	4.2	54.32	67.85	2.6
Rice bran	Sodium fluorosilicate.	4.2	55.54	81.18	3.6
Do	Potassium bisulfate.	4.2	51.90	80.45	2.6

Example 5

Two samples of the same ore used in the latter part of Example 3 and in Example 4 were treated using as reagents 1.64 lbs./ton of neutralized sulfonated castor oil, 2 lbs./ton of sulfuric acid and 3.52 lbs./ton of fuel oil. The first sample was conditioned at 70% solids and then diluted to flotation density, the second was conditioned at flotation density. The rougher concentrate was cleaned once in the first test and twice in the second test. The results are shown in Table 5.

Table 5

Concentrate, per cent Fe		Rougher tailing		Pulp density, per cent solids	
Assay	Distrib.	Assay, per cent Fe	pH	Conditioning	Flotation
52.36	90.50	1.38	2.9	70	22
39.86	83.02	4.13	2.8	22	22

The superior results obtained by conditioning at high solids are clearly shown.

Example 6

A number of samples of the same iron ore used in Example 5 was treated using different degrees of desliming. The promoter used was a neutralized sulfonated castor oil, "Aquasol AR–90," (American Cyanamid Company). Illustrative results are shown in the following table.

Table 6

Product	Per-cent weight	Assay, per-cent Fe	Per-cent Fe distrib.	Lbs./ton used		
				Sulfonated castor oil	H_2SO_4	Fuel oil
Essentially deslimed						
Calc. head	100.00	14.48	100.00	1.64	2.00	3.52
Slime	6.04	23.85	9.95			
Clean. conc	22.54	52.36	81.49			
Clean. tail	7.72	4.66	2.49			
Rgh. tail	63.70	1.38	6.07			
Partially deslimed						
Calc. head	100.00	14.41	100.00	1.92	2.50	4.40
Slime	3.76	29.89	7.80			
Clean. conc	22.42	53.00	82.46			
Clean. tail	6.65	3.92	1.81			
Rgh. tail	67.17	1.70	7.93			
Not deslimed						
Calc. head	100.00	14.65	100.00	2.74	2.50	11.00
Clean. conc	24.98	48.02	81.84			
Clean. tail	11.21	6.15	4.70			
Rgh. tail	63.81	3.09	13.46			

It will be noted that a fairly good cleaner concentrate was obtained even in the sample which was not deslimed at all, and that there was very little difference in grade and recovery between the essentially deslimed and partially deslimed samples. A comparison of the reagent consumption shows the advantage of desliming, the consumption being decreased as the degree of the desliming is increased.

Example 7

An additional sample of the same ore used in Example 6 was subjected to both desliming and scrubbing. The ore was first deslimed by hydraulic classification at about 25% solids and the sands scrubbed for several minutes in a Fagergren flotation machine with the air intake closed. The scrubbed sands were deslimed and conditioned at about 70% solids with 0.93 lbs./ton of the sulfonated castor oil, 2.0 lbs./ton of sulfuric acid and 2.20 lbs./ton of 22° Bé. fuel oil. The conditioned ore was then diluted to 22% solids and subjected to froth flotation, the rougher concentrate being cleaned twice without additional reagents and the cleaner tailings being combined. The results are shown in Table 7.

Table 7

Product	Per cent weight	Assay		Per cent distrib. of Fe
		Per cent Fe	Per cent insol.	
Calc. head	100.00	14.25		100.00
Prim. slime	5.22	25.97		9.52
Sec. slime	1.84	25.76		3.33
Clean. conc	21.90	53.42	17.90	82.13
Clean. tail	13.01	1.27		1.16
Rgh. tail	58.03	.95		3.86

Comparison of the results in Examples 6 and 7 show that at least a partial desliming is highly desirable but that the grade and recovery per se are not appreciably increased by further treatment. A comparison of the reagent consumption in Example 7 with the last test in Example 6 shows a tremendous decrease in reagent consumption. These savings combined with the advantages from the increased grade and/or recovery often warrant the use of the additional desliming operations in combination with scrubbing or polishing. If desired, the ore may be scrubbed and then deslimed or, as above, may be deslimed followed by scrubbing and further desliming.

Example 8

In order to show the utility of mixed sulfonated oils or mixtures of sulfonated oils with other sulfonated materials, a number of samples were treated with such mixtures. Illustrative results are shown in Table 8. In the first two tests the same ore used in the first tests of Example 2 was employed. In the remaining tests a beneficiation plant reject assaying about 15% Fe was used.

Table 8

Conditioning and flotation				Iron concentrate		
Sulfonated product	H_2SO_4	Fuel oil	Assay		Distrib., per cent Fe
			Per cent Fe	Per cent insol.	
	Lb./ton	*Lb./ton*	*Lb./ton*			
Mixture of oleic acid 1 part, peanut oil 1 part; commercial preparation (sulfonated)	2.4	2.4	4.8	57.62	10.88	77.44
A leather conditioning oil: Hydrogenated fish oil 4 parts, oleic acid 2 parts, peanut oil 2 parts, tallow 2 parts; commercial preparation (sulfonated)	2.5	2.5	5.0	59.18	10.00	80.80
Sulfonated castor oil 1 part (Aquasol AR-90) / Petronate 1 part (oil-soluble petroleum sulfonate—Sonneborn Sons)	1.75	2.3	4.1	60.53	6.66	96.17
Sulfonated castor oil 1 part (Aquasol AR-90) / SP-702 1 part (water-soluble petroleum sulfonate—Sanco Distributors, Inc.)	1.40	2.3	3.1	60.31	7.48	96.94
Sulfonated castor oil 1 part (Aquasol AR-90) / Sulfonated talloel 1 part	2.33	2.3	4.1	60.63	6.72	96.46
1 part oleic acid, 25 parts H_2SO_4 / 1 part soya oil, 60 parts H_2SO_4	2.33	2.3	4.1	58.83	9.48	96.42

Example 9

A number of different iron ore samples were treated using different sulfonated oils in order to illustrate the versatility of the present process. Illustrative results are shown in Table 9.

Table 9

Sulfonation			Lbs./ton used			Concentrate			Rougher tailing	
Oil used		H_2SO_4, parts				Assay		Per cent distrib. Fe	Assay, per cent Fe	pH
Type	Parts		Promoter	H_2SO_4	Fuel oil	Per cent Fe	Per cent insol.			
Castor, commercial preparation Aquasol A R-90 (American Cyanamid Co.)			2.00	2.61	4.13	61.16	7.46	91.22	3.92	2.7
Corn	100	50	1.96	1.96	4.31	55.12	10.62	89.81	1.51	2.75
Peanut	100	50	2.34	2.93	3.87	58.71	12.88	93.37	1.04	2.65
Rice bran	100	60	1.89	4.72	3.78	63.36	6.46	92.69	1.35	2.7
Do	100	60	1.93	4.82	3.86	65.38	7.10	90.64	1.62	2.7

DESCRIPTION OF ORES USED ABOVE

1st test—Washer tailing containing chiefly hematite, limonite and quartz; assaying about 30% Fe.
2nd test—Ore containing hematite, siderite, and goethite; assaying about 16% Fe.
3rd test—A taconite; assaying 22% Fe.
4th test—Ore containing martite; assaying about 22% Fe.
5th test—Ore containing magnetite; assaying about 21% Fe.
All concentrates were cleaned once, except in the last two tests where two cleanings were employed.

In the claims, the term "oxidized iron ores" is used in its commonly accepted meaning to include not only iron oxide ores such as those containing magnetite, hematite, etc., but also hydroxides, carbonates, etc.

We claim:

1. A method of beneficiating oxidized iron ores by froth flotation which comprises subjecting the ore to froth flotation in the presence of an effective amount of a collector containing as its essential collecting constituent a sulfonated saponifiable organic oil, characterized by the presence of an aliphatic group having at least twelve carbon atoms, and an effective amount of an acid substance, the anion of which is a constituent of an acid having a dissociation constant greater than 10^{-7}, whereby a concentrate relatively rich in iron mineral and a tailing relatively poor in iron is obtained.

2. A method according to claim 1 in which the sulfonated oil collecting agent is associated with at least one oiling agent selected from the group consisting of unsulfonated saponifiable oils, unsulfonated hydrocarbon oils and unsulfonated fatty acids.

3. A method of beneficiating oxidized iron ores by froth flotation which comprises subjecting the ore to froth flotation in the presence of an effective amount of a collector containing as its essential collecting constituent a sulfonated saponifiable organic oil of the fatty acid-glyceride type, characterized by the presence of an aliphatic group having at least twelve carbon atoms, and an effective amount of an acid substance, the anion of which is a constituent of an acid having a dissociation constant greater than 10^{-7}, whereby a concentrate relatively rich in iron mineral and a tailing relatively poor in iron is obtained.

4. A method according to claim 3 in which the sulfonated saponifiable oil is fish oil.

5. A method according to claim 3 in which the sulfonated saponifiable oil is soy bean oil.

6. A method according to claim 3 in which the sulfonated saponifiable oil is corn oil.

7. A method of beneficiating oxidized iron ores by froth flotation which comprises conditioning the ore at high solids with a reagent containing as its essential collecting constituent a sulfonated saponifiable organic oil, characterized by the presence of an aliphatic group having at least twelve carbon atoms and an effective amount of an acid substance, the anion of which is a constituent of an acid having a dissociation constant greater than 10^{-7}, diluting the conditioned ore to flotation density and subjecting it to froth flotation to produce a concentrate relatively rich in iron mineral and a tailing relatively poor in iron.

8. A method of beneficiating oxidized iron ores by froth flotation which comprises conditioning the ore at high solids with a reagent containing as its essential collecting constituent a sulfonated saponifiable organic oil, characterized by the presence of an aliphatic group having at least twelve carbon atoms and an effective amount of sulfuric acid, diluting the conditioned ore to flotation density and subjecting it to froth flotation to produce a concentrate relatively rich in iron mineral and a tailing relatively poor in iron.

ROBERT B. BOOTH.
EARL C. HERKENHOFF.