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FROTH FLOTATION OF IRON ORE WITH
SULFONATED FATTY ACID

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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 organic carboxylic acids are used as promoting agents.

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 fatty acid 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.

The subject matter of the present invention constitutes a continuation-in-part of our copending application for U. S. Letters Patent Serial No. 498,254 patented September 18, 1945 No. 2,385,054, filed August 11, 1943, which discloses the use of sulfonated talloel for the same purpose.

Throughout the specification and claims the term "sulfonated fatty acids" is used in its ordinary sense to designate the products obtained by treating a fatty acid with a sulfonating agent, usually strong sulfuric acid. Consequently, it is

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quite possible that the fatty acids may be either sulfonated or sulfated or both. There is no intention that the term "sulfonated fatty acids" shall be restricted to include only those compounds in which the sulfur is present in the form of sulfonic acid groups.

As pointed out in connection with sulfonated talloel in our above-mentioned copending application, useful results ordinarily depend upon an acid treatment of the ore, except possibly in those cases in which the fatty acid reagent is highly sulfonated. Such cases are not an exception since such promoters are usually 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 a change in the nature of the mineral surfaces. The exact nature of this change is not wholly understood and it is not meant that this invention be limited to any particular theory of operation. It does appear to be necessary that the fatty acid be sulfonated and that sufficient acid be used during the ore treatment to produce a pH 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 as martite, limonite, siderite, goethite and the like which are commonly present in iron ores also may be suc-

cessfully 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 the 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

containing principally hematite, limonite and quartz and assaying about 15% Fe was deslimed by hydraulic classification. The deslimed product, containing about 13% Fe, was divided into a number of samples and these were conditioned at about 67% solids with the flotation reagents, diluted to about 21-22% solids and subjected to froth flotation in a Fagergren flotation machine. The rougher concentrate was subjected to a cleaner flotation without the use of additional flotation reagents. As a promoter, oleic acid and sulfonated oleic acid were used in different tests. Various amounts of oiling agent and sulfuric acid were used. The results are shown in Table I.

Table I

Promoter			Lbs./Ton Used			Concentrate, Percent Iron		Rgh. Tailing	
Fatty Acid		Sulfuric Acid, Parts	Promoter	Sulfuric Acid	Fuel Oil	Assay	Distrib.	Percent Iron Assay	pH
Type	Parts								
Oleic.....	100	None	1.81	None	None	39.68	86.87	2.20	6.9
Do.....	100	None	1.81	1.59	None		No Promotion 55.48		
Do.....	100	None	1.81	1.59	2.50				
Do.....	100	None	1.81	None	2.50	37.00		6.35	6.9
Do.....	100	None	1.81	None	2.50				
Do.....	100	25	1.94	1.59	5.00	51.28	89.53	0.98	2.8
Do.....	100	25	0.97	None	None	15.75	72.68	10.74	6.9
Do.....	100	25	1.94	None	5.00	46.28	60.25	4.64	6.9
Do.....	100	25	1.94	1.59	None	44.20	74.68	3.30	2.8
Do.....	100	20	1.92	1.59	4.00	56.41	95.44	0.61	2.6
Do.....	100	20	1.92	None	4.00	54.84	83.90	2.32	6.7
Do.....	100	20	1.92	1.59	None	52.75	75.95	2.69	2.6
Do.....	100	10	1.73	1.59	4.00	59.83	87.24	1.22	2.7
Do.....	100	10	1.73	None	4.00	52.50	88.59	1.47	6.7
Do.....	100	5	3.54	1.59	None	60.20	55.13	3.79	2.7
Do.....	100	5	5.90	1.59	1.00	59.58	79.01	1.83	2.6
Do.....	100	34.5	1.78	1.59	4.00	59.46	93.18	0.85	2.6

¹ Prepared by the usual commercial procedure. Had been neutralized to methyl orange with NaOH after sulfonation. All other sulfonates were acidic (not neutralized) when added to conditioner.

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 of the fatty-acid glyceride type. 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 illustrative only and not by way of limitation. All parts are by weight unless otherwise noted.

EXAMPLE 1

A low-grade, Minnesota iron ore washer reject,

From the above results, it can be seen that an unsulfonated fatty acid such as oleic does not produce satisfactory results, even when making use of fuel oil in an acid circuit. Similarly, the second four tests, in which any residual sulfonating acid was neutralized before use, show that the presence of H⁺ ions in the circuit is essential in order to obtain acceptable grades and that the presence of an oiling agent also definitely improved the recovery. The remaining tests on unsulfonated sulfonated acids show that, while both a sulfonated acid promoter and H⁺ ions in the circuit are necessary, the degree of sulfonation of the promoter is not particularly critical, although the use of somewhat more oil is usually helpful in the case of the more highly sulfonated acids.

EXAMPLE 2

In order to show the similar results which are obtained on varying the sulfonated organic acid, the following procedure was carried out. A number of samples of the same ore treated in Example 1 were given the same preliminary preparation and subjected to froth flotation using as reagents various sulfonated organic acids, alone, with H₂SO₄, with fuel oil, and with both H₂SO₄ and fuel oil. In the last four tests, additional samples of a low grade Mesabi iron ore containing about 17% iron and containing principally hematite and quartz were subjected to the same procedure. The proportions of fatty acid and sulfuric acid used in sulfonating the fatty acid are shown in the following table along with the

metallurgical results. The sulfonating acid used was 95.5% H₂SO₄.

the ore used was a reject from an iron beneficiating plant, contained principally hematite and

Table 2

Promoter			Lbs./Ton Used			Concentrate, Per- cent Iron		Rgh. Tailing	
Fatty Acid		Sulfuric Acid, Parts	Promoter	Sulfuric Acid	Fuel Oil	Assay	Distrib.	Percent Iron Assay	pH
Type	Parts								
Dehydrated Ricinoleic Acid.....	100	20	3.77	1.59	1.51	58.36	84.01	2.20	2.6
Do.....	100	20	3.77	1.59	None	57.03	79.04	2.69	2.6
Do.....	100	20	3.77	None	1.51	57.65	80.10	2.81	4.1
Do.....	100	20	3.77	None	None	34.19	91.68	1.47	6.2
Do.....	100	20	3.77	None	None	42.49	68.30	5.34	8.5
Linseed Fatty Acids.....	100	20	3.72	1.59	3.00	59.85	88.71	1.16	2.6
Do.....	100	20	3.72	1.59	None	46.11	82.27	2.20	2.6
Do.....	100	20	3.72	None	None	29.31	90.41	1.71	4.8
Do.....	100	20	5.16	1.59	3.00	56.98	92.53	0.67	2.5
Undecylenic Acid.....	100	15	5.77	1.59	1.00	55.09	87.87	1.62	4.7
Do.....	100	15	5.77	1.59	None	59.73	90.41	0.92	2.6
Do.....	100	15	5.77	1.59	None	55.51	84.01	1.71	2.6
Do.....	100	15	5.77	None	1.00	57.16	91.17	1.34	4.0
Sulfonated Abietic Acid.....	100	15	5.77	None	None	48.49	90.11	1.34	3.8
Do.....	(Neopen Pont.)	SS-du	1.06	1.59	4.50	58.02	85.82	1.83	2.8
Do.....	(Neopen Pont.)	SS-du	1.06	1.59	None	23.45	19.02	12.21	2.6
Do.....	(Neopen Pont.)	SS-du	1.06	None	4.50	42.93	26.55	10.26	7.0
Do.....	(Neopen Pont.)	SS-du	1.06	None	None	19.60	14.84	12.52	7.0
Talcoel.....	100	40	1.62	1.62	3.23	55.23	90.67	1.19	2.7
Do.....	100	40	1.62	1.62	None	48.36	61.28	5.07	2.6
Do.....	100	40	1.62	None	3.23	35.83	92.62	1.43	5.8
Do.....	100	40	1.62	None	None	30.93	87.38	2.15	6.4
Undecylenic Acid.....	100	53	2.24	2.24	2.47	58.10	93.84	0.94	2.7
Do.....	100	53	2.24	2.24	None	47.05	89.31	2.02	2.7
Do.....	100	53	2.24	None	2.47	50.73	95.55	0.94	2.7
Do.....	100	53	2.24	None	None	23.59	96.05	1.82	6.6

* 0.8 lb./ton NaOH added to conditioner.

The results show that the process is not particularly critical as to the nature of the fatty acid which is sulfonated to form the promoter or as to the degree of sulfonation but that an acid circuit is necessary to obtain satisfactory results.

35 quartz, and assayed only about 14.5% Fe. The results, which further show the wide variety of fatty acids which may be sulfonated and used according to the process of the present invention, are shown in Table 3.

Table 3

Fatty Acid		Sulfuric Acid, Parts	Chloro-sulfonic acid, Parts	Lbs./Ton Used			Concentrate, Per Cent Iron		Rgh. Tailing	
Type	Parts			Promoter	Sulfuric Acid	Fuel Oil	Assay	Distrib.	Per Cent Iron Assay	pH
Fish Liver Oil Fatty Acids.....	100	60	None	1.76	4.68	9.40	47.93	61.89	4.19	2.8
Soya Fatty Acids.....	100	50	None	1.76	2.34	4.70	57.92	92.50	1.62	2.7
Naphthenic Acids.....	100	None	67	5.88	2.34	2.34	59.81	44.51	11.11	2.4
Palm Kernel Oil Fatty Acids.....	100	None	50	5.88	2.34	2.34	59.40	57.70	9.05	2.5
Stearic Acid.....	100	None	50	11.76	2.34	4.70	58.73	48.96	11.34	2.4
Lauric Acid.....	100	None	100	5.88	2.34	4.70	54.27	41.76	11.21	2.5
Cottonseed Oil Fatty Acids.....	100	None	50	5.88	2.34	4.70	59.00	69.58	5.94	2.6
Castor Oil Fatty Acids.....	100	50	None	1.76	2.34	4.70	59.81	84.40	3.65	2.4
Erucic Acid.....	100	58	None	1.76	2.34	4.70	59.67	84.82	3.51	2.4
Dehydrated Castor Oil Fatty Acids.....	100	50	None	1.76	2.34	4.70	57.51	93.41	1.49	2.4
Neo-Fat 3R, 59.0% Linoleic, 39.5% Oleic (Armour & Co.).....	100	50	None	1.76	2.34	4.70	49.82	78.74	2.16	2.7
"Roleic"—Mixed Vegetable Oil Fatty Acids (W. C. Hardesty & Co.).....	100	None	60	2.08	3.12	4.16	56.18	73.99	4.13	2.6
Animal Fatty Acids (W. C. Hardesty & Co.).....	100	None	67	2.08	3.12	4.16	57.35	84.24	2.22	2.4
Synthetic Fatty Acids (Standard Oil Development Co.).....	100	None	67	5.20	3.12	4.16	58.30	70.14	4.66	2.3
Crude Synthetic Fatty Acids (Standard Oil Development Co.).....	100	None	67	5.20	3.12	4.16	57.24	80.72	2.76	2.3
Palm Kernel Oil Fatty Acids.....	100	None	100	10.40	2.08	4.16	57.24	82.51	2.76	2.2
Naphthenic Acids.....	100	None	67	10.40	2.08	4.16	56.60	85.16	2.12	2.4
Fleshing Grease—50% Fatty Acids Glue by-Product—F. W. Tunnel & Co.....	100	None	67	2.0	3.0	4.0	59.35	76.84	2.76	2.6

EXAMPLE 3

A number of additional types of fatty acid, sulfonated with 95.5% sulfuric acid or with chloro-sulfonic acid, were used in carrying out the same procedural steps of Example 1. In the first eleven tests a Minnesota ore washer reject containing mainly hematite and quartz and assaying about 25% Fe was used. In the last seven tests

EXAMPLE 4

In order to show that it makes little practical difference whether the sulfonated fatty acid reagent is fed per se or as a metallic or organic salt thereof, a number of samples of the ore used in the last seven tests of Example 3, was subjected to the same procedural steps as in Example 1, but a number of different metallic and organic

salts of various sulfonated fatty acids were used as the promoter. These salts were prepared by adding an inorganic salt of a metal or an organic base to an aqueous solution of the sulfonated fatty acid and collecting the resultant precipitate by filtration, or decantation. The results of these tests, as shown in Table 4, clearly demonstrate that wholly acceptable results are obtained by feeding the sulfonated fatty acid as a salt thereof.

linoleic, and the like. They need not be saturated; oleic and erucic acids, for example, produce good results. They may even contain such a high degree of unsaturation as is found in the China-wood oil fatty acids. They need not be straight chain aliphatics as evidenced, for example, by the excellent results obtained using sulfonated abietic acid. Naphthenic acids, which may contain either monocyclic or bicyclic ring structures, produce good reagents after sulfona-

Table 4

Promoter Used				Lbs./Ton		Concentrate Percent Fe		Rougher Tailing	
Added As—	Parts, Fatty Acid	Parts, Sulfuric Acid	Lbs. Per Ton	Sulfuric Acid	Fuel Oil	Assay	Distrib.	Assay percent Fe	pH
Calcium Salt of Sulfonated Oleic Acid—precipitated with CaCl ₂	100	25	1.81	3.24	5.00	57.69	74.76	3.50	2.8
Ferric Sulfo-oleate—precipitated with FeCl ₃	100	25	2.76	2.70	6.18	44.35	84.41	1.89	2.7
Aluminum Sulfo-oleate—precipitated with AlCl ₃	100	25	2.16	3.24	5.47	55.00	88.82	1.69	2.6
Sulfonated Soya Fatty Acids—neutralized with monoethanolamine.....	100	60	2.16	2.70	5.23	52.71	89.04	1.69	2.7
Sulfonated Fish Liver Oil Fatty Acids—neutralized with Guanidine Carbonate.....	100	50	1.80	2.70	3.80	45.02	85.53	1.35	-----
Ammonium Sulfo-Ricinoate Beacon Co., Boston, Mass.....	-----	-----	1.71	2.63	2.55	53.06	86.71	1.88	2.8

EXAMPLE 5

In order to illustrate the use of highly unsaturated acids, 20 parts of China-wood oil fatty acids were mixed with 20 parts of fuel oil, and 10 parts of 95.5% H₂SO₄ were added thereto while maintaining temperature below about 35° C. The resultant product was made into an emulsion by admixture with 100 parts of water. This emulsion was fed to the conditioning step in the procedure of Example 1, using the same ore as was treated in the last tests of Example 2. The results are shown in Table 5.

Table 5

Sulfonated promoter, lbs./ton	7.00
Sulfuric acid, lbs./ton	2.33
Fuel oil, lbs./ton	7.00
Concentrate, assay, percent Fe	60.53
Concentrate, distrib., percent Fe	77.45
Rgh. tailing, assay, percent Fe	4.58
Rgh. tailing, pH	2.3

From the preceding examples, it is apparent that a wide variety of fatty acids may be sulfonated to form promoting reagents suitable for use in the present process. These acids in general should contain 11 or more carbon atoms in order to obtain the best results, since, otherwise, the fatty acid group on the reagent is not sufficiently non-polar to obtain best results in the acid circuit. These fatty acids may be straight chain aliphatics such as undecylenic, oleic, lauric,

tion. There is no necessity for using single purified acids, as evidenced by the successful results obtained with such mixtures as fish oil fatty acids, fish liver oil fatty acids, coconut oil fatty acids, soybean fatty acids, cottonseed oil acids, palm oil fatty acids, and the like, as well as the commercial fatty acid mixtures. High grade mixtures such as "Neo-Fat 3R" containing oleic and linoleic acids give good results also. However, it is not necessary that the mixtures be pure as is shown by the successful results obtained with the commercially-obtainable "Roleic" acid, which is a mixture of different vegetable oil fatty acids, and with mixtures of animal fatty acids, crude synthetic fatty acids, and fleshing grease such as is obtained in the leather trade and which contains about 50% of mixed fatty acids.

EXAMPLE 6

In order to show the effect of the use of various oiling agents and acids of different dissociation constants, the procedure of Example 1 was repeated on a number of samples of ore using various oiling agents and various acids to produce the necessary H⁺ ion concentration. In the first eight tests the ore used is the same as that used in the first part of Example 3. In the remaining tests a low grade Mesabi iron ore, the same as used in Example 4, was employed. It contained chiefly hematite and quartz and assayed about 14.5% Fe. The results are shown in Table 6.

Table 6

Promoter				Acid Used		Addition Agent		Concentrate, Percent Fe		Rough Tailing, pH
Fatty Acid		Sulfuric Acid, Parts	Lbs./Ton Promoter Used	Type	Lbs./Ton	Type	Lbs./Ton	Assay	Distrib.	
Type	Parts									
Fish Oil Fatty Acid.	100	50	1.76	Nitric.....	4.70	Talloe.....	4.70	57.38	79.54	2.
Do.....	100	50	1.76	Sulfurous.....	2.34	Coconut Oil.....	4.70	59.13	68.96	4.
Do.....	100	50	1.76	Hydrochloric.....	2.34	Chlorinated Kerosene.....	4.70	51.03	80.45	2.
Do.....	100	50	1.76	Sulfamic.....	2.34	Fuel Oil No. 2.....	4.70	55.22	94.20	3.
Soya Fatty Acids.	100	60	1.76	Formic.....	2.34	Methyl Ester of Talloe.....	4.70	54.00	86.74	3.
Do.....	100	60	1.76	Citric.....	2.34	Crude Oil.....	4.70	48.20	90.05	3.
Do.....	100	50	1.76	Sulfuric.....	2.34	Bunker C Fuel Oil.....	4.70	49.95	83.00	2.
Fish Oil Fatty Acids.	100	50	1.76	Acetic.....	2.34	Cottonseed Oil.....	4.70	51.03	80.57	4.

Table 6—Continued

Promoter				Acid Used		Addition Agent		Concentrate, Percent Fe		Rough Tailing, pH
Fatty Acid		Sulfuric Acid, Parts	Lbs./Ton Promoter Used	Type	Lbs./Ton	Type	Lbs./Ton	Assay	Distrib.	
Type	Parts									
Soya Fatty Acids.	100	60	1.57	Hydrofluoric	2.40	Fuel Oil No. 2.	4.17	58.32	80.98	3.2
Do	100	60	1.57	Phosphoric	2.09	Fish Oil	8.34	57.65	82.12	
Do	100	60	1.57	Citric	2.09	Fuel Oil No. 2.	4.17	55.89	66.71	
Do	100	60	1.57	Tartaric	2.09	do	4.17	53.87	72.85	
Do	100	60	1.57	Boric	5.10	do	4.17	15.50	90.60	
Do	100	60	1.57	CO ₂	Saturated	do	4.17	16.72	85.70	6.9
Oleic Acid	100	25	1.79	Sulfuric		2.68	Naphthenic Acid	5.90	52.71	
Do	100	25	1.79	do	2.68	Ethylene Glycol Mono-oleate.	6.68	56.35	58.59	2.7
Do	100	25	1.79	do	3.22	Saponified Talloel	4.58	50.15	66.27	2.7
Do	100	25	1.79	do	2.68	n-Heptaldehyde	6.50	47.58	67.55	
Do	100	25	2.09	do	2.68	Lauryl Mercaptan	8.14	58.10	59.97	
Do	100	25	2.09	do	2.68	22° Bé. Fuel Oil	5.75	52.03	93.14	

From the results it will be seen that carbonic acid which has a dissociation constant of approximately 10^{-7} is about the weakest acid that can be used, boric acid not giving any appreciable beneficiation.

It will be further noted that a wide variety of accessory reagents having oily characteristics were used in conjunction with the sulfonated fatty acids. Excellent results were obtained with hydrocarbon oils such as kerosene, fuel oil, crude oil, and halogenated hydrocarbons such as chlorinated kerosene. Various saponifiable oils of the glyceride type including coconut oil, fish oils, cottonseed oil and the like are wholly satisfactory. Similarly fatty acids, or derivatives thereof which yield acids in the circuit, such as talloel, oleic acid, and the soaps thereof may be used. Various organics showing oily characteristics may be used. Naturally, the hydrocarbons, saponifiable oils or fatty acids because of their availability and relatively low cost are preferable as the accessory reagents.

EXAMPLE 7

In order to show the utility of acid salts rather than acids per se, the procedure of Example 2 was repeated on the ore used in Example 4. Various acid salts were used. As a promoter 1.57 lbs./ton of sulfonated soyabean fatty acids, sulfonated with 60 parts per 100 of 95.5% H₂SO₄, was used and fuel oil No. 2 in the amount of 4.17 lbs. per ton was used as an oiling agent. Illustrative results are shown in Table 7.

should be a constituent of an acid having a dissociation constant greater than 10^{-7} . The acid salt should be used in sufficient quantity to provide the necessary pH.

Table 7

Acidic Material		Concentrate, Per Cent Fe		Rougher Tailing	
Type	Lbs./Ton	Assay	Distrib.	Assay Per Cent Fe	pH
Sodium Chloro-sulfonate	8.34	53.87	80.28	3.38	2.6
Sodium Silicofluoride	8.34	57.92	81.47	2.03	3.7
Potassium Bisulfate	5.21	42.12	84.73	2.50	2.8

EXAMPLE 8

The effect of desliming was demonstrated by repeating the procedure of Example 1 on low grade Mesabi iron ore tailing but varying the degree of desliming. The ore used contained about 14.5% iron, chiefly as hematite, in a gangue of principally quartz. In the first test, the ore was essentially deslimed, in the next test only partly deslimed, and in the last test no desliming was employed. As a promoter sulfonated oleic acid was used, which had been sulfonated with 25 parts per 100 of 95.5% sulfuric acid, followed by neutralization to methylorange by caustic soda. The results, which show the effective reagent savings which can be obtained by desliming, are shown in Table 8.

Table 8

Product	Percent Wt.	Assay		Percent Distrib. of Iron	Consumption, Lbs./Ton		
		Percent Fe	Percent Insol.		H ₂ SO ₄	Promoter	Fuel Oil
Essentially Deslimed:							
Calc. Head	100.00	14.44	-----	100.00	2.50	1.95	5.82
Slime	5.85	21.84	-----	8.85			
Clean. Conc.	23.57	52.03	20.02	84.90			
Clean. Tail	6.56	3.24	-----	1.47			
Rgh. Tail	64.02	1.08	-----	4.78			
Partially Deslimed:							
Calc. Head	100.00	14.29	-----	100.00	2.50	2.50	5.72
Slime	4.12	25.21	-----	7.27			
Clean. Conc.	23.62	51.09	21.62	84.44			
Clean. Tail	7.04	3.77	-----	1.85			
Rgh. Tail	65.22	1.41	-----	6.44			
Not Deslimed:							
Calc. Head	100.00	14.40	-----	100.00	3.00	2.78	9.68
Clean. Conc.	25.39	49.34	23.42	87.01			
Clean. Tail	10.32	5.53	-----	3.97			
Rgh. Tail	64.29	2.02	-----	9.02			

Obviously, the salts used must be strongly acidic and, as noted above, must not have a deleterious action on the flotation of iron minerals. In order to provide sufficient acidity, the anion

EXAMPLE 9

In order to demonstrate the effect of scrubbing, the procedure used in the first test of Example 8 was repeated except that after desliming the ore

was scrubbed in a flotation cell at about 25% solids with the air intake shut off and was again deslimed before being conditioned with the reagents. The reagents used were 2.5 lbs./ton of H_2SO_4 , 1.12 lbs./ton of neutralized sulfonated oleic acid and 2.64 lbs./ton of 22° Bé. fuel oil.

peated on a number of ore samples using as promoters a number of different sulfonated products in combination with a sulfonated fatty acid. Illustrative results are shown in Table 11. The ore was the same as that used in the last four tests of Example 2.

Table 11

Promoters	Lbs. Per Ton	Lbs./Ton		Concentrate, Percent Fe		Rougher Tailing	
Composition		Sulfuric Acid	Fuel Oil	Assay	Distrib.	Assay, Per Cent Fe	pH
1 Part oil-soluble petroleum sulfonate (Petronate—L. Sonneborn & Sons).....	1.86	2.33	4.10	59.85	96.21	0.74	2.9
1 Part sulfonated oleic acid (treated with 25% by weight concentrated sulfuric acid and neutralized after sulfonation).....	1.63	2.33	4.61	59.87	95.58	0.81	2.9
1 Part water-soluble petroleum sulfonate (SP-702—Stanco Distrib., Inc.).....	1.63	2.33	3.59	60.93	91.31	1.55	2.7
1 Part sulfonated oleic acid (as above).....							
1 Part sulfonated talloel (treated with 50% by weight concentrated sulfuric acid).....							
1 Part sulfonated oleic acid (as above).....							

The concentrate was cleaned twice without additional reagents. The results obtained are shown in Table 9.

Table 9

Product	Percent Weight	Assay		Percent Distrib. of Iron
		Percent Fe	Percent Insol.	
Calc. Head.....	100.00	14.55	-----	100.00
Prim. Slime.....	6.27	20.49	-----	8.83
Sec. Slime.....	2.71	19.28	-----	3.59
Clean. Conc.....	21.85	52.84	18.98	79.52
2nd Cl. Tail.....	4.79	4.04	-----	1.33
1st Cl. Tail.....	8.82	1.21	-----	0.74
Rgh. Tail.....	55.56	1.62	-----	6.18

Comparison of these results with those obtained in the test on the essentially deslimed feed in the first part of Example 8 shows the important savings in reagent consumption that can be effected by a thorough desliming, even though such steps are not necessary to obtain a commercially acceptable result.

EXAMPLE 10

In order to show the effect of conditioning at high pulp densities, the procedure of Example 4 was repeated on two samples, the first being conditioned at 65% solids and the second at flotation density. The ore was similar to that used in Example 8. The reagents used were 2.73 lbs./ton of H_2SO_4 , 2.12 lbs./ton of neutralized sulfonated oleic acid and 5.76 lbs./ton of 22° Bé. fuel oil. The rougher concentrate was cleaned once in the first test and twice in the second test. The results show the definite advantage of conditioning at high solids.

Table 10

Concentrate, Per Cent Fe		Tailing		Pulp Density, Per Cent Solids	
Assay	Distrib.	Assay Per cent Fe.	pH	Conditioning	Flotation
52.03	93.14	1.08	2.7	65	22
40.57	83.30	3.24	2.7	22	22

EXAMPLE 11

In order to show that the sulfonated fatty acids may be used in conjunction with other sulfonated materials, the procedure of Example 1 was re-

EXAMPLE 12

A Minnesota iron ore, a washer overflow containing mainly hematite and quartz, portions of which were locked, and assaying about 15% Fe, was deslimed, conditioned at about 65% solids with 1.57 lbs. of sulfonated soya fatty acids (100 parts fatty acid: 60 parts 95.5% H_2SO_4), 4.0 lbs./ton fuel oil No. 2, and 2.09 lbs./ton sulfuric acid, and floated in a Fagergren flotation machine. The resulting rougher concentrate contained about 34% of the flotation feed by weight and assayed 33.8% Fe and about 49% insoluble. The flotation tailing, about 66% by weight, assayed 2.43% Fe.

This concentrate was conditioned with 2.0 lbs./ton of lime and 2.0 lbs./ton of quebracho and then was deslimed using 2.0 lbs./ton of sodium silicate. The deslimed product was conditioned with 0.08 lb./ton of a higher alcohol frother, B-23, and with 0.05 lb./ton of a cationic-type reagent, lauryl amine hydrochloride, and then floated for 1 minute to remove the silica. This treatment was followed by two stage-additions of 0.05 lb./ton of lauryl amine hydrochloride, conditioning and flotation for the further removal of silica. This treatment produced an iron product (i. e. flotation tailing) assaying 57.51% Fe, and representing a recovery of 50.55% of the iron. Further cleaning of the silica concentrate, using additional 0.027 lb./ton B-23 and 0.02 lb./ton lauryl amine hydrochloride, gave a middling product containing 15.41% of the iron and assaying 34.70% Fe.

EXAMPLE 13

In order to show the applicability of the present process to different types of iron ore, in addition to those used in the preceding examples, a number of various ores were ground to flotation size, if necessary, and then were subjected to a procedure similar to that of Example 1. The rougher concentrates were cleaned once in all except the last test where two cleanings were employed. The results are shown in the following table. It will be noted that acceptable results were readily obtained from a number of types of products or ores which contained a wide variety of iron minerals.

Table 12

Promoter Used				Lbs./Ton		Type of Ore	Feed Assay, Per Cent Fe	Concentrate, Per Cent Fe		Rougher Tailing, pH
Fatty Acid		Parts Sulfuric Acid	Lbs. Per Ton	Sul-furic Acid	Fuel Oil			Assay	Distrib.	
Type	Parts									
Oleic Acid.....	100	25	2.44	2.73	6.10	A washer tailing containing mainly hematite, limonite and quartz.	30.43	58.91	95.88	2.75
Ammonium Sulfuricinoleate (Beacon Co., Boston, Mass.).	-----	-----	2.50	2.76	4.07	A table concentrate containing chiefly magnetite, martite and quartz.	64.44	68.34	95.92	3.3
Soya Fatty Acids.....	100	50	1.75	2.06	3.62	An ore containing martite, magnetite and hematite.	22.07	61.33	96.42	2.7
Fish Liver Oil Fatty Acids...	100	50	2.18	2.73	2.84	A taconite containing principally hematite and quartz.	21.47	54.73	95.62	2.65
Soya Fatty Acids.....	100	50	2.00	2.50	5.06	An ore containing goethite, siderite and hematite.	15.85	51.30	92.61	2.6

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 consisting essentially of a sulfonated aliphatic fatty acid selected from the group consisting of the aliphatic fatty-acids having at least eleven carbon atoms and mixtures of such acids, only, and an amount of an acid substance the anion of which is a constituent of an acid having a dissociation constant greater than 10^{-7} effective to produce in the flotation tailing a pH of from 2 to 6, 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 fatty acid reagent 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 according to claim 1 in which the collecting reagent is a sulfonated oleic acid.

4. A method according to claim 1 in which the collecting reagent is a sulfonated fish oil fatty acid.

5. A method according to claim 1 in which the collecting reagent is a sulfonated soya bean oil fatty acid.

6. A method of beneficiating oxidized iron ores by froth flotation which comprises conditioning the ore at high solids with a reagent consisting essentially of a sulfonated acid selected from the group consisting of the aliphatic fatty-acids having at least eleven carbon atoms and mix-

tures of such acids, only, and an amount of an acid substance, the anion of which is a constituent of an acid having a dissociation constant greater than 10^{-7} effective to produce in the flotation tailing a pH of from 2 to 6, diluting the conditioned ore to flotation density and subjecting it to froth flotation, whereby a concentrate relatively rich in iron mineral and a tailing relatively poor in iron is obtained.

7. 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 reagent consisting essentially of a sulfonated acid selected from the group consisting of the aliphatic fatty-acids having at least eleven carbon atoms and mixtures of such acids, only, and an amount of sulfuric acid effective to produce in the flotation tailing a pH of from 2 to 6, whereby a concentrate relatively rich in iron mineral and a tailing relatively poor in iron are produced.

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The following references are of record in the file of this patent:

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Certificate of Correction

Patent No. 2,475,581

July 12, 1949

ROBERT B. BOOTH ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Columns 7 and 8, Table 4, eighth column thereof, for "85.53" read *89.53*; columns 9 and 10, Table 8, eighth column, for "5.82" read *5.28*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of February, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.