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BENEFICIATION OF IRON ORES

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This invention relates to a process for beneficiating iron ores. More particularly, it relates to a process for beneficiating low-grade iron oxide-bearing ores by a sequence of steps of conditioning and froth flotation of ore pulps with the aid of a new and effective collecting agent produced by sulfonating a particular type of polyalkylated aromatic hydrocarbons.

In the course of the last few decades, deposits of high-grade iron ore have been diminishing at a rapid rate owing to the steadily increasing demand of expanding manufacturing industries. Deposits of high-grade ore containing iron oxide material, such as hematite, magnetite and the like, residually concentrated through natural leaching out of siliceous components thereof and suitable for direct shipment to the smelters, remain few in number and their eventual exhaustion looms alarmingly ahead in not too distant a future. Whenever the siliceous impurity is not completely leached out owing to the particular nature of the ore involved, or because of some other factors, additional beneficiation may be secured by physical separation processes such as screening, log-washing, classification, heavy media separation, jigging, etc. Unfortunately, these processes are generally ineffective with materials finer than about 65 mesh in size, and thus a large proportion of the weight of the ore must be discarded and is lost as tailings containing from about 50 to 60% of the weight of the original iron.

In view of the growing scarcity of high-grade iron ores suitable for direct shipment to the smelters, the problem of developing efficient methods of beneficiating the low-grade iron oxide-bearing "wash-ores" and "jig-ores," as well as the heretofore unused low-grade iron formations found in nature, such as taconite, acquires great importance.

My invention offers a simple and economical process for beneficiating low-grade iron ores by the application of a new and effective collecting agent for froth flotation of iron oxide material from such ores. It permits of effectively recovering iron oxides from ore fines such as are obtained in the overflow of iron washer plants and in the rejected waste products from heavy media separation, and, in general, from ores which have been comminuted, as by grinding, in order to

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unlock the iron mineral from its surrounding gangue.

The description which follows teaches the preparation of my new collecting agent and the method of applying it to ore pulps in order to obtain optimal iron recoveries from the froth flotation of low-grade iron ores.

As mentioned hereinbefore, in its general aspects my invention relates to the flotation of particles of iron oxide mineral with the aid of a collecting agent obtained by sulfonation of a certain type of polyalkylated aromatic hydrocarbons. These polyalkylated aromatic hydrocarbons are the bottoms fraction from the alkylation of mononuclear aromatic hydrocarbons such as benzene, toluene, or a xylene, with olefins, or olefin polymers, containing from 9 to 18 carbon atoms and boiling between about 250° F. to about 585–600° F., and preferably with those containing from 12 to 15 carbon atoms and boiling between about 350° F. to about 520° F. Polymers of propylene or butylene, or mixtures of propylene and butylene polymers, are particularly satisfactory for the purpose, although other olefins containing from 9 up to 18 carbon atoms and boiling between about 250° F. to about 600° F., for instance, those olefins obtainable by the Fischer-Tropsch synthesis, may also be used for the alkylation of the aromatic nucleus. In the preparation of olefin polymers suitable for the alkylation of aromatic hydrocarbons, purity of the olefin stock is not essential; thus, for instance, instead of substantially pure propylene, mixtures of propylene with saturated low molecular weight hydrocarbons, and even those mixtures containing some ethylene, may be successfully employed. The olefin stock is employed to alkylate the mononuclear aromatic hydrocarbons under alkylating conditions in the presence of a catalyst such as hydrogen fluoride or boron trifluoride or of other suitable alkylation catalysts, and in such a way as to leave at least one position on the aromatic nucleus available for the entry of a sulfonic acid group. The resulting alkylate is fractionated in order to remove excess unreacted aromatic hydrocarbon and fractions boiling between about 175° F. and about 600° F. The remaining bottoms fraction consists of polyalkylated mononuclear aromatic hydrocarbons boiling above the boiling point of a monoalkylated aromatic hydro-

carbon in which the alkyl portion corresponds to the olefin employed for alkylation. This bottoms fraction is withdrawn to be converted by sulfonation into the collecting agent of the present invention.

The sulfonation treatment of these polyalkylated aromatic bottoms is effected in a suitable apparatus with strong (fuming) sulfuric acid at a temperature below about 160° F., the acid being employed in an amount suited to the particular requirements of each case, and preferably in amounts from about 3 to about 20 mols of the acid per 1 mol of the polyalkylated aromatic hydrocarbon bottoms. A mixture of polyalkylated mononuclear aromatic sulfonic acid and of sulfuric acid is obtained. The polyalkylated mononuclear aromatic sulfonic acid in this mixture is not water-soluble, but only water-dispersible. However, this fact does not affect the effectiveness of the sulfonic acid as a collecting agent when the mixture of acids is employed in the froth flotation of iron oxide ores.

Olefin polymers suitable for the alkylation of mononuclear aromatic hydrocarbons which are to be converted by sulfonation into collecting agents of my invention are produced by polymerizing olefins, such as propylene, in the presence of a catalyst. Generally, an acid polymerization catalyst, such as a phosphoric acid catalyst will be used.

In the preferred embodiment of the preparation of flotation agents of my invention, substantially pure propylene is polymerized at a temperature from about 375° F. to about 475° F. and a pressure, e. g., from about 200 to about 600 p. s. i., in the presence of a catalyst consisting of a charcoal support saturated with orthophosphoric acid. The resulting product is a polypropylene boiling between about 65° F. and about 720° F. A fraction thereof containing from 12 to 15 carbon atoms per molecule and boiling between about 375° F. and about 510° F. is employed to alkylate a mononuclear aromatic hydrocarbon, e. g., benzene, in the presence of a catalyst, preferably hydrogen fluoride, under appropriate alkylating conditions: temperatures between about 50° and about 100° F., molar excess of benzene over polypropylene, and a large amount of the catalyst (from 200 to 800 mol per cent of hydrogen fluoride) based on the polypropylene feed. The alkylate is then distilled to remove excess benzene and lighter alkyl aromatic hydrocarbons boiling up to about 500° F., followed by the so-called "heart cut" which boils between about 500° F. to about 600° F. and consists predominantly of monoalkylated aromatic hydrocarbons having from 12 to 15 carbon atoms in the alkyl chain. The remaining heavy bottoms fraction boiling above 600° F. and up to about 725° F. is a polyalkylated benzene fraction and consists predominantly of paradialkyl benzenes. It is sulfonated in a suitable apparatus with 20% fuming sulfuric acid in a ratio of about 3 to about 20 mols of the acid per 1 mol of polyalkylated benzene. The ultimate sulfonation product is a mixture of a substantially water - dispersible polyalkylated mononuclear aromatic sulfonic acid and sulfuric acid.

Hereinafter in this specification whenever the term "sulfonic acid collecting agent or collector" is mentioned, it will designate the mixture of polyalkylated mononuclear aromatic sulfonic acid and sulfuric acid as obtained by sulfonating the bottoms fraction of polyalkylated aromatic hydrocarbons, such as paradialkyl benzenes, in accordance with the process described hereinabove. Accordingly, the amounts of "sulfonic acid" given in the following description and in the tables will represent the content of polyalkylated mononuclear aromatic sulfonic acid in the sulfonation reaction mixture.

In recovering iron oxide materials from the low-grade iron ores, such as wash-ore tailings, in accordance with the invention, an aqueous free-flowing ore pulp is formed and subjected first to a desliming treatment, in order to remove the extremely fine colloidal slime material of less than about 18–20 microns in size. This desliming treatment may be effected by any of the conventional methods of the art, for instance, by employing a hydroseparator followed by a bowl classifier. The deslimed pulp containing preferably about 25% by weight solids is then ready for conditioning and flotation in accordance with the process of my invention.

The conditioning of the iron ore pulp ordinarily is carried out at high dilution (of the order of 25% solids). Usually it is preferred to effect flotation in an acid circuit. Should the sulfonic acid-sulfuric acid mixture fail to impart sufficient acidity corresponding to a pH of about 2 to 4 to the ore pulp, additional sulfuric acid may be added during the conditioning treatment to insure the desired pH in the flotation circuit. Conditioning of the ore pulp at high dilution, however, is not always necessary for an effective flotation, and in certain cases, depending on the nature of the ore and other circumstances, it may be desirable to condition the ore pulp at a much lower dilution (as high as 60 to 75% solids by weight of the pulp), and then to dilute the conditioned pulp to the desired flotation density of not less than 20% solids by weight of the pulp. Conditioning of the ore-pulp is effected in special conditioning or mixing vessels; however, if so desired under the circumstances of a particular case, the various flotation reagents may be added directly into flotation cells or at various points during the flotation treatment.

In the practice of my invention the collecting effect of the sulfonic acid collector is further enhanced by the addition of an unsaponifiable, non-volatile hydrocarbon oil.

This unsaponifiable non-volatile hydrocarbon oil is preferably a neutral, petroleum hydrocarbon oil, such as a furnace oil or a fuel oil having an A. P. I. gravity from about 30° to about 35°, although heavier oils having an A. P. I. gravity as low as 10° are also satisfactory. Petroleum oils are preferred because of their availability and relative cheapness, but other hydrocarbon oils which are non-volatile and unsaponifiable under the conditions of use in accordance with the invention may also be utilized.

In conditioning the ore pulp, the admission of the sulfonic acid collecting agent into the pulp is followed by the addition of a neutral hydrocarbon oil. The relative proportions of the sulfonic acid collector and of the hydrocarbon oil depend on the type of ore being treated, its structure (crystallinity), and the quantity of fines and slimes in the ore. Ordinarily, good results are obtained by employing a polyalkylated mononuclear aromatic sulfonic acid collecting agent in amounts from about 0.5 to about 4.5 pounds per each ton of deslimed ore, and neutral non-volatile hydrocarbon oil, such as a fuel oil, in an amount from about 1 to about 8 pounds per each ton of deslimed ore. These amounts, however, are merely illustrative of the preferred range and

may vary outside this range. Thus when the ore is unusually slimy, a greater content of polyalkylated mononuclear aromatic sulfonic acid up to 5 and 6 pounds per each ton of ore may be necessary. The optimum weight ratio of the sulfonic acid collecting agent to the neutral hydrocarbon oil for an effective flotation may vary from 1:1 to 4:1, depending on the nature of the ore to be treated and other conditions of each particular case.

As mentioned hereinbefore, whenever the sulfonic acid collector of the present invention is not sufficiently acid to impart the desired degree of acidity (pH from about 2 to about 4) to the ore pulp undergoing flotation treatment, additional sulfuric acid in amounts ranging from about 1 to about 4 pounds of sulfuric acid per each ton of the deslimed ore being conditioned may be added to secure the desired pH in the flotation circuit.

Other suitable collectors and flotation reagents such as frothers, promoters and the like may be employed in conjunction with the sulfonic acid collector of my invention for the purpose of recovering iron oxides by froth flotation in proportions which may be varied in accordance with the needs of each particular case.

At this point it may be noted that, contrary to previous experience of froth flotation, complete desliming is not necessary. In order to obtain the optimal results it is entirely sufficient to remove slimes finer than about 10 microns in size.

In agreement with the customary practice of froth flotation, the rougher concentrate from the first flotation stage which is seldom of the final grade may be cleaned and recleaned as many times as desired. Likewise, the tailings from the initial flotation treatment may be scavenged repeatedly to yield the maximum recovery of iron before being rejected as final tailings.

The operation of my invention and the advantages secured thereby will be better understood upon consideration of the following illustrative test data.

Example I.—The olefin feed for this test is the product of polymerization of a propylene gas mixture, containing 21.6% by weight of propylene, the remainder being saturated low-boiling hydrocarbons 72.4%, butylene 0.5% and ethylene 5.5%. Polymerization is effected at about 375° F. and 250 pounds pressure in the presence of a catalyst formed by saturating a charcoal support with 75% orthophosphoric acid. Benzene is alkylated with the resulting C_{12}–C_{15} polypropylene in the presence of a hydrogen fluoride catalyst and at a temperature of about 70° F., whereupon the bottoms fraction boiling above 600° F. is separated from excess benzene and the light heart cut. This polyalkylated aromatic bottoms fraction boils between 638° F. and 751° F. It is sulfonated at a temperature of less than 160° F. with 20% fuming sulfuric acid in a mol ratio of 3 mols of acid per 1 mol of polyalkylated aromatic bottoms. Wash plant tailings (500 grams), after removal of slimes finer than about 20 microns in size (slimes amounting to about 25–27% by weight based on dry ore), have an iron content of 14.5% by weight on dry deslimed basis. This deslimed material is charged into a flotation cell with enough water to form a pulp containing 25% solids. The resulting ore pulp is then conditioned in this flotation cell by adding 2 pounds of the sulfonic acid collecting agent, prepared as described hereinabove and equivalent to 0.6 pound of polyalkylated aromatic hydrocarbons, followed by 3 pounds of fuel oil (gravity=10° A. P. I.) per each ton of the ore. Since in this case the mixture containing the sulfonic acid collector is not sufficiently acid to impart the preferred pH of about 2 to about 4 to the flotation circuit, 3 pounds of sulfuric acid per each ton of ore is added to the pulp being conditioned. After conditioning for about 2 to 3 minutes, air is admitted into the flotation cell, and a froth rich in iron oxide is removed. This initial froth is subjected to a second flotation without additional reagents and yields the final concentrate.

Upon redistribution of the middling remaining as a residue from this second flotation or cleaning treatment, an ore concentrate is obtained which is equal to 23.1% of the weight of the original solid ore feed and contains 59.1% iron. A very satisfactory recovery of iron equal to 94.2% of the metal originally present in the dry feed is obtained.

Example II.—In this example, the same sulfonic acid collector as in Example I is employed to recover iron oxide material from a difficult type of weathered or "painty" ores. These ores are wash plant tailings containing hematite, limonite and considerable quartz gangue stained with adherent iron oxide. This stained quartz is a particularly difficult material to separate. An ore pulp formed from 500 grams of such substantially deslimed tailings having an iron content equal to 23.7% by weight on dry deslimed basis contains 25% solids and is conditioned in a flotation cell for about 2 minutes with 3.5 pounds of the sulfonic acid collector, equivalent to 1.9 pounds of polyalkylated aromatic bottoms, 3 pounds of furnace oil having a gravity of 31° A. P. I., and 3 pounds of sulfuric acid per each ton of ore. Thereupon air is admitted into the cell, and the mineral-laden froth is removed. This flotation is repeated three times with no further addition of reagents. The concentrate obtained upon redistribution of the middling contains 60.5% iron and is equal to 35% of the weight of the original feed. The recovery of iron amounts to 89.1% of the metal originally present in the ore.

Example III.—In this test, the sulfonic acid collector is prepared by treating the polyalkylated aromatic bottoms fraction of Example I with 20% fuming sulfuric acid at a temperature below 160° F. but in a molar ratio of 6 mols of sulfuric acid to 1 mol of hydrocarbons. The same type of deslimed weathered ore as in Example II is introduced in an amount equal to 500 grams into a flotation cell with sufficient water to form a pulp containing 25% solids. After conditioning this pulp for 2 to 3 minutes with 3.5 pounds of the aforementioned sulfonic acid collector, equivalent to 1.3 pounds of polyalkylated aromatic hydrocarbons, followed by 3 pounds of fuel oil having a gravity of 31° A. P. I., per each ton of dry ore, air is admitted into the pulp, and the iron oxide-bearing froth is removed. In this instance, the ratio of the number of mols of sulfuric acid employed for sulfonation per each mol of polyalkylated aromatic bottoms is sufficiently large to impart a pH of 2 to 4 to the flotation circuit, and thus no additional sulfuric acid is required in the conditioning step. The froth product is cleaned by three successive flotations without further addition of the reagents. After redistribution of the middling, a recovery of 91.4% iron is secured in a concentrate product which analyzes to contain 60.5% iron and amounts to 34.4% of the original weight of the ore.

Example IV.—In this case, the deslimed ore and the reagents for the flotation thereof are similar to those of Examples II and III, except for the fact that the mol ratio of sulfuric acid to polyalkylated aromatic hydrocarbon bottoms in the preparation of the sulfonic acid collector is 11.8:1. The product of this sulfonation in an amount equal to 3.5 pounds, equivalent to 0.86 pounds of polyalkylated aromatic bottoms, is added into the flotation cell, followed by 4.5 pounds of fuel oil (gravity=31° A. P. I.), per each ton of the ore, and the conditioning and flotation treatments are carried out as indicated in the previous examples. The recovery of iron, after distribution of the middling, is found to be equal to 95.5% of the original feed. The concentrate contains 60.0% iron and represents 36.2% of the weight of the original ore. The following Table I summarizes the data obtained in Examples I, II, III and IV.

TABLE I

Data on flotation of wash plant tailings (500 grams, deslimed)

Example No.	I	II	III	IV
Molar ratio of sulfuric acid employed for sulfonation to polyalkylated benzene bottoms	3:1	3:1	6:1	11.8:1
Reagents in Lbs./Ton of Ore:				
Sulfonic acid collector	2.0	3.5	3.5	3.5
Neutral Hydrocarbon Oil (Fuel oil; gravity=31° A. P. I.)	3.0	3.0	3.0	4.5
H_2SO_4 (96%) to secure desired pH	3.0	3.0	None	None
Feed: Iron content, in per cent by weight	14.5	23.7	22.8	22.7
Product (based on deslimed feed):				
Iron content of final concentrate, in per cent	59.1	60.5	60.5	60.0
Weight of final concentrate, in per cent of feed	23.1	35.0	34.4	36.2
Recovery of Iron, in per cent of feed	94.2	89.1	91.4	95.5

The next series of tests with a low-grade weathered iron-bearing ore (wash plant tailings) are made to illustrate the optimal operating conditions for the effective froth flotation of iron oxides from iron-bearing ores in accordance with my invention. In these tests I have varied the type of polyalkylated aromatic hydrocarbon bottoms fraction employed for the preparation of the sulfonic acid collector, the mol ratio of sulfuric acid to polyalkylated aromatic bottoms, the amount of neutral hydrocarbon oil, the extent of desliming, and, in some tests, I have added a flotation activator to the ore pulp. Numerous test data defining these optimal conditions could be adduced, but it is believed that those several representative tests as are described and tabulated hereinafter will be sufficient.

The sulfonic acid collector for these tests illustrated in Tables II–V is obtained by sulfonating a fraction of polyalkylated aromatic hydrocarbons, namely, the bottoms fraction produced in the alkylation of benzene with C_{12} to C_{15} polypropylene and boiling from 603° F. to above 700° F. This bottoms fraction possesses the following characteristics: gravity = 28.3° A. P. I.; aniline point = 125; viscosity at 100° F. = 198.8 S. S. U. Its sulfonation is obtained by employing 20% fuming sulfuric acid in a molar ratio of 10 mols of the acid to 1 mol of polyalkylated benzene hydrocarbons, unless otherwise specified. In all cases the quantity of H_2SO_4 used for sulfonation is sufficient to secure the desired pH of about 2 to about 4 in the flotation treatment. In most of these tests, slimes finer than 10 microns in size are removed prior to the conditioning treatment, unless otherwise indicated, and all the material coarser than 65 mesh is eliminated by screening. As will be shown further on in Table II, it is unnecessary to remove slime particles larger than 10 microns in size to insure satisfactory recovery of iron values. On the other hand, desliming to less than 10 micron size will ultimately result in unsatisfactory flotation. For the sake of stability and ease in dispensing, the sulfonic acid-sulfuric acid mixture is diluted with water in a concentration equivalent to 0.0625 gram of polyalkylated benzene bottoms per one milliliter of diluted solution prior to the conditioning of the ore pulp.

The ore is submitted to the following sequence of treating steps: (1) desliming to a desired degree; (2) elimination of material coarser than 65 mesh by screening; (3) formation of an aqueous iron ore pulp; (4) conditioning of this ore pulp at flotation density (of the order of 25% solids); and (5) froth flotation of the conditioned iron ore pulp in successive flotation cells. As pointed out already, the rougher concentrate is seldom of the final grade and, therefore, it is submitted to three stages of cleanings, yielding the final concentrate and the cleaner tailings which are returnable to the process. The rougher tailings are scavenged as frequently as desired and yield a low-grade scavenger concentrate likewise returnable to the process. In some cases, an additional flotation step is interposed between the rougher and the scavenging treatment to produce a middling which may also be retreated at least once to prevent build-up of middlings.

Table II below combines the data on the reagents used for flotation, the procedure followed, and the results obtained by employing a sulfonic acid collector produced by sulfonation of undistilled polyalkylated benzene bottoms boiling between 603°–700° F., a 50% overhead fraction thereof boiling between 603°–665° F. and a 75% overhead fraction boiling between 603°–684° F. It is noted that the weight recovery and the metal recovery of the product are substantially increased by employing the fraction boiling between 603°–684° F. The grade of the product is likewise improved.

TABLE II

Effect of boiling range of polyalkylated benzene bottoms employed to prepare sulfonic acid collector on recoveries of iron by flotation

Test No.	144-3	146	151
Boiling range of polyalkylated benzene bottoms, °F.	603–700	603–665	603–684
Molar ratio of sulfuric acid employed for sulfonation to polyalkylated benzene bottoms	10:1	10:1	10:1
Reagents in Lbs./Ton of Ore:			
H_2SO_4 (20% fuming) employed for sulfonation	8.4	5.5	8.4
Sulfonic acid collector	3.7	2.45	3.7
Neutral hydrocarbon oil (Furnace oil of 31° API gravity)	1.5	4.0	8.0
Feed:			
Maximum size of slimes removed, in microns	25	25	25
Iron content, in per cent	22.8	22.1	22.1
Product (Based on Deslimed Feed):			
Iron content of final concentrate, in per cent	53.4	59.5	58.5
Weight of final concentrate, in per cent of feed	25.0	30.8	33.6
Recovery of iron, in per cent of feed	58.5	83.0	88.9

Table III shows the effect of different mol ratios of sulfuric acid employed for sulfonation to polyalkylated benzene bottoms in preparing the sulfonic acid collector and also the effect of different degrees of slime removal on ultimate iron recoveries. An exceptionally high recovery of 96.1% of iron is obtained when the mol ratio of sulfuric acid to polyalkylated benzene bottoms in the sulfonation reaction is equal to about 10:1. Furthermore, the same table indicates that extensive desliming treatment is not critical for a satisfactory iron oxide recovery, and that the best recoveries are obtained upon removal of slimes not larger than 10 microns in size.

TABLE III

Effect of molar ratio of sulfuric acid to polyalkylated benzene bottoms and of degree of desliming on recoveries of iron oxide from low-grade iron ore

Test No.	185	187	174	155
Molar ratio of sulfuric acid employed for sulfonation to polyalkylated benzene bottoms	10:1	6:1	10:1	10:1
Reagents in Lbs./Ton of Ore:				
H_2SO_4 employed for sulfonation (20% fuming)	11.7	7.8	9.8	12.2
Sulfonic acid collector	4.29	4.29	4.29	2.45
Neutral hydrocarbon oil (furnace oil of 31° API gravity)	7.0	7.0	7.0	5.0
Feed:				
Maximum size of slimes removed, in microns	10	10	5	25
Iron content, in per cent	24.3	24.4	25.2	22.0
Product (based on deslimed feed):				
Iron content of final concentrate, in per cent	61.1	60.4	56.7	57.2
Weight of final concentrate, in per cent of feed	38.2	36.2	42.4	37.1
Recovery of iron, in per cent of feed	96.1	89.5	95.5	94.0

Table IV contains the data relative to the effect of varying amounts of unsaponifiable, neutral hydrocarbon oil which is added to assist the sulfonic acid collector upon the recovery of iron oxides from the ore by the process of the present invention. It is noted that an increase in the amount of hydrocarbon oil substantially improves the recovery of iron and tends to raise the grade of the concentrate.

TABLE IV

Effect of varying amounts of neutral hydrocarbon oil on recovery of iron ore

Test No.	138-3	138-4	155	158
Molar ratio of sulfuric acid to polyalkylated benzene bottoms	10:1	10:1	10:1	10:1
Reagents in Lbs./Ton of Ore:				
H_2SO_4 employed for sulfonation (20% fuming)	5.5	5.5	9.6	12.2
Sulfonic acid collector	2.45	2.45	2.45	2.45
Neutral hydrocarbon oil (Furnace oil: Gravity=31° API)	1.5	4.0	5.0	7.0
Feed:				
Maximum size of slimes removed, in microns	25	25	25	25
Iron content, in percent	21.9	21.7	22.0	22.6
Product (based on deslimed feed):				
Iron content of final concentrate, in per cent	54.5	54.6	57.2	60.0
Weight of final concentrate, in per cent of feed	32.4	34.2	37.1	35.4
Recovery of iron, in per cent of feed	80.5	85.7	94.0	94.1

Table V contains the results of tests with and without iron chloride as an activator of flotation. It is observed that the presence of about 2 to 5 pounds of iron chloride per ton of ore improves the recovery as well as the grade of the ore.

TABLE V

Effect of addition of $FeCl_3$ on flotation results

Test No.	162	178	164
Molar ratio of sulfuric acid to polyalkylated benzene bottoms	10:1	10:1	10:1
Reagents in Lbs./Tons of Ore:			
H_2SO_4 employed for sulfonation (20% fuming)	10.4	10.4	10.4
Sulfonic acid collector	3.7	3.7	3.7
Neutral hydrocarbon oil (Furnace oil: Gravity=31° API)	6.0	6.0	6.0
$FeCl_3$ activator	0.0	5.0	2.0
Feed:			
Size of slimes removed, in microns	10	5	10
Iron content, in per cent	23.6	24.5	23.5
Product (based on deslimed feed):			
Iron content of final concentrate, in per cent	61.5	58.5	58.5
Weight of final concentrate, in per cent of feed	34.2	39.0	36.9
Recovery of iron, in per cent of feed	89.1	93.0	96.0

Table VI provides a comparison between the flotation results obtainable with the sulfonic acid collector of the present invention and the results obtained by employing a well-known collector of cationic type, namely, normal dodecyl amine acetate, which floats the quartz away from hematite in taconite or in a similar low-grade iron ore.

TABLE VI

Comparison of flotation results obtained with a cationic collector

Test No.	163	210.4
Molar ratio of sulfuric acid employed for sulfonation to polyalkylated benzene bottoms	10:1	------
Reagents in Lbs./Ton of Ore:		
H_2SO_4 employed for sulfonation (20% fuming)	10.4	------
Sulfonic acid collector	3.7	------
Furnace oil (Gravity=31° API)	6.0	------
Methyl amyl alcohol frother	------	0.1
Dodecyl amine acetate	------	1.8
Feed:		
Maximum size of slimes removed, in microns	10	<15
Iron content, in per cent	23.6	23.4
Product (based on deslimed feed):		
Concentrate grade, per cent Fe	61.5	49.8
Weight of concentrate, in per cent of feed	34.2	19.8
Recovery of Fe, in per cent	89.1	42.1

The above data show a definite superiority of flotation agents containing the sulfonic acid collector of my invention over the cationic dodecyl amine acetate collector with respect to the weight of final concentrate recovered, the amount of iron recovery in per cent of the feed and the grade of the final concentrate.

The last Table VII contains a comparison of test results from froth flotation of iron ore of approximately the same grade in accordance with the present invention [Tests (b) and (g)], and also by employing other collecting agents used in the art, such as water-soluble and oil-soluble petroleum sulfonates, unsulfonated tall oil, unsulfonated tall oil plus a normal alkyl amine, and normal dodecyl betaine. The examination of the data assembled in this table definitely shows that the results obtained with my sulfonic acid collector are superior to those obtainable with other collecting agents. For an equivalent grade of the ore, the sulfonic acid collector of my invention secures superior recoveries. Thus, it is found that the sulfonic acid collector provides an economical and effective means for the recovery of iron oxide from ores, particularly from low-grade iron ores, and

that the application of this collector in froth flotation yields high-grade final concentrates and secures recoveries which compare advantageously with the other flotation processes of the art.

TABLE VII

Comparison with various collectors

Test	Type of Ore	Type of Process	Collecting Agent Employed	Amount, in Lbs./Ton of Ore	Grade of Final Concentrate, in Per Cent Fe	Recovery, Per Cent Total Fe
(a)	Wash Ore, 17.7% Fe	Cationic; silica removal	N-dodecyl betaine	0.48	Average 56.9	75
(b)	Wash Ore, 24.3% Fe	Anionic; iron oxide removal.	Polyalkylated benzene sulfonic acid collector+neutral oil.	4.3 sulfonic acid+7.0 oil.	61.1	96.1
(c)	Wash Ore, 20.2% Fe	do	Petroleum sulfonate (water-soluble).	1.96	60.2	85.0
(d)	Wash Ore, 19.6% Fe	do	Petroleum sulfonate (oil-soluble)	2.90	58.2	85.5
(e)	Wash Ore, 23.8% Fe	Combined anionic and cationic.	Tall oil+C^{18} amine	1.5 tall oil+0.10 amine	57.2	33.9
(f)	Wash Ore, 21.7% Fe	Anionic; silica removal	Tall oil	2.00	59.2	82.3
(g)	Wash Ore, 22% Fe	do	Polyalkylated benzene sulfonic acid collector+neutral oil.	2.45 sulfonic acid+5.0 oil.	57.2	94.0

The application of my novel sulfonic acid collector is by no means limited to the recovery of hematite and magnetite. Other iron minerals such as martite, limonite, siderite, goethite and the like may be also successfully floated in accordance with this invention. Generally speaking, the application of my sulfonic acid collector permits of recovering commercially acceptable concentrates from tailings heretofore rejected in the conventional processes of iron-ore beneficiation.

In conclusion, it is to be understood that the test data in the aforegiven examples and tables are merely illustrative, and that the invention is not limited thereby, but only by the definitions of the appended claims.

1. A process for the recovery of iron oxide minerals from iron-bearing ores, which comprises forming an aqueous pulp of an iron oxide-bearing ore and effecting froth flotation of said aqueous pulp in the presence of a polyalkylated mononuclear aromatic sulfonic acid, said acid being a sulfonated bottoms fraction from the alkylation of a mononuclear aromatic hydrocarbon with an olefin containing from 9 to 18 carbon atoms and boiling between about 250° F. to about 600° F., said bottoms fraction boiling above the boiling point of a monoalkylated aromatic hydrocarbon in which the alkyl portion corresponds to said olefin.

2. A process as defined in claim 1, wherein the ore pulp subjected to froth flotation has a pH from about 2 to about 4.

3. A process as defined in claim 6, wherein said froth flotation is effected in the presence of said polyalkylated mononuclear aromatic sulfonic acid and of an unsaponifiable nonvolatile hydrocarbon oil.

4. A process as defined in claim 1, wherein said froth flotation is effected in the presence of said polyalkylated mononuclear aromatic sulfonic acid and of a neutral petroleum hydrocarbon oil characterized by a gravity from about 10 to about 35° A. P. I.

5. A process as defined in claim 1, wherein said froth flotation is effected in the presence of said polyalkylated mononuclear aromatic sulfonic acid and of a neutral nonvolatile petroleum hydrocarbon oil, and wherein the ratio of said polyalkylated mononuclear aromatic sulfonic acid to said neutral petroleum hydrocarbon oil is comprised between 1:1 and 4:1.

6. A process as defined in claim 1, wherein said froth flotation is effected at a dilution of the ore pulp corresponding to not less than 20% solids.

7. A process as defined in claim 1, wherein said froth flotation is effected in the presence of sufficient sulfuric acid to impart a pH of about 2 to about 4 to the ore pulp.

8. A process as defined in claim 1, wherein said olefin is an olefin containing from 12 to 15 carbon atoms and said mononuclear aromatic hydrocarbon is benzene.

9. A process as defined in claim 1, wherein said olefin is a polymer of propylene containing from 12 to 15 carbon atoms and said mononuclear aromatic hydrocarbon is benzene.

10. A process for the recovery of iron oxide minerals from iron-bearing ores, which comprises forming an aqueous pulp of an iron oxide-bearing ore, removing colloidal slimes therefrom, conditioning the deslimed aqueous ore pulp with a polyalkylated mononuclear aromatic sulfonic acid, said acid being a sulfonated bottoms fraction from the alkylation of a mononuclear aromatic hydrocarbon with an olefin containing from 9 to 18 carbon atoms, said bottoms fraction boiling above the boiling point of a monoalkylated aromatic hydrocarbon in which the alkyl portion corresponds to said olefin, effecting froth flotation of the conditioned ore pulp in an acid circuit having a pH from about 2 to about 4, and recovering the iron oxide-bearing froth.

11. A process as defined in claim 10, wherein the colloidal slimes removed are slimes less than 10 microns in size.

12. A process for the recovery of iron oxide minerals from iron-bearing ores, which comprises forming an aqueous pulp of an iron-bearing ore, conditioning said pulp at low dilution corresponding to 75% or less solids with a polyalkylated mononuclear aromatic sulfonic acid, said acid being a sulfonated bottoms fraction from the alkylation of a mononuclear aromatic hydrocarbon with an olefin containing from 9 to 18 carbon atoms and boiling between about 250° F. to about 600° F., said bottoms fraction boiling above the boiling point of a monoalkylated aromatic hydrocarbon in which the alkyl portion corresponds to said olefin, and effecting froth flotation of the conditioned pulp at high dilution of not less than 20% solids.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
Re. 22,548	Brandt	Sept. 26, 1944

UNITED STATES PATENTS

Number	Name	Date
2,164,063	Handy	June 27, 1939
2,202,601	Reid	May 28, 1940
2,230,565	Gaylor	Feb. 4, 1941
2,385,054	Booth et al.	Sept. 18, 1945
2,410,376	Booth	Oct. 29, 1946
2,410,377	Booth et al.	Oct. 29, 1946

Number	Name	Date
2,414,714	Booth et al.	Jan. 21, 1947
2,456,119	Friedman	Dec. 14, 1948
2,461,875	Booth et al.	Feb. 15, 1949
2,475,581	Booth et al.	July 12, 1949
2,480,592	Mitchell	Aug. 30, 1949
2,467,176	Zimmer	Apr. 12, 1949
2,475,581	Booth	July 12, 1949