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FROTH FLOTATION OF NONSULFIDE ORES WITH A MIXTURE OF OIL-SOLUBLE AND WATER-SOLUBLE PETROLEUM SULFONATES

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This invention relates to a new class of anionic promoters for non-sulfide ores and to processes of froth flotation using these promoters.

In the past there have been occasional proposals to use as froth flotation promoters certain so-called petroleum sulfonates which are by-products in the refining of petroleum lubricating oil fractions by sulfonating agents such as sulfuric acid, oleum, and the like. Because of the low price and large supply of these materials in normal times, they would be commercially very desirable. However, the procedures of using these compounds in froth flotation have, in the past, achieved little, if any, real success. Petroleum sulfonates are normally divided into two classes: the oil-soluble variety, which are frequently referred to as mahogany oils or mahogany soaps or mahogany acids and the substantially water soluble variety, some of which are usually referred to as green acids. The former have been proposed for use as promoters for certain members of the class of non-sulfide minerals. When used in the flotation of iron oxide and garnet, the petroleum sulfonates alone have not achieved any practical use as recoveries and grades were commercially not acceptable. In our Patents Nos. 2,410,376 and 2,410,377, October 29, 1946, we have described the flotation of iron oxide minerals with oil soluble and water soluble petroleum sulfonates, respectively. The novelty consisted in subjecting the ore to a treatment with a strong acid such as, for example, sulfuric acid. The improvement is extraordinary and opens up the field of iron ore beneficiation to practical froth flotation processes using anionic collectors. In a similar manner, the sulfonates are of great value in the froth flotation of acid treated garnet ores. The garnet flotation is the subject matter of a copending application of Booth and Pickens, Ser. No. 502,982, September 18, 1943.

While for the first time commercially useful grades and recoveries were obtainable with petroleum sulfonates in the flotation of acid treated iron ores, the individual sulfonates generally left something to be desired. In general, the oil soluble sulfonates showed somewhat better results. However, the products are often more expensive and in some cases less readily available, since they have a variety of uses. The water soluble sulfonates also showed good promoting activity but were open to the disadvantage that in some cases they were required in larger amounts than in the case of oil soluble sulfonates. In some cases the quality of the froth was also not as good as might be desired.

The present invention is based on the discovery that when mixtures of oil and water soluble petroleum sulfonates are used much better results are obtained than with either used alone in the same amounts. The results are quite striking, in some cases permitting better recovery and grade with less reagents and in other cases giving equal or better metallurgy with mixtures containing a large portion of the cheaper water soluble sulfonates.

It is not intended to limit the present invention to any theory. Petroleum sulfonates, both mahogany and green acids, are not pure chemical compounds. They are mixtures of indeterminate chemical constitution varying with different oils and with different refining procedures. The tremendous number of variables present makes any attempt at formulating a theory of action out of the question.

We have found, however, that within wide limits, mixtures of oil soluble and water soluble sulfonates give markedly improved results in the froth flotation of non-sulfide minerals amenable to anionic promoters. Strangely enough, the improvement seems to occur generally with various mixtures within wide limits in spite of the fact that particular mahogany sulfonates and green acids or other water soluble petroleum sulfonates may vary widely in their nature and this is an important advantage of the present invention as it creates no problem of supply.

While we have not determined what it is with certainty, there must be some cooperation between the two types of sulfonates because the mixtures appear to be applicable over a wide field of froth flotation of non-sulfide minerals which respond to anionic collectors. The most important improvements commercially at the moment are iron ore flotation and the flotation of garnet and pebble phospate. However, the reagent mixtures of the present invention are also useful with a wide variety of non-sulfide ores. For example, good results are obtained in the beneficiation of cement rock, limestone, rhodochrosite, coal, barite, scheelite, celestite, cassiterite, kyanite, chromite, fluorite, etc.

The mixtures appear to be generally applicable to non-sulfide ores amenable to anionic flotation but the relative importance of the improvements obtained will, of course, vary with different ores.

The mixed sulfonate promoters of the present invention appear to act as improved sulfonates and not to have changed their basic characteristics. In other words, the mixed promoters of the present invention should be used under the same conditions which have been found to give the best results with individual petroleum sulfonates. Thus, for example, in the case of iron and garnet, the ore should be acid treated before flotation. In some cases where the addition of fuel oil and other froth modifying substances are desirable they should be used with the mixed promoters of the present invention. However, in the case of fuel oil or other oiling agents it is sometimes possible to dispense with them when a mixture is used or to use smaller amounts. This is not universally true but, where applicable, constitutes an additional saving of the present invention.

Because of the extremely wide range of characteristics of oil and water soluble petroleum sulfonates a large number of compositions are possible. Naturally, different mixtures will give different results, but it is a surprising fact that in very many cases a good mixed promoter is obtained from a mixture of sulfonates neither of which alone would be commercially attractive. In other cases it is possible by the addition of a small amount of effective sulfonate to make a mixed promoter out of an extremely low grade sulfonate which, although very cheap, is practically useless alone. This is particularly striking in the case of some acid treated iron ore flotations where certain sulfonated residues can be used in a mixture although alone they are worthless.

In addition to improved metallurgical results and reduced reagent consumption which are generally obtainable by the use of the present invention, the mixtures in many cases show improved general flotation characteristics. Thus, for example, the quality of the froth is often better when a mixture is used than when either one is used alone and the mixtures in general are more readily dispersed in water. Some are so readily dispersed that they may be fed in water solution or dispersion, thus simplifying the feeding of the reagent. In many cases markedly improved feeding, distributing and froth characteristics are obtained in mixtures which contain a relatively small proportion of one or the other of the two kinds of sulfonates.

In general it is an advantage of the present invention that the proportion of the two kinds of sulfonates may be varied within wide limits. Many of the best mixtures are those in which the two sulfonates are present in substantially equal amounts. However, under favorable circumstances and particularly in the froth flotation of acid treated iron ore the range may be from 25 parts of oil soluble sulfonate to 1 part of water soluble sulfonate to 1 part oil soluble sulfonate to 25 parts water soluble sulfonate. However, it is not preferred in general to use the extremes and the preferred range is from 10 parts of oil soluble sulfonate to 1 part water soluble to 1 part oil soluble to 10 parts water soluble. In the case of certain sensitive mixtures and in certain flotation operations decrease in efficiency may even be noted with ratios as low as 6 to 1. The wide range permits formulation of mixed promoters according to the present invention having desired characteristics and particularly it is possible in many cases to use a mixture containing a small portion of more expensive sulfonate and a large portion of cheap sulfonate. The wide range of proportions are also valuable as safety factors because commercial petroleum sulfonates are not always uniform and may vary from day to day.

Throughout the specification and claims the term "petroleum sulfonate" is used in the loose sense in which this term is employed in the petroleum art. While, as has been stated above the constitution of various sulfonates is not accurately determined, it is probable that much of the combined acid is present in the form of the sulfate group rather than sulfonate group. Many unsaturated hydrocarbons of lubricating oil stocks in the refining procedure give rise to sulfuric acid half-esters. This is particularly true in the case of some of the water soluble sulfonates. However, the art uses a single term to cover the products obtained and this term will be used throughout the specification and claims, it being understood that the sulfur-containing acid groups are not limited to sulfonic groups. While the term "petroleum sulfonate" is used loosely as far as the sulfur containing acid groups are concerned, it is limited to products obtained by refining petroleum lubricating oil stocks with sulfonating agents. It does not include acid sludges obtained by the sulfuric acid treatment of fuel fractions such as kerosene.

The petroleum sulfonates of commerce are not pure chemical compounds. Thus, for example, the oil-soluble petroleum sulfonates are commercially sold in the form of dispersions in unsulfonated oil and the commercial products referred to in the application are of this nature. Water-soluble petroleum sulfonates are also for the most part mixtures and are not chemically pure substances. Throughout the specification and claims the term "petroleum sulfonate" is used to include the impure commercial products which are customarily sold.

It is an advantage of the present invention that in general the froth flotation procedure is not materially changed by the use of the promoters of the present invention and other adjuncts such as dispersing agents, depressants and the like will normally be employed where their use with a particular ore has been found to be generally desirable. In some cases, notably in the addition of oiling agents such as hydrocarbon oils, glyceride oils and the like, optimum conditions will vary with different mixtures of sulfonates and often are not identical with optimum conditions for individual components. In this respect, the mxed promoters of the present invention behave in a manner which is common in non-sulfide flotation. In the more specific descriptions in the examples in every case optimum conditions are used. The determination of optimum conditions, as is well known, is not difficult or critical but should be made in every case as is standard practice in the art. It is a further advantage of the present invention that the general behavior of the froth flotation is similar to known froth flotations of the same ore and the operator does not have to learn new techniques.

Since many of the various oil soluble and water soluble petroleum sulfonates are of indeterminate structure they cannot be identified by chemical formula and, therefore, in the examples the products will be identified by their trade names and source of supply. This is the only method of identification practical with petroleum sulfonates and it should be understood that in some cases sulfonates having practically the same characteristics may be supplied by different manufacturers under different names. However, in the specific examples which are to follow, numerous types of sulfonates have been used and no two sulfonates are of identical flotation characteristics. The petroleum sulfonates of the examples are, however, all true petroleum sulfonates, that is to say, products obtained from the refining of lubricating oil fractions with sulfonating agents.

It is an advantage of the present invention that the feeding of the mixed sulfonates is not critical. They may be mixed and fed as a mixture. Water soluble and oil soluble sulfonates may be fed separately and one, or both, or the mixture may be dissolved in oil or dispersed in water. When a mixture is being dispersed it is a further advantage that some of the water soluble sulfonates act as dispersing or solubilizing agents for the oil soluble sulfonates.

The dispersing effect of some of the water soluble sulfonates represents an operating advantage as dispersions can be made up in a much shorter time and, in some cases, in more concentrated form. Within wide limits the metallurgy does not appear to be adversely affected by the method of feeding the reagents so long as thorough mixing with the ore is effected.

The invention will be described in greater detail in conjunction with the following specific examples which show results obtainable in the froth flotation of six types of non-sulfide ores.

Example 1

A Minnesota iron ore, a washer reject, containing about 30.5% Fe, was deslimed and the pulp treated with acid, promoter and, in some cases, fuel oil, the treatment being at high solids (60–70%) which has been found to be the most effective conditioning for this type of ore. After conditioning was completed, the thick pulp was diluted to froth flotation density and was subjected to a rougher float and followed by a single cleaning using Fagergren flotation machines. The results of the tests giving the amount of reagent used appear in the following table of metallurgical results. In every case about 2.6 lbs. per ton of sulfuric acid was used and the pH of the rougher tailing was in the neighborhood of 3.0.

Oil-Soluble Petroleum Sulfonate		Water-Soluble Petroleum Sulfonate		Lbs./Ton Fuel Oil	Concentrate		Rgh. Tailing Assay Per Cent Fe
Type	Lbs./Ton	Type	Lbs./Ton		Assay Per Cent Fe	Distrib. of Fe, Per Cent	
Calol Sodium Sulfonate (Standard Oil Co. of Cal.).	2.31	None		None	60.21	83.13	6.48
Do	2.31	do		1.17	59.94	93.41	2.30
Do	0.95	do		0.95	63.34	67.84	10.42
None		Green Sulfonic Acids—Neutralized (Sun Oil Co.).	8.40	2.78	58.59	93.90	3.51
Do		do	6.10	2.01	60.39	91.85	4.26
Do		do	4.20	1.39	60.35	78.08	7.97
Calol Sodium Sulfonate (Standard Oil Co. of Cal.).	1.05	do	1.05	1.16	60.48	83.66	5.27
Do	0.95	do	0.95	1.85	61.16	92.91	2.57
Oronite #2 (Oronite Chem. Co.)	4.12	None		4.15	59.01	96.63	1.73
Do	4.12	do		2.26	58.46	81.99	7.83
Do	3.10	do		3.18	60.45	95.97	1.85
Do	1.55	do		1.59	63.69	45.01	15.52
Do	1.05	Green Sulfonic Acids—Neut	2.10	3.25	59.67	96.34	1.76
Do	0.71	do	1.42	2.09	61.56	61.84	13.37
O-Emulsifier (Sonneborn Sons, Inc.)	4.22	None		None	60.89	92.61	3.11
Do	1.53	do		None	64.50	48.29	16.44
Do	1.53	Green Sulfonic Acids—Neut	1.53	2.25	60.35	94.89	2.43
Eldrol (Penna. Oil Prod.)	4.17	None		None	63.32	25.29	24.57
Do	2.08	do		None	No Useful Promotion		
Do	1.61	Green Sulfonic Acids—Neut	1.61	1.89	61.02	91.00	3.78

It will be noted that in every case the same or better grade and recovery is obtainable with a mixture in amounts considerably smaller than that required if water soluble sulfonates alone are used and in some cases materially smaller than when oil soluble sulfonates alone are employed. In each case the amount of fuel oil represents that which will give optimum results with the particular reagent combination employed.

Example 2

A low grade Minnesota iron ore containing about 17% Fe, mainly as hematite, was conditioned as described in Example 1. A series of tests was carried out, the metallurgical results of which appear in the following table. The amount of sulfuric acid used was about 2.3 lbs. per ton, the pH of the rougher tailing being slightly below 3. The amount of fuel oil used in each case represents the optimum for the reagent combination employed. In general, as in the other examples, the best operating conditions were employed for each combination.

Oil-Soluble Petroleum Sulfonate		Water-Soluble Petroleum Sulfonate		Lbs./Ton Fuel Oil	Concentrate		Rgh. Tailing Assay Per Cent Fe
Type	Lbs./Ton	Type	Lbs./Ton		Assay Per Cent Fe	Distrib. of Fe, Per Cent	
Reagent 407 (Sherwood Ref'g Co.)	4.00	None		None	61.29	90.95	1.62
Do	2.86	do		None	61.97	86.49	1.89
None		SP-702 (Stanco Distrib., Inc.)	2.34	1.29	58.86	95.82	0.81
Do		do	1.34	0.63	61.95	76.16	2.90
Reagent 407	1.42	do	1.42	None	57.65	96.13	0.81
Do	1.31	do	1.31	None	59.41	96.83	0.58
Petroleum Sulfonates (Shell Oil Co.)	2.27	None		1.50	61.16	88.55	1.62
None		Sonesal Green Acids—(Sonneborn Sons, Inc.).	2.10	1.78	59.81	95.08	1.08
Do		do	0.90	0.84	61.49	95.96	0.81
Do		do	0.56	0.49	61.95	91.14	1.27
Petroleum Sulfonates	0.85	do	0.85	2.22	59.00	96.13	0.81
Do	0.57	do	0.57	1.51	61.03	95.49	0.69
Crude Naphtha Sulfonic Soap (Shell Oil Co.).	4.58	None		None	62.10	76.70	3.65
Do	2.29	do		None	No Useful Promotion		
None		SP-702	2.34	1.29	58.86	95.82	0.81
Do		do	1.34	0.63	61.95	76.16	2.90
Crude Naphtha Sulfonic Soap	1.69	do	1.69	None	58.19	97.51	0.54
Eldrol (Penna. Oil Prod. Ref'g Co.)	4.93	None		None	62.10	89.48	1.79
Do	2.29	do		None	62.37	83.76	2.43
None		Oronite #3 (Oronite Chem. Co.)	5.80	4.08	43.61	25.05	13.50
Eldrol	1.73	do	1.73	None	62.10	85.69	2.03
Petronate (Sonneborn Sons, Inc.)	1.82	None		None	62.10	92.63	1.08
None		SP-702	2.34	1.29	58.86	95.82	0.81
Do		do	1.34	0.63	61.95	76.16	2.90
Petronate	0.74	do	0.74	None	61.70	94.35	0.95
SP-312 (Stanco Distrib., Inc.)	2.30	None		None	62.37	89.08	1.22
None		MP-189 (du Pont)	3.02	5.83	60.89	93.39	0.54
SP-312	1.12	do	1.12	1.48	61.43	95.12	0.68
Oronite #2 (Oronite Chem. Co.)	2.96	None		2.08	60.16	92.08	0.92
Do	2.96	do		3.64	60.50	90.22	0.81
None		Green Sulfonic Acids—Neut. (Sun Oil Co.).	2.86	3.24	61.88	89.64	1.84
Oronite #2	0.24	do	2.71	3.35	58.79	97.90	0.35
None		Neutralized Water-Soluble Tarry Fraction from Green Sulfonic Acids (Sun Oil Co.).	12.20	1.56	56.89	91.21	1.89
Oronite #2	1.47	do	1.47	3.33	60.85	95.76	0.69
None		Acidic Water-Soluble Tarry Fraction from Green Sulfonic Acids (Sun Oil Co.).	9.38	1.55	57.29	92.56	1.62
Oronite #2	1.50	do	1.50	3.42	60.73	97.10	0.46

It will be noted that the sulfonate mixtures of the present invention produce in every case iron concentrates of merchantable grade with excellent recoveries in spite of the fact that the ore is very low grade. In fact the results are as good or better with this low grade ore as with the higher grade ore of Example 1. Possibility of treating such low grade ores is an important advantage of the present invention.

Example 3

The ore of Example 1 was conditioned as described therein and was submitted to a series of tests with mixtures of water soluble and oil soluble sulfonates in varying proportions. The metallurgical results appear in the following table. In every case the amount of sulfuric acid used was about 2.6 lbs. per ton of ore and the amount of fuel oil chosen was the optimum for the given reagent combination. The pH of the rougher tailing remained slightly below 3.0.

Sulfonate Mixture Used				Lbs./Ton		Concentrate			Rgh. Tailing, Assay Per Cent Fe
Oil-Soluble Sulfonate		Water-Soluble Sulfonate		Promoter	Fuel Oil	Assay Per Cent Fe	Assay Per Cent Insol.	Per Cent Distrib. Fe	
Type	Parts	Type	Parts						
Oronite #2 (Oronite Chem. Co.)	100	None		4.12	2.26	58.46	12.56	81.99	7.83
Do	100	do		4.12	4.15	59.01	11.54	96.63	1.73
Do	100	do		1.55	1.59	63.69	4.80	45.01	15.52
None		Green Sulfonic Acids—Neutralized (Sun Oil Co.).	100	8.40	2.78	58.59	12.00	93.90	3.51
Do		do	100	4.20	1.39	60.35	9.48	78.08	7.97
Oronite #2	1	Green Sulfonic Acids—Neut	1	3.14	3.23	59.47	9.74	96.35	1.73
Do	1	do	2	3.14	3.34	60.04	9.72	96.56	1.61
Do	1	do	3	3.14	3.69	60.96	8.54	95.07	2.30
Do	1	do	4	3.14	3.69	60.50	9.06	96.11	1.61
Do	1	do	4	3.14	2.98	59.58	10.56	97.03	1.38
Do	1	do	1	3.14	4.61	59.24	10.84	97.37	1.27
Do	1	do	8	3.14	3.69	60.39	9.02	96.61	1.84
Do	1	do	25	3.14	3.69	60.16	9.44	95.91	2.19
Do	2	do	1	3.14	3.23	59.81	9.50	96.72	1.73
Do	4	do	1	3.14	3.23	59.58	10.60	96.52	1.84
Do	8	do	1	3.14	3.23	59.93	9.90	96.43	1.73
Do	25	do	1	3.14	3.23	58.78	11.22	96.18	1.84
Reagent 407 (Sherwood Ref'g Co.).	100	None		3.31	None	62.30	6.98	87.79	4.52
Do	100	do		2.10	None	64.62	4.60	31.53	22.23
Do	100	do		2.07	1.82	62.88	6.38	54.05	18.64
None		SP-702 (Stanco Distrib., Inc.)	100	2.64	1.86	59.41	11.36	94.90	2.32
Do		do	100	2.06	1.81	59.98	10.24	94.41	2.66
Do		do	100	1.23	0.91	64.50	5.14	14.56	21.54
Reagent 407	1	do	1	2.06	1.81	61.26	8.52	94.81	2.08
Do	3	do	1	2.06	1.81	61.95	7.74	89.98	3.71
Do	3	do	1	2.10	1.11	62.42	7.02	88.22	3.82
Do	6	do	1	2.06	0.54	63.46	5.88	74.83	8.11

It will be apparent that, with one of the best combinations, ranges from 1 part oil soluble to 25 parts water soluble and vice versa showed practically no falling off in results. Grades are comparable within normal experimental error. Even with a combination of sulfonates which is particularly sensitive, serious falling off did not take place until the ratio reached 6 to 1. These mixtures represent approximately the two extremes, most mixtures falling between the ranges.

Example 4

A low grade iron or containing hematite, siderite, and goethite assaying about 16% Fe was ground and then prepared as described in Example 1. The reagents were added as a 12% aqueous dispersion. The sulfuric acid was just under 2 lbs. per ton and the pH of the rougher tailing just below 3.0.

Promoter Used		Lbs./Ton Fuel Oil	Concentrate		Rgh. Tailing, Assay Per Cent Fe
Type	Lbs. Per Ton		Assay Per Cent Fe	Distrib. of Fe, Per Cent	
Eldrol (Oil-Sol.—Penna. Oil Prod.)	2.86	None	56.36	75.17	4.14
SP-702 (Water-Sol.—Stanco Distrib., Inc.)	2.26	1.24	52.22	89.23	1.73
1:1 Mixture of Eldrol and SP-702	2.35	0.64	54.17	88.86	1.84
Do	1.98	None	56.36	73.10	3.91

These tests with respresentative mixed sulfonates show the effectiveness of the new reagent on a very refractory low grade iron ore. The results are, of course, not quite as good as with the more easily floatable ores of Examples 1–3 but demonstrate the fact that even extremely refractory ores may be treated with the mixed promoters of the present invention to obtain reasonable recoveries in fairly high grade products.

Example 5

A high grade table concentrate containing principally magnetite, martite and silicate gangue and analyzing about 66% Fe was conditioned and floated as described in Example 1. The reagent was added as a 6% aqueous dispersion. The amount of sulfuric acid was 4 lbs. per ton and the amount of fuel oil just under 2 lbs. per ton. The pH of the rougher tailings was about 2.5. The following table tells the metallurgical results.

Promoter Used		Concentrate		Rgh. Tailing, Assay Per Cent Fe
Type	Lbs. Per Ton	Assay Per Cent Fe	Distrib. of Fe, Per Cent	
Calol (Oil-Sol.—Standard Oil Co. of Cal.)	2.50	69.48	93.83	36.58
Green Sulfonic Acids—Neutralized (Water-Sol.—Sun Oil Co.)	6.00	67.40	16.76	64.87
1:1 Mixture of Calol and Green Sulfonic Acids—Neutralized	2.50	69.58	91.44	40.26

It will be apparent that although the water soluble acids gave a very poor recovery with only slight increase in grade, the mixture gave the same or slightly higher grade with almost as good recovery as the oil soluble sulfonate alone. This test is particularly severe because the oil soluble sulfonate was one of the very best when used alone and the water soluble sulfonate gave no useful result even when used in much larger amounts.

Example 6

A garnet ore from the northeastern United States, containing about 26% garnet mainly as almandite with a hornblende, quartz, feldspar, biotite and pyrite gangue, was ground to flotation size and deslimed. The deslimed ore was conditioned with 5 lbs. per ton of sulfuric acid and petroleum sulfonate in the amount of 1.0 lb. per ton. The sulfonates used here were Calol Sodium Sulfonate diluted with 10% secondary butyl alcohol and a typical green acid from the Sun Oil Company. Flotation was effected in a Fagergren flotation machine, a rougher float being taken and the rougher concentrate cleaned after conditioning with 0.5 lb. per ton of sulfuric acid. The cleaner concentrate was then conditioned with 1 lb. per ton of sulfuric acid and recleaned. The following table gives the results of the three tests.

Reagent Used, Type	Test No.		
	1	2	3
	Calol	Conc. Green Sulfonates	7 parts Calol, 5 parts Conc. Gr. Sulf.
Conc.—Assay, Per Cent Garnet	92.2	40	99
Conc.—Recovery, Per Cent Garnet	81.6	60	87.3

In the case of test 2, cleaning was omitted as the rougher concentrate was so poor and the recovery so low that the procedure was not practical. The marked increase in grade obtained with mixed sulfonates is particularly important with garnet because the ore is relatively cheap and the demand is for a very high grade concentrate. In this type of flotation, therefore, the grade is considerably more important than the recovery. A higher grade was made with about 6% increase in recovery in the case of the mixture of sulfonates, as compared to the results obtained with the better of the components of the mixture.

Example 7

A rake classifier product of pebble phosphate from the Lakeland, Florida district, assaying about 36.5% B. P. L., was conditioned with 0.75 lbs. per ton of a 1:1 mixture of neutralized green sulfonic acids and Calol sodium sulfonate and with 0.99 lb. per ton of talloel together with 4.86 lbs. per ton of fuel oil. Conditioning was effected at high solids in the common manner but differed from the usual Florida practice in that the anionic promoter was used without any caustic soda. After diluting to flotation density the pulp was floated in a Fagergren flotation machine, a rougher concentrate was obtained and was then cleaned. Separate tests were made with each of the components of the mixture described. The green acids alone gave no flotation either in the amount present in the mixture, 0.37 lb. per ton, or in the amount of 0.75 lb. per ton. The following table shows metallurgical results.

Product	Calol Sodium Sulfonate	1:1 Mixture
Cleaner Conc., Per Cent BPL Assay	77.42	78.73
Cleaner Conc., Per Cent Insol. Assay	3.21	3.65
Cleaner Conc., Per Cent BPL Distribution	71.90	85.75
Middling Product, Per Cent BPL Assay	39.52	41.58
Middling Product, Per Cent BPL Distribution	2.48	5.10
Tailing, Per Cent BPL Assay	14.80	6.10
Tailing, Per Cent BPL Distribution	25.62	9.15

It will be noted that while commercially useful results are obtained with Calol sodium sulfonate alone, substantially the same grade was obtained with a marked increase in recovery when the mixture was used. The flotation feed contained considerably more slimes than are usual in flotation operations on this ore in Florida, and it is to be noted that the mixed sulfonates appear to show low slime sensitivity, an important practical advantage.

In the examples dealing with iron ore and garnet ore sulfuric acid has been described as the acid treating agent. As described in our copending applications referred to above, sulfuric acid gives excellent results and its cheapness makes it the preferred material. However, other strong acids which do not contain anions that adversely affect flotation give similar results and it is an advantage of the present invention that the mixed sulfonates are likewise not sensitive to the particular strong acid used in the present treatment of the ore. Instead of a strong acid certain strong acid salts such as sodium bisulfate and the like may be employed.

In the foregoing examples the mixed sulfonates of the present invention have been used as promoters in froth flotation processes. This is the most important practical field for the compositions and the one in which they show their greatest advantage. However, it should be understood that the mixed sulfonates of the present invention are also usable in other wet separation processes involving agglomeration such as tabling, belt tabling, film flotation and the like.

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 a non-sulfide ore amenable to anionic froth flotation which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a collector for the non-sulfide material, said collector containing as its essential collecting component a mixture of 4–96% of oil soluble petroleum sulfonates and 96–4% of water soluble petroleum sulfonates and recovering a concentrate rich in the desired non-sulfide material and tailing poor in the same, the petroleum sulfonates being obtained in the refining of petroleum lubricating oils.

2. A method of beneficiating a non-sulfide ore amenable to anionic froth flotation which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a collector for the non-sulfide material, said collector containing as its essential collecting component a mixture of 10–90% of oil soluble petroleum sulfonates and 90–10% of water soluble petroleum sulfonates, and recovering a concentrate rich in the desired non-sulfide material and tailing poor in the same, the petroleum sulfonates being obtained in the refining of petroleum lubricating oils.

3. A method of beneficiating an acid treated oxidized iron ore which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a collector for the acid treated iron ore, said collector containing as its essential collecting component a mixture of 4–96% of oil soluble petroleum sulfonates and 96–4% of water soluble petroleum sulfonates, and recovering a concentrate rich in iron and tailing poor in iron, the petroleum sulfonates being obtained in the refining of petroleum lubricating oils.

4. A method of beneficiating an acid treated oxidized iron ore which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a collector for the acid treated iron ore, said collector containing as its essential collecting component a mixture of 10–90% of oil soluble petroleum sulfonates and 90–10% of water soluble petroleum sulfonates, and recovering a concentrate rich in iron and tailing poor in iron, the petroleum sulfonates being obtained in the refining of petroleum lubricating oils.

5. A method of beneficiating an acid treated garnet ore which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a collector for the acid treated garnet ore, said collector containing as its essential collecting component a mixture of 4–96% of oil soluble petroleum sulfonates and 96–4% of water soluble petroleum sulfonates, and recovering a concentrate rich in garnet and tailing poor in garnet, the petroleum sulfonates being obtained in the refining of petroleum lubricating oils.

6. A method of beneficiating an acid treated garnet ore which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a collector for the acid treated garnet ore, said collector containing as its essential collecting component a mixture of 10–90% of oil soluble petroleum sulfonates and 90–10% of water soluble petroleum sulfonates, and recovering a concentrate rich in garnet and tailing poor in garnet, the petroleum sulfonates being obtained in the refining of petroleum lubricating oils.

7. A method of beneficiating a sulfuric acid treated oxidized iron ore which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a collector for the sulfuric acid treated iron ore, said collector containing as its essential collecting component a mixture of 4–96% of oil soluble petroleum sulfonates and 96–4% water soluble petroleum sulfonates, and recovering a concentrate rich in iron and tailing poor in iron, the petroleum sulfonates being obtained in the refining of petroleum lubricating oils.

8. A method of beneficiating a sulfuric acid treated oxidized iron ore which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a collector for the sulfuric acid treated iron ore, said collector containing as its essential collecting component a mixture of 10–90% of oil soluble petroleum sulfonates and 90–10% of water soluble petroleum sulfonates, and recovering a concentrate rich in iron and tailing poor in iron, the petroleum sulfonates being obtained in the refining of petroleum lubricating oils.

9. A method of beneficiating a sulfuric acid treated garnet ore which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a collector for the sulfuric acid treated garnet ore, said collector containing as

its essential collecting component a mixture of 4–96% of oil soluble petroleum sulfonates and 96–4% of water soluble petroleum sulfonates, and recovering a concentrate rich in garnet and tailing poor in garnet, the petroleum sulfonates being obtained in the refining of petroleum lubricating oils.

10. A method of beneficiating a sulfuric acid treated garnet ore which comprises subjecting an aqueous pulp of the ore to froth flotation in the presence of a collector for the sulfuric acid treated garnet ore, said collector containing as its essential collecting component a mixture of 10–90% of oil soluble petroleum sulfonates and 90–10% of water soluble petroleum sulfonates, and recovering a concentrate rich in garnet and tailing poor in garnet, the petroleum sulfonates being obtained in the refining of petroleum lubricating oils.

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