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CATIONIC FROTH FLOTATION OF IRON ORE

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This invention relates to the separation of silicious gangue particles from oxidic iron mineral particles by a froth flotation process of the "cationic" type wherein the silicious particles are induced to float and the iron mineral particles are induced to sink. More particularly, the invention is concerned with the application of this separatory process to pulps of oxidic iron-bearing materials containing fine oxidic iron particles whereby markedly to depress or inhibit the floatability of the latter and hence to give a cleaner separation between the same and the fine silicious particles associated therewith.

It heretofore has been proposed to beneficiate silicious low-grade iron-bearing material by a process which, in essence, consists in subdividing the material to size of liberation, forming an aqueous pulp of the subdivided material, adding a relatively small amount of a readily water-dispersible cationic collector—without, or preferably with, added frothing agent—to a body of the aqueous pulp, and subjecting the resulting mixture to agitation and aeration in a froth flotation cell, whereby to develop a froth rich in silica and poor in iron, and separating the froth from the unfloat residue. Such a process is described and claimed in my copending now abandoned application entitled "Beneficiation of iron ores," Serial No. 500,002, filed August 25, 1943. This "cationic" type of froth flotation process operates very well on pulps whose liberated oxidic iron particles are relatively coarse and which have either been freed from colloidal matter ("silmes") or have had their colloidal matter rendered relatively innocuous by recourse to a flocculation treatment or suitable "conditioning" treatment. The application of this process, however, to pulps having a substantial content of fine oxidic iron particles has the disadvantage that undesirably large amounts of the cationic collector (usually a rather expensive chemical) are required: moreover, the resulting concentrates tend to run too high in silica and too much iron mineral is discarded in the tailings.

It is an object of the present invention to provide an improved cationic type of froth flotation process which is effective for application to crude pulps of silicious iron-bearing material. Another inventive object is to modify the conventional cationic flotation process in such manner as to depress the iron mineral fines, i. e., to inhibit the flotation of these fines.

It has now been found that the above disadvantages may be obviated, and that the above and other inventive objects may be realized by including in the charge to the flotation cell, e. g., by incorporating into the pulp a relatively small amount of a modified starch product (hereinafter to be more specifically described), and conducting the cationic froth flotation operation upon the resulting mixture. By so modifying the convention-

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al procedure the iron contents of the resultant tailings are desirably lowered and the resulting concentrates are of higher grade and also contain a greater proportion of the total iron in the feed; moreover, this modified procedure permits a desirable economy in the amount of collector used per unit of ore treated, and also makes possible the selection of operable cationic collector from a larger group of the latter than was available under the prior practice.

By the expression "modified starch product" is here meant a starch, consisting mostly (i. e., about 75% or better) of relatively large moleculcd, branched components, which has been only moderately degraded, by one or another of known processes of degradation, to the point where

(1) the starch granule structure has been substantially weakened or destroyed to allow good dispersibility in water, so that the starch product has acquired a 5 to 80% solubility in cold water, and

(2) the ferricyanide reducing value of the starch product lies between about 20 and about 250, optimum 35 to 80.

Relative to the first criterion, it is to be noted that modified starch products having less than a 5% solubility in cold water include most thin-boiling "starches," "oxidized starches" and so-called "soluble starches." This limitation excludes about 80% of the very many modified starch products tested by me. The upper limit of 80% solubility is imposed because products with higher than 80% cold water solubility usually have suffered too extensive chemical degradation and are composed of, or contain a large proportion of, carbohydrate molecules too small in molecular size to function as depressors of the iron mineral fines in the cationic flotation process.

In connection with the second criterion above, it is noted that a good measure of the extent of chemical degradation—or the degree to which the starch molecule has been broken or hydrolyzed into smaller fragments—is the test described by Farley and Hixon in "Indus. & Eng. Chem., Anal. Ed.," vol. 13, p. 616 (1941). With this test, which primarily is a means for determining aldehyde groups, it is possible to correlate average molecular size with the ferricyanide reducing value of the product. The ferricyanide reducing value of unmodified starch is 10, and that of glucose is 2800; ferricyanide reducing value is proportional to extent of hydrolysis up to a value of about 1500. Many of the modified starch products found to be very effective as depressors of iron mineral fines have ferricyanide reducing values of 80 or less, whereas some modified starch products, commercially styled "dextrins," found to have only slight depressing effect have ferricyanide reducing values of the order of 250 and higher.

A low sugar content (i. e., not more than 2% and preferably much less than 2%, expressed as dextrose) also is a desirable quality of a modified starch product effective as a depressor in the present relation. A substantial sugar content is indicative of too extensive degradation of the starch molecules and is reflected in high ferricyanide reducing value of the modified starch product.

Ancillary to the above criteria, I have found that the depressor effect of an operable modified starch product is to be attributed to its content of branched components, and that the linear components of the starch are without the depressor effect and probably are to be assessed as were "dilutents" therein. These facts have been established by me on the basis of experimental data involving the use of separated fractions of branched components and linear components and use of admixtures of the two. Modified starch products prepared from corn starch (e. g., the product known as "Amioca") from "waxy maize" corn, composed almost entirely of branched molecules, have higher depressor efficiency than modified starch products similarly processed and having the same ferricyanide reducing value and same cold water solubility but derived from corn starch containing 72-75% of branched molecules.

Included within the scope of the above definition of operable modified starch products, but not exhaustive of the latter, are: some "British gums" or heat dextrins, and an "acidified starch" or "acid-modified starch" prepared by heating the unmodified starch with a small amount of mineral acid in dilute aqueous solution, e. g., in the proportions of about 5 grams of the unmodified starch and 100 ml. of water containing about 0.5 ml. of concentrated sulphuric acid, the heating being continued for several minutes, without the necessity of boiling, until the dispersion became relatively clear.

In connection with this latter product, it is noted that the resulting solution is used in the flotation procedure directly, that is to say without neutralization. The effect of the acid modification is to weaken the granule structure (as shown by its very low paste viscosity) and to disperse it in the water with relatively little chemical degradation of the molecules: it still gives a blue iodine color, and its ferricyanide reducing value falls within the range 35-50.

Other specific modified starch products answering the above criteria and found to have excellent depressor effect in the present relation are:

(a) A modified corn starch product, of the "heat dextrin" type, having a cold-water solubility of 70% and a ferricyanide reducing value of 76;

(b) A modified starch, of the "soluble starch" type, having a cold-water solubility of 10% and a ferricyanide reducing value of 76; and

(c) A modified corn starch product, of the "British gum" type, having a cold-water solubility of about 50% and a ferricyanide reducing value of about 75.

The effect of the above described "acidified starch" is shown in the batch tests data of Table No. 1 following, in which the starting material employed, the identities and relative amounts of collector and of frother, and the conditions of operation were as follows: The "acidified starch" was a product produced by heating corn starch in water containing about 1% HCl, based

on the weight of the starch, for about 15 minutes. The pulp was conditioned with the "acidified starch" for about 10 minutes, prior to carrying out the batch flotation step. In this series of batch operations the starting material operated upon was a washing plant tailing from the Danube mine washing plant. This tailing product analyzed 35.2% Fe (mostly hematite, with a small amount of limonite) and a gangue composed largely of chert and quartz. This starting material was finely divided (minus 60 mesh) as received, and was not further subdivided; it contained a substantial amount of ultra-fine particles ("slimes"). The starting material was not deslimed or subjected to a flocculation treatment. The separations were effected in a standard mechanically agitated flotation cell, 500 grams of the starting material being used per batch with sufficient water to yield a pulp containing about 25% solids. In each test there were used:

- (a) As cationic collector, 0.4 lb. a cationically acting amine collector, more particularly described below, per ton ore, and
(b) As frother, 0.104 lb. methyl amyl alcohol per ton ore.

The cationically acting amine collector referred to above is a mixture of primary aliphatic amines corresponding in alkyl chain length to fatty acids of coconut oil, the amines mixture being converted to the corresponding hydrochlorides or acetates or other water-soluble derivatives thereof for the sake of improved solubility. The collector was used in dilute aqueous solution, and was added to the cell contents in small increments during the carrying out of the flotation step.

TABLE 1

Effect of "acidified starch" in amine flotation—Danube tailings

Acidified Starch, lb./ton	Product	Percent Weight	Assay, Percent		Percent of Total Iron
			Iron	Silica	
None	Tailings.....	27.43	12.88	-----	9.98
	Middlings.....	38.97	34.25	-----	37.77
	Concentrates.....	33.60	54.96	18.17	52.25
	Total.....	100.00	35.35	-----	100.00
.4	Tailings.....	26.30	7.98	-----	5.86
	Middlings.....	24.00	22.47	-----	15.03
	Concentrates.....	49.70	57.06	15.30	79.11
	Total.....	100.00	35.85	-----	100.00
.8	Tailings.....	25.66	7.81	-----	5.54
	Middlings.....	24.14	21.49	-----	14.37
	Concentrates.....	50.20	57.63	15.32	80.09
	Total.....	100.00	36.12	-----	100.00
1.6	Tailings.....	30.64	5.86	-----	4.99
	Middlings.....	20.58	19.21	-----	11.00
	Concentrates.....	48.78	61.72	8.88	84.01
	Total.....	100.00	35.88	-----	100.00
2.0	Tailings.....	34.26	4.07	-----	3.95
	Middlings.....	15.97	18.07	-----	8.18
	Concentrates.....	49.77	62.10	8.13	87.87
	Total.....	100.00	35.22	-----	100.00
3.0	Tailings.....	25.99	6.01	-----	4.22
	Middlings.....	17.29	12.18	-----	5.67
	Concentrates.....	56.72	58.79	13.92	90.11
	Total.....	100.00	37.01	-----	100.00

It will be observed that improvement (in grade and in quantity of concentrate) followed the progressive increases in amounts of "acidified starch" employed, up to an optimum of about

2.0 lb./ton (between 1.6 and 3.0 lb./ton) of the "acidified starch." As the amount of acidified starch exceeds the optimum, the silica particles are also inhibited from floating and tend to contaminate the concentrate.

Continuous tests (instead of the above batch tests), made at the rate of 1 ton per hour, in commercial sized float machine, have demonstrated that metallurgical results similar to those recited above are securable with a collector consumption, and with a consumption of "acidified starch," of only about one-half those amounts employed in the batch tests. Thus, in continuous tests paralleling the batch tests recited in Table 1, optimum results were secured with a collector consumption of 0.18 lb./ton and 1.0 lb./ton of "acidified starch": as little as 0.2 lb./ton of the "acidified starch" exerted a real improvement in the grade and quantity of the concentrate.

It has been found that best results are attained by adjusting the alkalinity of the circuit, containing the modified starch product, to suit the particular ore being treated. Thus, it has been found that in operating on certain ferruginous cherts (e. g., those found in northeastern Minnesota and locally known as "taconite" and "oxidized taconite") it is desirable if not absolutely necessary that the circuit be maintained alkaline (e. g., at an alkalinity equivalent to a pH of 8 or more). On the other hand, it has been found that best results in operating on certain washing plant tailings follow adjustment of the alkalinity of the circuit to neutral or only very slightly alkaline (pH 7-7.5). This latter observation is illustrated in the data, of Table 2 following, of batch tests performed on a low grade washing plant tailing conditioned with about 2 lbs./ton of "acidified starch":

TABLE 2

Effect of alkalinity in amine flotation of danube tailings using "acidified starch"

Acid or Alkali Added	pH-Pulp	Product	Percent Weight	Assay, Percent		Percent of Total Iron
				Iron	Silica	
Sulphuric acid	5.9-6.1	(Tailings.....	37.92	6.35	-----	14.30
		(Middlings.....	40.12	5.70	-----	13.59
		(Concentrates.....	21.96	55.35	16.47	72.11
		Total.....	100.00	16.79	-----	100.00
None	7.0-7.3	(Tailings.....	59.78	4.23	-----	15.33
		(Middlings.....	22.58	13.02	-----	17.82
		(Concentrates.....	17.64	62.52	5.76	66.85
		Total.....	100.00	16.50	-----	100.00
Soda Ash	7.7-8.0	(Tailings.....	53.37	4.41	-----	14.42
		(Middlings.....	28.21	9.63	-----	16.70
		(Concentrates.....	18.42	60.91	8.50	68.88
		Total.....	100.00	16.29	-----	100.00
Do	8.7-9.0	(Tailings.....	43.40	4.74	-----	12.72
		(Middlings.....	38.20	10.20	-----	24.09
		(Concentrates.....	18.40	55.60	17.22	63.19
		Total.....	100.00	16.19	-----	100.00

Conditions of test:

Ore charge—500 gm.

Collector—the previously recited amine mixture, 0.4 lb./ton ore

Frother—methyl amyl alcohol, 0.104 lb./ton ore

Acid or alkali addition as indicated.

The improved results obtained by using a nearly neutral pulp may be seen by comparing the following test with the fifth test of Table 1, noting

that the only difference in conditions is that of the alkalinity of the pulp (i. e., pH 7.5 in the following test against pH 8 in Table 1):

Danube washing plant tailings

Product	Percent Weight	Assay, Percent		Percent of Total Iron
		Iron	Silica	
Tailings.....	33.35	5.55	-----	5.03
Middlings.....	19.19	21.23	-----	11.06
Concentrates.....	47.46	65.07	5.04	83.91
Total.....	100.00	36.80	-----	100.00

Reagents:

Collector recited above—0.4 lb. per ton;

"Acidified starch"—2.0 lb. per ton;

Methyl amyl alcohol—104 lb. per ton.

The "modified starch product" may be a commercial "soluble starch" having a cold water solubility greater than 5% and not greater than 80% and having a ferricyanide reducing value falling within the range 20-250. Illustrative are the following data of a batch test using a soluble starch of commerce; the same having a cold water solubility of about 10% and a ferricyanide reducing value of 76. In this test the starting material was identical with that described in reference to Table 2 above, and the conditions were identical with those observed in the second test of Table 2, with the exception that 1.0 lb./ton of

65 the commercial soluble starch was used in place of 2.0 lb./ton of the "acidified starch":

Product	Percent Weight	Assay, Percent		Percent of Total Iron
		Iron	Silica	
Tailings.....	65.83	5.37	-----	21.18
Middlings.....	21.47	23.93	-----	30.83
Concentrates.....	12.70	63.00	4.44	47.99
Total.....	100.00	16.67	-----	100.00

With some ores, the modified starch product can be added directly to the head of the flotation circuit, while with other ores it is advantageous to condition the pulp with the modified starch product for some minutes prior to the actual flotation operation.

While in the above illustrative specific examples the cationic collectors employed were primary aliphatic amines such as mixtures of water-soluble forms of primary aliphatic amines corresponding in alkyl chain length to fatty acids of coconut oil, above referred to, and commercial dodecylamine hydrochloride, it is to be understood that the above described modified starch products exert their selectivity-enhancing (specifically, iron oxide-depressing) properties in the presence of cationic collectors generally.

The following specific example illustrates the applicability of the principles of the invention in the flotation of silica from hematite in a batch test using a well-known quaternary ammonium compound as collector.

The feed was a deslimed washing plant tailing from Danube mine above referred to. In size it was substantially all finer than 65 mesh, and was not further subdivided. In test 682-A, there was used as collector a quaternary ammonium chloride derivative from myristic acid. The collector, used in the form of a 2% aqueous solution, was added in three equal portions to the rougher cell and in one further portion to the cleaner cell. As the frother there was used a higher alcohol product, which frother was added to the cleaner cell in a single addition. In test 682-B the same collector and frother were used, but there also was used, as iron oxide depressor, the above referred to modified starch product having a cold-water solubility of 70% and a ferricyanide reducing value of 76.

The batch tests data of test No. 682-A follow:

Product	Wt. in Grams	Per Cent Weight	Assay Per Cent			Per Cent of Total Iron
			Iron	Silica	Units	
Underflow.....	75.00	15.11	63.31	5.66	9.57	56.93
Cleaner Overflow.....	29.80	6.00	23.01	-----	1.38	8.21
Rougher Overflow.....	391.70	78.89	7.43	-----	5.86	34.86
Total.....	496.50	100.00	16.81	5.66	16.81	100.00

Conditions of test:

Ore charge—500 gm.
Collector—the above-recited quaternary ammonium compound—0.28 lb./ton
Frother—a higher alcohol—0.05 lb./ton
Pulp density—25%
pH of pulp—7.1.

The batch tests data of test No. 682-B follow:

Product	Wt. in Grams	Per Cent Weight	Assay Per Cent			Per Cent of Total Iron
			Iron	Silica	Units	
Underflow.....	109.5	21.87	61.69	7.62	13.49	79.82
Cleaner Overflow.....	31.6	6.31	15.50	-----	0.98	5.80
Rougher Overflow.....	359.5	71.82	3.39	-----	2.43	14.38
Total.....	500.6	100.00	16.90	7.62	16.90	100.00

Conditions of test:

Ore charge—500 gm.
Collector—same quaternary ammonium compound—0.32 lb./ton
Frother—same higher alcohol—0.05 lb./ton
Depressor—same modified starch product as was used in test No. 682-A—2.5 lb./ton
Pulp density—25%
pH of pulp—7.1.

It will be noted that while in both of the above tests high-grade concentrates were made, the rougher overflow (or tailing) contained, in test 682-A, 7.43% of iron, whereas in test 682-B, in which the modified starch product was used, the iron content of the rougher overflow fell to only 3.39%; also, that when the modified starch product was used the weight recovery of concentrates was 21.87%, as contrasted with only 15.11% when the modified starch product was omitted. With use of the latter agent, the overall iron recovery was 79.82%, whereas it was only 56.93% when the modified starch product was omitted. As will be obvious, the modified starch product definitely sharpened and improved the separation. It will be noted also that although somewhat more collector was used in the -B test than in the -A— from which fact it was to have been predicted that more iron would be carried into the froth in -B than in -A—there actually was carried into the froth only one-half as much of the iron as in the -A test, this being explainable only on the basis of the strong depressing effect of the modified starch product on the flotation of the hematite particles.

The previously given examples have shown the application of this improved process to the concentration of washing plant tailings. It has been found, surprisingly, that the improved process admirably is adapted for use in the beneficiation

of ferruginous cherts such as those deposits known in northeastern Minnesota as "taconites" and "oxidized taconite." The concentration of these latter materials is much more difficult than the concentration of, say, wash ores or washing plant tailings in which the particles of iron oxide and silica are relatively free, one from another, at say minus 65 mesh. In the taconites the locking between the minerals is much more intimate and even with 200-mesh grinding there is a con-

siderable intergrowth of iron and silicious minerals.

The following data of batch tests are illustrative of the application of the present process to such a starting material. The starting material in these tests was an oxidized taconite from the Majorca mine, analyzing about 26.60% Fe (mostly as hematite, with minor amount of limonite). The aqueous pulps contained about 25% solids. In all except the control test, the pulps were conditioned for some minutes with the modified starch product before conducting the flotation operation.

TABLE 3

Effect of modified starch product addition on amine flotation of an oxidized taconite

Acidified Starch, lb./ton ore	Product	Percent Weight	Assay, Percent		Percent of Total Iron
			Iron	Silica	
None	Tailings	43.57	14.91	-----	24.35
	Middlings	40.34	28.51	-----	43.09
	Concentrates	16.09	53.99	17.81	32.56
	Total	100.00	26.69	-----	100.00
0.5	Tailings	50.02	11.93	-----	22.30
	Middlings	45.01	39.64	-----	66.84
	Concentrates	4.97	58.47	9.45	10.86
	Total	100.00	26.75	-----	100.00
1.0	Tailings	53.82	11.09	-----	22.53
	Middlings	30.50	35.16	-----	42.06
	Concentrates	15.68	59.86	8.62	35.41
	Total	100.00	26.50	-----	100.00
2.0	Tailings	45.36	9.79	-----	16.64
	Middlings	31.60	27.60	-----	32.79
	Concentrates	23.04	58.55	11.11	50.57
	Total	100.00	26.68	-----	100.00

Reagents:

500 g. Majorca taconite, at minus 100 mesh, not previously deslimed;

0.2 lb./ton commercial dodecylamine hydrochloride, collector;

0.05 lb./ton methyl amyl alcohol, frother; Modified starch product addition as indicated in above table.

Alkalinity in all tests of this table, pH 8.2.

From the above table it is evident that use of the aforesaid modified starch product made it possible to secure cleaner concentrates and simultaneously to increase the recovery. As the amount of starch product was increased the inhibiting effect of the reagent on the flotation of the hematite could be judged by noting the progressive increase in the weight of the concentrate and the progressive decrease in the grade of the tailings (froth product).

The above data are illustrative of the applicability of the improved process of the present invention to difficultly concentratable ferruginous cherts and slates and other silicious iron-bearing materials generally.

From a consideration of the role played by the aforesaid "modified starch product," it is concluded that an important function of the material is that of an inhibiting agent, tending to prevent the flotation of the iron oxide minerals. This is particularly striking in the effect of preventing the flotation of the more finely divided iron oxide particles (e. g., minus 200 mesh). In any froth flotation process the separation tends to be a "size" separation, in that there is a natural tendency for the finer material to be segregated in the froth while the coarser material

sinks. If the separation is not sharp, there is a tendency for the finer iron minerals to be carried over in the froth and for the coarse silica particles to remain in the underflow together with the more granular portion of the iron oxides.

As will be noted in the following comparative sizing analyses, the use of the aforesaid modified starch product in a cationic flotation operation desirably improves the separation of iron mineral from the finer material ("slimes") of the ore pulp. These sizing analyses were made of the tailings (froth product) of two tests identical except for the fact that in one case, "test B," modified starch product was used, whereas in the other, "test A," the modified starch was omitted. Both A and B were continuous mill tests made with a 6-cell "#12 Denver Sub-A" flotation machine, the feed in each case being at the rate of 1 long ton per hour. In both tests there was used as cationic collector 0.182 lb./ton of the mixed amines product used in the tests reported in Table 1 above, and as frother 0.074 lb./ton of a commercial higher alcohol frother. In test B the ore pulp was conditioned, for 11 minutes prior to flotation, with 1.14 lbs./ton of the aforesaid "acidified starch."

Sizing analysis of flotation tailings

Mesh	Test A		Test B	
	Per cent Wt.	Per cent Fe	Per cent Wt.	Per cent Fe
+65	0.96	2.93	0.61	2.77
+100	4.34	3.42	3.32	1.30
+150	11.79	2.77	9.74	1.14
+200	12.62	2.44	12.49	0.98
+250	70.29	11.72	73.84	5.54
Total	100.00	9.05	100.00	4.38

From the above data it will be noted that although the acidified starch tends to prevent the floating of the iron mineral at all sizes the effect is most marked on the material finer than 200 mesh. The chief advantage of using the modified starch product is that it exerts a marked depressing effect on the fine iron minerals which have a tendency to come up in the froth because of their fine size. Accordingly, in most cases desliming is obviated by the use of the modified starch product, although in some instances it may be economically advantageous preliminarily to deslime the pulp.

I have found that certain other colloids, viz., crude (i. e., raw) starch, many boiled starches, starch products high in raw starch, starch products having a substantial content of sugars (e. g., a modified starch sold by Arnold, Hofmann & Co. under the designation "Starch CC"), certain colloidal polymerized organic salts of sulfonic acids of the alkyl aryl type, gum tragacanth, gelatin, gum acacia, casein, glue, and water-soluble sugars (e. g., dextrose and maltose), do not answer the hereinbefore-recited combination of criteria (i. e., do not have a ferricyanide reducing value between 20 and 250 and a cold water solubility of from 5 to 80%), and do not give any improvement in the cationic froth flotation of gangue from oxidic iron mineral; in most cases their presence in the circuit is positively harmful rather than helpful. Thus, the presence of 1.0 lb./ton of sucrose in the circuit was found to impair rather than enhance the selectivity of a commercial collector consisting essentially of a mixture of primary aliphatic amines corresponding in alkyl chain length to fatty acids of coconut

oil, in water soluble form, as did the presence of 0.5 lb./ton of gum tragacanth. Illustrative of the indifferent or even positively harmful effects resulting from the presence of raw corn starch in the pulp circuit are the batch tests data recited in the following table:

TABLE 4

*Effect of raw corn starch in amine flotation—
Danube tailings*

Raw Starch, lbs./ton	Product	Percent Weight	Assay, Percent		Percent of Total Iron
			Iron	Silica	
None	(Tailings.....)	27.43	12.88	-----	9.98
	(Middlings.....)	38.97	34.25	-----	37.77
	(Concentrates.....)	33.60	54.96	18.17	52.25
	Total.....	100.00	35.35	-----	100.00
.2	(Tailings.....)	24.46	9.80	-----	6.65
	(Middlings.....)	36.78	31.27	-----	31.86
	(Concentrates.....)	38.76	57.24	15.20	61.49
	Total.....	100.00	36.09	-----	100.00
.4	(Tailings.....)	25.04	9.12	-----	6.33
	(Middlings.....)	29.21	27.35	-----	22.17
	(Concentrates.....)	45.76	56.33	16.44	71.50
	Total.....	100.00	38.04	-----	100.00
.8	(Tailings.....)	22.63	9.93	-----	6.24
	(Middlings.....)	26.27	25.23	-----	18.37
	(Concentrates.....)	51.10	53.24	20.53	75.39
	Total.....	100.00	36.08	-----	100.00
1.6	(Tailings.....)	22.52	9.46	-----	5.93
	(Middlings.....)	28.28	23.65	-----	18.61
	(Concentrates.....)	49.20	55.13	18.35	75.46
	Total.....	100.00	35.94	-----	100.00
2.0	(Tailings.....)	29.55	7.66	-----	6.22
	(Middlings.....)	30.26	35.23	-----	29.32
	(Concentrates.....)	40.19	58.31	13.08	64.46
	Total.....	100.00	36.35	-----	100.00
3.0	(Tailings.....)	25.02	8.15	-----	5.74
	(Middlings.....)	32.06	29.68	-----	26.74
	(Concentrates.....)	42.92	55.94	17.00	67.52
	Total.....	100.00	35.56	-----	100.00

Conditions of tests:

Ore charge—500 gm. pH maintained at 8.0

0.4 lb. a commercial collector consisting essentially of a mixture of primary aliphatic amines corresponding in alkyl chain length to fatty acids of coconut oil, in water soluble form, per ton ore

—104 lb. methyl amyl alcohol per ton ore

The raw starch was raw corn starch which had been heated in water to form a hydrous jelly.

By a "ton" of ore is here meant 2240 pounds of ore which has been dried to constant weight at 105° C.

It is to be understood that the above recitations of particular cationic collectors and of particular frothing agents are not to be considered as limitative of the scope of the present invention, but merely as illustrative of the latter.

While the improved cationic flotation process of the present invention has been described herein with particular reference to the beneficiation of washing plant tailings, it is of course to be understood that this process is not restricted to this latter starting material, and that the same is applicable in the beneficiation of high grade and low grade iron ores generally, stock pile lean ores, and tailings from gravity plants. I contemplate the incorporation of the present process in plants which employ gravity, washing, jigging, float-and-sink, magnetic separation or any other known

iron ore-concentrating method, as an additional step in the recovery of iron values from natural mill fines, reground low grade mill products and other iron-bearing materials of too low grade to be called "iron ores."

This application contains subject-matter in common with my application Serial No. 505,697, filed October 9, 1943, and is a continuation-in-part of my application Serial No. 516,287, filed December 30, 1943.

I claim:

1. In the beneficiation of silicious iron-bearing material by a froth flotation procedure in which silicious gangue particles are floated from a pulp of the iron mineral, which pulp contains particles of various sizes including very fine oxidic iron particles, by the aid of a readily water-dispersible cationic collector, the improvement which consists in effecting the flotative separation in a non-acid pulp circuit, in the presence of a modified starch product having a cold water solubility of from 5 to 80% and a ferricyanide reducing value of from 20 to 250, said modified starch product not containing more than 2% of water-soluble sugars and being substantially free from raw starch, whereby the fine oxidic iron particles are depressed into the underflow.

2. In the beneficiation of silicious iron-bearing material by a froth flotation procedure in which silicious gangue particles are floated from a pulp of the iron mineral, which pulp contains particles of various sizes including very fine oxidic iron particles, by the aid of a readily water-dispersible cationic collector, the improvement which consists in effecting the flotative separation in a non-acid pulp circuit, in the presence of an aqueous solution of acid-treated starch having a cold water solubility of from 5 to 80% and a ferricyanide reducing value falling within the range 35-50, said modified starch product not containing more than 2% of water-soluble sugars and being substantially free from raw starch, whereby the fine oxidic iron particles are depressed into the underflow.

3. In the beneficiation of silicious oxidic iron-bearing material by a froth flotation procedure in which silicious gangue particles are floated from an aqueous pulp of the iron mineral, which pulp contains silicious gangue and oxidic iron particles of various sizes including very fine oxidic iron particles, by the aid of an aliphatic amine collector in water-soluble form and a frother, the step of improving the selectivity of the flotative separation by suppressing the floatability of the very fine oxidic iron particles with respect to the floatability of the silicious gangue particles by the expedient of pre-conditioning a neutral to alkaline pulp of the material, in which pulp any alkalinity thereof is due to the presence therein of an alkaline-acting compound of an alkali metal, with an aqueous solution of a modified starch product having a cold water solubility of from 5 to 80% and a ferricyanide reducing value of from 20 to 250, said modified starch product not containing more than 2% of water-soluble sugars and being substantially free from raw starch.

4. Process of recovering by cationic froth flotation an oxidic iron concentrate from a pulp of silicious iron-bearing material which pulp is composed of particles of various sizes including very fine oxidic iron particles, which comprises conditioning an aqueous slurry of the material with an aqueous solution of a modified starch product having a cold water solubility of from 5 to 80%

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and a ferricyanide reducing value of from 20 to 250, said modified starch product not containing more than 2% of water-soluble sugars and being substantially free from raw starch, establishing an aqueous, neutral to alkaline flotation pulp of said conditioned material in which pulp any alkalinity is due to the presence of an alkaline acting compound of an alkali metal, subjecting the pulp to agitation and aeration while adding thereto a frother and portion by portion an aliphatic amine collector in water-soluble form, whereby oxidic iron particles including the very fine oxidic iron particles tend to be depressed into the underflow while the silicious gangue particles float, removing a silicious gangue froth product poor in oxidic iron particles of all sizes, and recovering a concentrate of oxidic iron from the underflow.

5. Process of beneficiating taconite and similar ferruginous cherts by a froth flotation procedure in which silicious gangue material selectively is floated from an aqueous pulp of the taconite consisting of silicious gangue and iron mineral particles including very fine iron mineral particles, which comprises maintaining the pulp at an alkalinity of at least pH 8.0, and effecting the flotative separation using a readily water-dispersible cationic collector and a frother in the presence of an aqueous solution of a modified starch product having a cold water solubility of from 5 to 80% and a ferricyanide reducing value of from 20 to 250, said modified starch product not containing more than 2% of water-soluble sugars and being substantially free from raw starch, whereby very fine mineral particles are depressed into the underflow.

6. Process of beneficiating taconite and similar ferruginous cherts by a froth flotation procedure in which silicious gangue material selectively is floated from an aqueous pulp of the taconite consisting of silicious gangue and iron mineral

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particles including very fine iron mineral particles, which comprises maintaining the pulp at an alkalinity of at least pH 8.0 by the use of an alkaline-acting compound of an alkali metal, conditioning the alkaline pulp with an aqueous solution of a modified starch product having a cold water solubility of from 5 to 80% and a ferricyanide reducing value of from 20 to 250, said modified starch product not containing more than 2% of water-soluble sugars and being substantially free from raw starch, subjecting the so-conditioned pulp to agitation and aeration while adding thereto portion by portion an aliphatic amine collector in water-soluble form and a frother, whereby very fine iron mineral particles are depressed into the underflow while the floatability of the silicious gangue particles is not adversely altered, and recovering from the underflow an iron mineral concentrate.

7. The improved beneficiation process defined in claim 1, wherein there is employed an amount of the modified starch product corresponding to from about 0.2 to about 3.0 lbs./ton of the iron-bearing starting material.

8. The improved beneficiation process defined in claim 2, wherein there is employed an amount of the acid-treated starch corresponding to from about .4 to about 2.0 lb./ton of the iron-bearing starting material.

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REFERENCES CITED

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

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