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FROTH FLOTATION WITH AN AMINE COMPOSITION

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This invention relates to the concentration of minerals by froth flotation. More particularly it relates to a novel froth flotation process wherein flotation is conducted in the presence of a novel combination of collector agents comprising an amine and a crude mixture of heterocyclic nitrogen compounds obtained from a mineral known as "gilsonite."

The invention has wide application to froth flotation processes and is useful wherever amines are used as a component of the collector. For example, the invention has application to the concentration of phosphate minerals from silica, such as normally occur in the Florida phosphate area, in the "western" deposits in Idaho, and in other phosphate deposits, as in Tennessee, and to the recovery of oxidic iron minerals from iron ore.

In customary Florida phosphate mining processes, two flotation steps are used. After the ore is washed and deslimed, it is conditioned with caustic soda, and a hydrocarbon, such as fuel oil or kerosene. A fatty acid collector, such as tall oil, is then added and the mixture subjected to a first flotation. Phosphate product is obtained as a rougher concentrate. This concentrate is then "deoiled" or freed of reagents by scrubbing with mineral acid. It is again deslimed in preparation for a second flotation step.

The second step involves flotation of the deoiled, deslimed rougher concentrate with a cationic amine collector. Here, the undesired silica is floated away from the phosphate mineral and is discarded. The underflow, or unfloated portion of the ore remains as the desired phosphate product.

In the flotation of ores of the western deposits, no second or amine flotation step is used. Instead, only a fatty acid collector, tall oil, is used to float a rougher concentrate which is then upgraded by re-flotation. However, no additional collector chemical need be used. The undesired silica and other non-phosphate minerals "drop out" and report in the underflow which is either discarded or recycled.

Although it is feasible within the prior art encompassed by froth flotation to consider the use of amine collector chemicals to float silica away from phosphate minerals in the western ores, it has generally been found impractical or uneconomical to do so due to the limitations of efficiency of known amine flotation processes. When amines have been used as the sole collector chemical in known flotation processes to treat ores of the same general type as the western phosphate ores, either the grade of the phosphate concentrate has been lower than required or the loss of phosphate mineral has been too high to be economical.

In the flotation of iron ore or magnetic iron ore concentrates from mixtures of oxidic iron minerals, the silica and miscellaneous cherts and siliceous minerals are floated away in a one-step process. Such flotation normally involves grinding the ore, pulping it in water, preconditioning with a starch or dextrin product which functions as a depressant for iron minerals, adding a small amount of readily water-dispersible cationic collectors and a frothing agent, and subjecting the pulp to froth flotation. The silica-rich froth is separated from the silica-poor unfloated iron mineral residue.

Considerable effort has been expended in each of the

above described flotation techniques and in others, to devise a more efficient and more economical method of operation, the objective, in all instances, being to make as complete a separation as possible resulting in high grade concentrates with a minimum loss of valuable minerals, and in so doing, to consume as little of the relatively costly amine collectors as possible. To date, such an ultimate in flotation processing has not been attained.

Indeed, the use of amine flotation procedures on some ores is frequently impractical because of economics. Either the grade of the desired concentrate is lower than required or else the loss of desired mineral is too high to make a flotation process based on amine practical from an economic viewpoint.

It is, therefore, an object of this invention to provide a more efficient flotation process.

Another object is to provide a novel flotation reagent.

Still another object is to provide a novel material for dissolving higher melting amines so that they may be used as liquid free-base amine material in froth flotation processes, said novel solvent material also producing other unique beneficial effects in the flotation process.

Another object is to provide desirable economy by reducing the amount of primary amine collector normally required for conventional amine-type froth flotation.

Another object is to provide a novel process for the concentration of phosphate minerals in high yield and in high phosphate content from all types of ore deposits.

A still further object is to provide a cationic froth flotation process for the separation of siliceous materials from oxidic iron materials.

Another object is to provide a cationic froth flotation process utilizing an amine reagent not requiring any iron depressant such as starch or dextrin for the selective separation of siliceous materials from oxidic iron materials.

Other objects will in part be obvious and will in part appear hereinafter.

It has now been found that minerals can be more efficiently concentrated by a froth flotation process wherein amine collector is used in the presence of crude mixed heterocyclic nitrogen material derived from the mineral gilsonite and obtained by distillation, acid extraction or other well known extraction techniques. Such crude mixed heterocyclic nitrogenous material occurs as a by-product in the manufacture of petroleum products from the aforementioned mineral "gilsonite" by The American Gilsonite Company. It has been described as containing predominantly mixed alkylated pyridines, pyrroles, indoles, and quinolines, with some of the substituent carbon chains being olefinic. It also contains some unidentified non-nitrogenous material. However, it is believed to be an inordinately complex mixture of chemical structures. Well over one hundred different compounds are indicated as being present in the mixture, based on gas chromatographic procedures. The extreme complexity of such a mixture of materials renders a complete qualitative analysis almost prohibitive.

Utilization of all crude, semi-purified or purified by-products and having a boiling point of greater than about 200° F. resulting from the refining of gilsonite, are utilizable with the amine. Naturally, the composition of such mixed heterocyclic nitrogenous by-products will vary with the composition of the original gilsonite, the point in the refining process from which they are extracted, the boiling range in which they are extracted, and the like. The invention herein described presupposes utilization of all such mixed heterocyclic nitrogenous compounds either in crude or in purified forms. The preferred mixed heterocyclic nitrogen compounds in the practice of this invention are those which have a boiling range of about 200° F.

to about 750° F. and particularly those which have an average boiling point within the range of about 450° to about 750° F.

The American Gilsonite Company has assigned descriptive nomenclature to various fractions of this type material as follows:

(1) Light bases from HBF (hydrocarbon feed)—Extracted from a naphtha stream of approximately 283° F. volumetric average boiling point and 222° F.–400° F.

(2) Intermediate bases from PFB (prefractionater bottoms)—Extracted from a heavy naphtha stream of approximately 422° F. volumetric boiling point and 400° F. to 590° F. boiling range.

(3) Medium bases from LGO (light gas oil)—Extracted from a gas-oil stream of about 520° F. volumetric average boiling point and 460° F. to 665° F. boiling range.

(4) Semi-purified acid extracted nitrogen compounds:

(a) Nitrogen bases I—Boiling range 491° F. to 509° F. at 760 mm.

(b) Nitrogen bases II—Boiling range 610° F. to 641° F.

(c) Nitrogen compounds III—Boiling range 700° F. to 710° F.

(d) Nitrogen compounds IV—Boiling range 745° F. to 755° F.

(e) Bottoms V—Boiling range 755° F. and higher.

(5) Nitrogen distillate—A crude mixture of nitrogen bases obtained by distillation and representative of 4(a) through 4(c) inclusive as above, plus some non-nitrogenous compounds.

The amines, conventionally used as collectors in froth flotation processes, are aliphatic in character and generally contain from about 8 to about 20 carbon atoms. Typically, the aliphatic amines derived from various petroleum, animal and vegetable oils are most commonly used. Specifically, octyl amine, decyl amine, dodecyl amine, tetradecyl amine, hexadecyl amine, octadecyl amine, octadecenyl amine and octadecadienyl amine are useful. Quaternary amines such as dodecyl trimethyl ammonium chloride, coco trimethyl ammonium chloride, tallow trimethyl ammonium sulfate are also useful. Mixed amines, diamines and quaternary amines, such as tallow amine, hydrogenated tallow amine, coconut oil or cocoamine, soybean oil or soya-amine, tall oil amine, rosin amine, tallow diamine, coco diamine, soya diamine or tall oil diamines and the like, and quaternary ammonium compounds derived from these amines, are also useful. Amido amines and imidazolines such as those derived from the reaction of an amine and a fatty acid can also be used.

The amine collectors are usually partially or wholly neutralized by a mineral or organic acid such as hydrochloric acid or acetic acid. Such neutralization facilitates dispersibility in water. In the alternative, the amine may be used as a free base amine by dissolving it in a larger volume of a suitable organic solvent such as kerosene, pine oil, alcohol, and the like before use. It should be noted that these solvents sometimes have undesirable effects in flotation such as reducing flotation selectivity or producing uncontrollable frothing.

Amine in an amount of about 0.01 pound to about 2.0 pounds per ton of ore is usually used in froth flotation practice, the preferred range in most instances being about 0.05 pound to about 1.0 pound per ton. The preferred amount of gilsonite material utilized in the practice of this invention encompasses approximately the same ranges, but may vary from ore to ore. It is well known that the character of any ore governs the amounts of flotation reagents utilized in order to provide best results.

The gilsonite material may be applied to the flotation pulp in several ways. First, since it usually occurs as a free-flowing liquid at low temperatures, it may be separately added to the pulp at the same time that the amine collector is added. In the preferred way, however, the gilsonite material is first blended with the amine collector and then a sufficient amount of acetic acid or hydrochloric acid is added to neutralize the primary amine collector to the desired degree, followed by dissolving or dispersing the blend to a suitable concentration in make-up water prior to addition to the pulp. An even more preferred way is to disperse a blend of gilsonite material and amine collector in warm make-up water, followed by addition to the make-up water of enough acetic ar hydrochloric acid to solubilize or disperse the blend prior to addition to the pulp. In still another way, a blend of amine collector and gilsonite material is prepared, in such a ratio that the blend exists as a free-flowing liquid with a low freezing point, the gilsonite material acting as a liquifying agent for the primary amine collector which usually occurs as a paste or crystalline solid without considerable heating to melt the amine. In such a form, the gilsonite material and amine are added as a liquid blend, with very little or no heating, directly to the flotation pulp without the undesirable necessity for prior solubilizing or dispersing the amine collector in make-up water.

Although it is preferred to conduct conventional amine floation in the presence of the mixed heterocyclic nitrogen compounds, the invention also contemplates utilization of the subject mixed heterocyclic nitrogen compounds as a primary and sole collector agent in the process, for minerals such as clay, talc, mica, coal, and the like.

The following examples illustrate the advantages obtained by the practice of this invention:

Example I

Test samples, of 730 grams each, of a wet phosphate ore charge (average calculated head assay: 28.06% acid insoluble-59.28% bone phosphate lime (BPL)) were each washed, deslimed and subjected to flotation in a laboratory Denver Sub-A flotation cell at pH 8.1±0.1 using Chicago tap water. Each sample was diluted to 16% solids and conditioned for one quarter minute with the reagent amounts indicated below and then subjected to flotation for one and one-half minutes.

Test No.	Reagent Amounts (lbs./ton of feed)			
	Pine Oil	Kerosene	Armeen T	Gilsonite Additive
3A	.0958	1.0	.5	None
3	.0958	1.2	.6	None
3B	.0958	1.4	.7	None
5	.0958	1.0	.42	.08
4	.0958	1.2	.5	.10

The results were as follows:

Test No.	Product	Percent Weight Original Ore Feed	Assay of Product		Metallurgical BPL Units	Percent Recovery of BPL
			Percent Insol.	Percent BPL		
3A	Concentrate	75.1	7.5	74.8	56.2	95.9
	Tail	24.9	90.5	9.78	2.4	
3	Concentrate	73.1	4.6	78.52	57.4	95.7
	Tail	26.9	88.0	9.64	2.6	
3B	Concentrate	71.3	4.2	79.48	56.7	95.6
	Tail	28.7	88.4	8.92	2.6	
5	Concentrate	73.7	6.0	77.25	56.9	97.3
	Tail	26.3	92.54	5.92	1.6	
4	Concentrate	72.9	4.5	77.25	56.3	97.1
	Tail	27.1	91.04	6.34	1.7	

The percent BPL recovery of Tests 4 and 5 was better when utilizing the gilsonite material, and less amine collector was required to produce desirable percent insoluble content in the concentrate. Thus an economy was effected in the process.

Example II

Test samples, of 710 grams each, of wet phosphate ore charge (average calculated head assay: 25.78% acid insoluble-59.48% BPL) was washed, deslimed and subjected to flotation in a laboratory Denver Sub-A flotation cell at pH 8.2±0.1 using Chicago tap water. Each sample was diluted to 16% solids and conditioned for one quarter minute with reagents as indicated below and then subjected to flotation for two minutes.

Test No.	Reagent Amounts (lbs./ton of feed)			
	Pine Oil	Kerosene	Armoflote P	Gilsonite Additive
7	.0958	1.0	.5	None
8	.0958	1.2	.6	None
9	.0958	1.4	.7	None
43	.0958	1.0	.45	.05
44	.0958	1.2	.54	.06
45	.0958	1.3	.485	.065

The following results were obtained:

Test No.	Product	Percent Weight Original Ore Feed	Assay of Product		Metallurgical BPL Units	Percent Recovery of BPL
			Percent Insol.	Percent BPL		
7	Concentrate	75.3	4.94	78.23	58.9	95.8
	Tail	24.7	86.85	10.55	2.6	
8	Concentrate	73.2	6.5	73.56	53.3	91.5
	Tail	26.8	76.5	18.54	5.0	
9	Concentrate	59.8	3.2	77.40	46.3	78.1
	Tail	40.2	56.7	32.45	13.0	
43	Concentrate	76.6	5.1	72.95	55.9	96.2
	Tail	23.4	88.4	9.50	2.2	
44	Concentrate	74.1	3.4	76.66	56.8	95.3
	Tail	25.9	86.3	10.72	2.8	
45	Concentrate	71.8	4.1	75.83	54.4	91.3
	Tail	28.2	78.1	18.3	5.3	

Again economies were effected by utilization of the gilsonite additive. In all cases where gilsonite is used, either higher percent recovery of BPL results or lower percent insoluble content in the concentrate, or both, occurs.

Example III

A wet phosphate ore charge (average calculated head assay: 25.23% acid insoluble-57.77% BPL) was scrubbed, washed, deslimed and subjected to floation in a laboratory Denver Sub-A flotation cell at pH 8.0 using Chicago tap water. Each sample was diluted to 16% solids and conditioned for one quarter minute with reagents as indicated below and then subjected to flotation of one and one-half minutes.

Test No.	Reagent Amounts (lbs./ton of feed)			
	Pine Oil	Kerosene	Armoflote P	Gilsonite Additive
7	.0958	1.4	.73	None
8	.0958	1.5	.75	None
9	.0958	1.2	.6	None
10	.0958	1.4	.63	.07
11	.0958	1.2	.549	.061
12	.0958	1.5	.675	.075

The following results were obtained:

Test No.	Product	Percent Weight Original Ore Feed	Assay of Product		Metallurgical BPL Units	Percent Recovery of BPL
			Percent Insol.	Percent BPL		
11	Concentrate	75.9	4.88	75.39	57.2	96.8
	Tail	25.1	89.51	7.95	1.9	
10	Concentrate	69.6	3.74	74.56	51.9	91.1
	Tails	30.4	76.58	16.93	5.1	
12	Concentrate	64.6	3.24	78.19	50.5	83.9
	Tails	35.4	63.77	27.47	9.7	
9	Concentrate	76.6	5.25	72.71	55.7	97.5
	Tail	23.4	91.62	6.18	1.4	
7	Concentrate	73.0	3.54	73.03	53.3	94.3
	Tail	27.0	83.16	11.77	3.2	
8	Concentrate	69.9	3.15	73.62	51.5	90.8
	Tail	301.0	75.82	17.41	5.2	

Again economies were effected by utilization of the gilsonite additive. In all cases where gilsonite material is used, either higher percent recovery of BPL results or lower percent insoluble content in the concentrate, or both occurs.

Example IV

Test samples, of 650 grams each, of a wet phosphate ore charge (average calculated head assay: 17.96% acid insoluble and 28.77% P_2O_5), sampled from an ore, characteristic of those found in the Western United States, were each ground to flotation sizing, deslimed and subjected to flotation in a Fagergren laboratory flotation cell at pH 8.8±0.1 using Chicago tap water. Each sample was diluted to 16% solids and conditioned for one quarter minute with reagents as indicated below and then subjected to flotation for one and three quarter minutes.

Test No.	Reagent Amounts (lbs./ton of feed)			
	Pine Oil	Kerosene	Armeen C	Gilsonite Additive
1	0.1	0.64	0.30	None
2	0.1	0.80	0.40	None
3	0.1	0.48	0.22	0.22
4	0.1	0.56	0.286	0.286
4A	0.1	0.72	0.374	0.374

The following results were obtained:

Test No.	Product	Percent Weight Original Ore Feed	Assay of Product			Metallurgical P_2O_5 Units	Percent Recovery of P_2O_5
			Percent Insol.	Percent P_2O_5	BPL		
1	Concentrate	92.94	14.92	29.73	64.93	27.63	96.95
	Tail	7.06	59.94	12.36		0.87	
2	Concentrate	90.65	13.74	30.00	65.52	27.20	95.64
	Tail	9.35	57.29	13.23		1.24	
3	Concentrate	95.41	15.38	30.89	67.46	29.47	98.40
	Tail	4.59	65.61	10.42		0.48	
4	Concentrate	92.58	14.58	30.97	65.67	27.84	97.00
	Tail	7.42	62.36	11.57		0.86	
4A	Concentrate	89.57	13.85	30.43	66.46	27.26	94.78
	Tail	10.43	57.72	14.39		1.50	

It will be observed that in each case where gilsonite material was present in the flotation system, a higher percent P_2O_5 grade of concentrate was produced, a higher recovery of phosphate mineral was obtained, and less of the primary amine collector was required to produce these improved results.

Example V

A 500 gram sample of a magnetic iron ore concentrate, with an average analysis of 62.0% Fe and 13.5% acid insolubles and consisting of about 90% minus 325 mesh sized material, was subjected to froth flotation in a standard laboratory flotation machine using dodecylamine acetate as the collector. Flotation was also conducted on an additional 500 gram sample of the same ore in the presence of gilsonite material. In the latter instance, gilsonite material was used as a blend with the dodecylamine acetate. The blend was applied to the ore pulp as a dilute aqueous solution.

The test procedure consisted of first pulping the 500 gram sample of ore in water to flotation density of about 20% solids in the flotation cell. This was followed by incremental addition to the pulp of appropriate amounts of collector and methylisobutyl carbinol (MIBC) as a frothing agent so as to cause flotation of silica and siliceous minerals in several stages After addition of flotation reagents in each stage of the flotation step, the pulp was conditioned for 30 seconds. The flotation pulp was allowed to remain at a natural value of 8.2±0.2.

The following results were obtained:

Gilsonite Additive, lb./ton	Dodecyl Amine Acetate, lb./ton	MIBC, lb./ton	Flotation Product	Percent Weight	Assay of Product		Percent Distrib. of Fe
					Percent Fe	Percent Acid Insol.	
None	0.03	0.06	1st froth	3.4	25.90	63.30	1.42
	0.03		2d froth	9.6	33.79	52.40	5.22
	0.02	0.03	3d froth	9.1	54.16	24.43	7.95
	0.02		4th froth	6.0	62.69	12.42	6.16
			Concentrate	71.9	68.37	4.67	79.25
	0.10	0.09	Totals	100.0			100.00
0.003	0.027	0.06	1st froth	2.9	22.01	68.11	1.03
0.003	0.027		2d froth	8.0	30.95	56.21	3.98
0.002	0.018	0.03	3d froth	9.6	51.62	26.64	7.97
			Concentrate	79.5	68.14	5.31	87.02
0.008	0.072	0.09	Totals	100.0			100.00
0.0125	0.0375	0.06	1st froth	10.41	25.13	63.68	4.23
0.0075	0.0225		2d froth	7.97	51.20	27.37	6.73
			Concentrate	81.62	67.39	4.96	89.04
0.0200	0.0500	0.06	Totals	100.00			100.00

From the test results it is shown that the presence of the gilsonite additive in the flotation pulp results in a more selective separation of minerals, causes a desirable increase in the quantity of high grade iron concentrate produced, and simultaneously, causes a desirable decrease in the amount of the more costly amine collector required to produce the high grade iron concentrate.

Example VI

Using the same ore and same general test procedure as in Example V, a series of tests were conducted to show the effect on amine collector consumption and on the selectivity of the flotation separation as a result of increasing the amount of gilsonite material added to the ore pulp in relation to the amount of amine collector used. In this series of tests, the dodecylamine and gilsonite material were added drop-wise as a liquid amine blend directly to the flotation pulp, thus by-passing the usual requirement in the flotation treatment of iron ores

of first forming the water soluble or dispersible acetate or hydrochloride salt of the amine.

The results were as follows:

Gilsonite Additive, lb./ton	Dodecyl Amine Acetate, lb./ton	MIBC, lb./ton	Flotation Product	Percent Weight	Assay of Product		Percent Distrib. of Fe
					Percent Fe	Percent Acid Insol.	
0.0132	0.0398	0.06	1st Froth	17.39	34.61	50.88	9.73
			Concentrate	82.61	67.63	5.41	90.72
0.0132	0.0398	0.06	Totals	100.00			100.00
0.0264	0.0264	0.06	1st Froth	8.81	23.54	66.31	3.33
0.0264	0.0264		2d Froth	10.07	48.25	31.09	7.81
			Concentrate	81.12	68.16	4.43	88.86
0.0528	0.0528	0.06	Totals	100.00			100.00
0.0725	0.0243	0.06	1st Froth	8.90	24.42	64.74	3.51
0.0363	0.0121		2d Froth	4.73	44.03	37.89	3.35
0.0363	0.0121	0.03	3d Froth	4.93	53.81	23.84	4.27
			Concentrate	81.44	67.67	5.30	88.87
0.1451	0.0485	0.09	Totals	100.00			100.00

From the results of the data in this example, it can be observed that the gilsonite material serves a dual purpose of acting as an amine solvent and at the same time actually improves flotation selectivity as compared to other common solvents such as kerosene which usually decreases flotation selectivity.

Example VII

In each of several tests, a 560 bram sample of a taconite iron ore containing hematite as a major iron mineral with an average anaylsis of 39.0% Fe and 38.0% acid insolubles, and consisting of about 87.5% minus 325 mesh sized material, was subjected to froth flotation in a standard laboratory flotation machine. The general test procedure consisted of pulping the ore sample in water to flotation density of about 20% solids in the flotation cell; followed by incremental addition to the pulp of appropriate amounts of coco amine collector, pine oil, and gilsonite material when desired; allowing a short conditioning time of from 15 to 30 seconds before aeration, and flotation was carried out in this manner in each of several stages; from 2 to 4 stages constituting a single test. The pH of the pulp was allowed to remain at a natural value of from 7.8 to 8.0. In the following tabulation, (and in Examples VIII and IX), all reagent addition rates are expressed in pounds per long ton (2,240) pounds of ore.

Test No.	Gilson. Add., lb./LT	Amine, lb./LT [1]	Pine Oil, lb./LT	Flotation Concentrate	Percent Weight	Assay of Product		Percent Distr. of Fe
						Percent Fe	Percent Insol.	
1	None	Armac C, 0.135	0.08	1st Rougher Conc	67.31	50.11	20.46	86.55
	None	Armac C, 0.135	0.08	2d Rougher Conc	38.84	57.08	9.29	56.89
	None	Armac C, 0.135	0.08	3d Rougher Conc	12.83	59.17	4.95	19.48
4	0.141	Armeen C, 0.141	0.08	1st Rougher Conc	75.61	47.34	24.52	92.36
	0.141	Armeen C, 0.141	0.08	2d Rougher Conc	48.77	56.47	10.13	71.07
	0.141	Armeen C, 0.141	0.08	3d Rougher Conc	29.30	59.08	5.28	44.67

[1] Pounds per long ton.

In Test No. 4, it can be seen that although slightly more amine collector was used which usually causes a lower recovery of iron, the presence of the gilsonite material in the pulp caused a 44.67% recovery of iron vaules in the 3rd rougher concentrate compared to 19.48% in Test No. 1, the third rougher concentrates in the two tests having almost identical percent iron grade.

Example VIII

The same ore and test procedure were used as in Example VII, except that distilled rosin amine was used instead of coco amine as the collector.

Test No.	Gilson. Add., lb./LT	Rosin Amine Acetate, lb./LT	Pine Oil, lb./LT	Flotation Concentrate	Percent Weight	Assay of Product		Percent Distrib. of Fe
						Percent Fe	Percent Insol. Acid	
2	None	0.135	0.08	1st Rougher Conc	70.37	47.92	22.88	88.30
	None	0.135	0.08	2d Rougher Conc	43.37	55.20	10.66	63.47
	None	0.135	0.08	3d Rougher Conc	16.40	57.25	5.53	24.59
7	0.12	0.135	0.08	1st Rougher Conc	67.07	50.56	20.44	86.13
	0.12	0.135	0.08	2d Rougher Cnoc	28.34	59.84	6.10	43.08

Comparison of the above Test Numbers 2 and 7 illustrate that the gilsonite material is also effective with rosin amine as collector. Again, a much higher recovery

of iron values is obtained in Test 7 using the gilsonite material, and in this case the percent Fe grade of the concentrate is higher; e.g., 59.84% Fe with 43.08% recovery compared to 57.25% Fe with 24.59% recovery. Also, less rosin amine collector is required to produce these better results

Example IX

A quaternary amine, Arquad 12–50, was used as collector using the same ore and procedure as in Example VII. The result of this test is as follows:

Test No.	Gilsonite Additive, lb./LT.	Arquad 12-50, lb./LT.	Pine Oil, lb./LT.	Flotation Concentrate	Percent Weight	Assay of Product, Percent Fe	Percent Distribution of Fe
6	0.045	0.09	0.08	1st Rougher Conc	97.19	39.90	98.65
	0.045	0.09	0.08	2d Rougher Conc	76.80	46.55	90.94
	0.045	0.09	0.08	3d Rougher Conc	58.35	54.12	80.34
	0.045	0.09	0.08	4th Rougher Conc	47.10	58.35	69.91

Example X

Tests were also conducted in which the gilsonite material was utilized in conjunction with dodecylamine acetate, but where the rougher flotation froth product was subjected to a cleaning step to recover iron minerals which floated with silica and this iron was recycled back into rougher flotation for ultimate recovery. In this testing, the same ore as in Examples V and VI; i.e., a magnetic iron ore concentrate, was used. A "locked" bench flotation test procedure was used; i.e., one in which several individual batch tests are conducted but flotation products from each test are combined into the next test to simulate recycle of products in continuous commercial operations.

In each of five batch flotation tests, a 500 gram sample of the same magnetic iron ore concentrate used in Example V was pulped in water to about 20% solids. To the ore pulp was added 0.054 lb./ton dodecylamine acetate, 0.006 lb./ton gilsonite material, and 0.03 lb./ton methylisobutyl carbinol as a frother. Rougher flotation was then conducted to obtain a rougher iron concentrate and a rougher froth product containing mostly silica but also containing some recoverable iron values. This rougher froth product was reground in a laboratory ball mill and then was subjected to reflotation without further addition of reagents to obtain a siliceous froth product as a final tails and a "cleaner concentrate." The cleaner concentrate containing recovered iron values was added to 500 grams of fresh ore for the next batch test. This procedure was repeated, combining the cleaner froth products together and combining the rougher iron concentrates produced, until five 500 gram samples of ore had been treated. The final products obtained were an iron concentrate containing 67.75% Fe and 5.37% acid insolubles, a final cleaner concentrate containing 55.68% Fe and 21.60% acid insolubles (a recycle product), and a final cleaner froth product or tailing containing 17.09% Fe and 72.91% acid insolubles. By calculation, 96.99% of the iron content of the ore was recovered in the iron concentrate. This process is illustrative of the generally excellent flotation metallurgy and low collector requirements produced by use of the gilsonite material.

In summary, all of the laboratory test examples with respect to flotation of iron ore indicates that the presence of gilsonite material in the flotation pulp during the cationic flotation treatment causes a more selective separation of silica from the iron minerals and requires less amine collector to produce desired levels of iron recovery and grade of concentrate. The gilsonite material produces improved metallurgical results regardless of the type of amine used as collector. It has also been shown to produce a more selective flotation separation on two types of iron ore exhibiting widely different flotation properties.

In the examples above, certain trademarks are used to designate the collector utilized. These refer to amines manufactured by Armour and Company and may be defined as follows:

Armac C—Coconut oil amine acetate.
Armeen C—Coconut oil amine.
Armeen T—Tallow amine.
Armoflote P—Blend of nitrile pitch amine blended with Armeen T.
Arquad 12–50—Trimethyldodecyl quaternary ammonium chloride.

Testing has shown that the various gilsonite materials used by themselves in the absence of the common amine collectors, when applied to iron ore or phosphate ore, do not function efficiently as cationic collectors under the usual conditions of flotation applied in such cases. This is not unusual, in view of the negative results obtained using as collectors such materials as pyridine, lutidines, and collidines, which are believed to be present in the gilsonite material. The manner in which gilsonite functions in flotation has not been determined.

Now that the invention has been described, we claim:

1. In a process for separating finely-divided minerals by froth flotation, the improvement comprising utilization of effective quantities of a fatty amine having about 8 to 20 carbon atoms and a mixture of heterocyclic nitrogen compounds as contained in the crude, semi-purified or purified by-products having a boiling point of about 200° F. to 750° F. resulting from refining of gilsonite.

2. In a process for separating finely-divided minerals by froth flotation, the improvement comprising utilization of effective quantities of about .01 to 2 pounds/ton of feed of fatty having about 8 to 20 carbon atoms of amine and about .01 to 2 pounds/ton of feed of a mixture of heterocyclic nitrogen compounds as contained in the crude, semi-purified or purified by-products having a boiling point of about 200° to 750° F. resulting from refining of gilsonite.

3. The process of claim **1** wherein the amine comprises dodecylamine acetate.

4. The process of claim **1** wherein the amine comprises coconut oil amine.

5. The process of claim **1** wherein the amine comprises tallow amine.

6. The process of claim **1** wherein the amine comprises a quaternary ammonium halide.

7. The process of claim **1** wherein the amine comprises a blend of nitrile pitch amine blended with tallow amine.

8. The process of claim 1 wherein the amine comprises rosin amine.

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