Oct. 8, 1968 C. L. RAY ET AL 3,404,777

FROTH FLOTATION WITH SECONDARY-ALKYL PRIMARY AMINES

Filed May 7, 1965

2 Sheets-Sheet 1

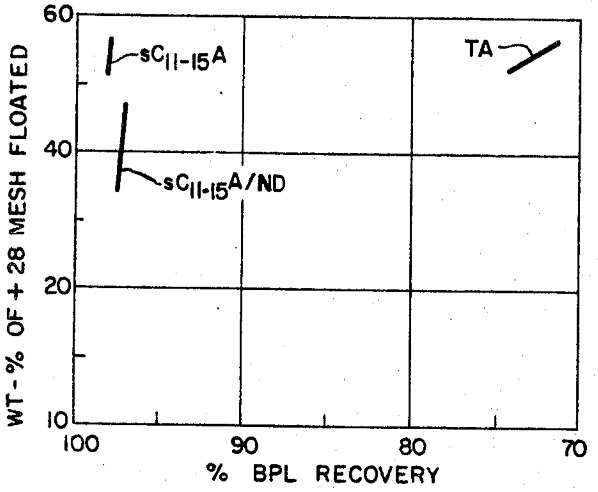

FIG. I

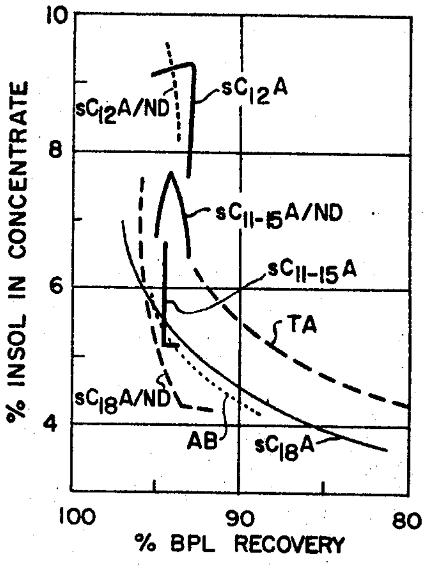

FIG. II

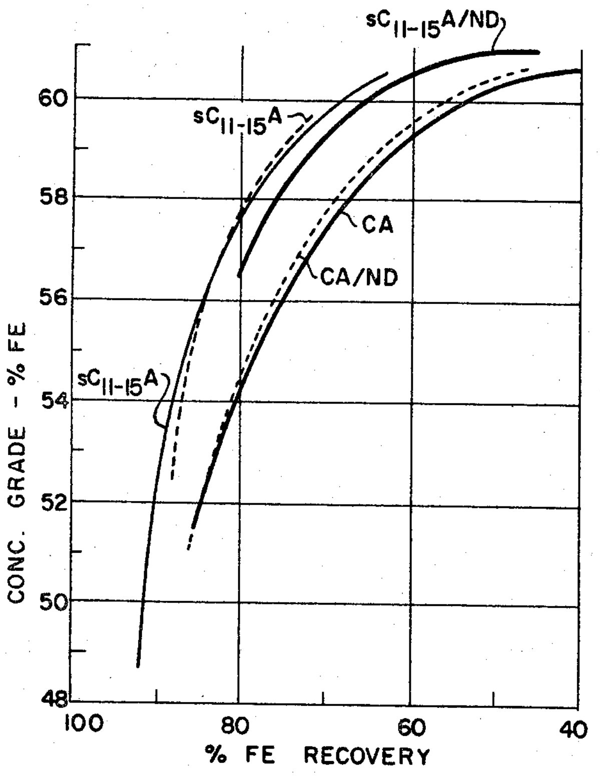

FIG. III

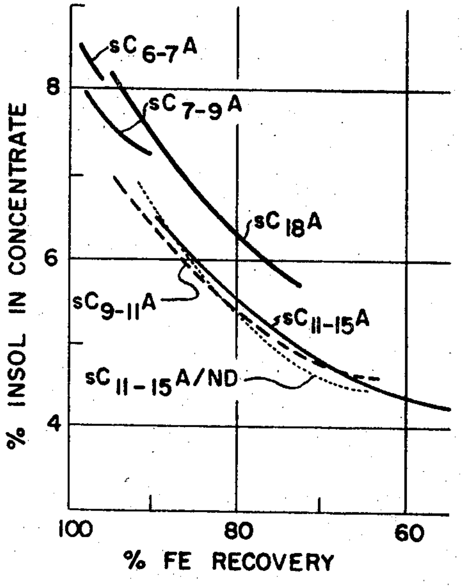

FIG. IV

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FROTH FLOTATION WITH SECONDARY-ALKYL PRIMARY AMINES

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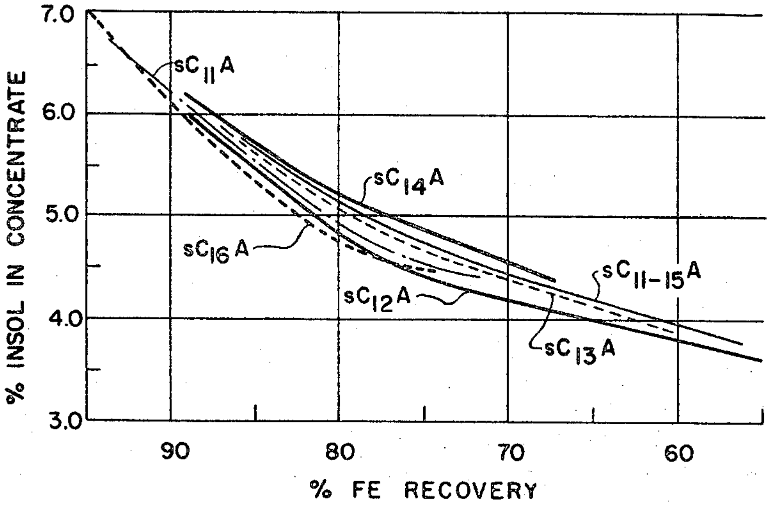

FIG. V

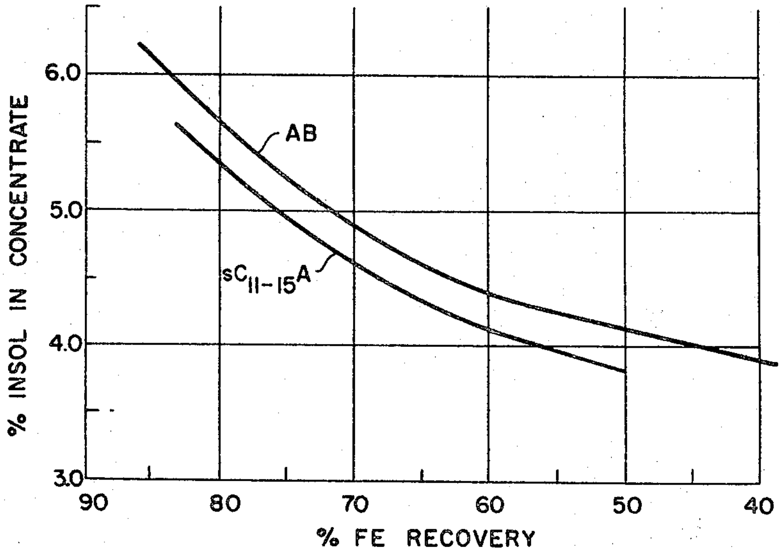

FIG. VI

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FROTH FLOTATION WITH SECONDARY-ALKYL PRIMARY AMINES

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Filed May 7, 1965, Ser. No. 454,155
5 Claims. (Cl. 209—166)

ABSTRACT OF THE DISCLOSURE

Secondary-alkyl primary amines of a specific configuration and chain length, alone or in admixture with heterocyclic nitrogen compounds derived from gilsonite, are used as froth flotation collectors.

This invention relates to the concentration of minerals by froth flotation and more particularly, to a novel froth flotation process wherein flotation is conducted in the presence of an unusually effective amine collector. The collector accomplishes a better percent grade of concentrate and a better recovery of the desired mineral per unit weight of amine used. And, by admixing the amine with a crude mixture of heterocyclic nitrogen compounds obtained from a mineral known as gilsonite, further enhancement in the percent grade and percent recovery can be effected.

While the invention has wide application to froth flotation processes and is useful wherever amines are used as collectors, it has particular applicability to iron ore and phosphate ore flotation.

In iron ore or magnetic iron ore recovery from mixtures of oxidic iron minerals, it is the undesirable silica and miscellaneous cherts and siliceous minerals that are floated away. The desired ore remains behind.

Prior to flotation, the ore is ground, pulped in water, and sometimes, depending on the nature of the ore being treated, preconditioned with starch or dextrin, which is a depressant for the desired iron portion of the ore. It is generally preferred not to use a depressant. Then, a small amount of an amine collector which is preferably readily water-dispersible, and a frothing agent, is added, and the pulp subjected to flotation. The silica rich froth is floated away from the desired iron mineral residue, in one and generally several steps.

In phosphate flotation, one or more steps are used dependent upon the ore being treated. In the two step process, the ore is washed, deslimed, and then 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 one step process, such as presently practiced in treating "western" phosphate ore, only a fatty acid collector, tall oil, is used to float rougher concentrate which is then upgraded by reflotation. However, no additional collector chemical need be used. The undesired silica and other nonphosphate minerals "drop out" and report in the underflow which is either discarded or recycled.

Considerable effort has and is being expended to devise more efficient and more economical methods of operation, the objective, in all instances, being to make as complete a separation as possible and to produce a higher grade concentrate with minimum loss of desired mineral, while consuming as little of the relatively costly amine collector as possible.

An object of this invention is to provide a novel amine collector for froth flotation.

Another object is to provide a novel collector mixture which, per unit amount, is even more efficient than said novel amine collector.

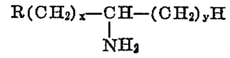
Still another object is to provide a more efficient iron ore flotation process.

Another object is to provide a more efficient phosphate flotation process.

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

It has now been found that the use of certain specific secondary-alkyl primary amines, alone (that is, as singular compounds or in admixture with similar secondary-alkyl primary amines), or preferably in combination with crude mixed heterocyclic nitrogen material derived from the minearl gilsonite, effects a marked improvement in mineral separation. These secondary-alkyl primary amines, may be represented by the formula:

FORMULA I



$$R(CH_2)_x—\underset{\displaystyle NH_2}{\underset{|}{C}}H—(CH_2)_yH$$

wherein

R is selected from the group consisting of hydrogen, an aliphatic radical, a carboxyaliphatic radical, an aminoaliphatic radical, and mixtures thereof,

x and y are positive integers having a sum from 2 to about 47, the total carbon atoms of the compound not exceeding 48.

Typical secondary-alkyl primary amines falling within the above formula are sec-undecylamine, sec-dodecylamine, sec-tridecylamine, sec-tetradecylamine, sec-pentadecylamine, sec-hexadecylamine, sec-heptadecylamine, sec-octadecylamine and all the isomeric versions thereof as well as mixtures of sec-alkyl primary amines and their isomeric forms such as would be derived from various unsaturated hydrocarbons including but not limited to the mixed C_6 to C_7, the C_7 to C_9, the C_9 to C_{11}, the C_{11} to C_{15}, the C_{20} to C_{48}, the C_9 to C_{10}, the C_{11} to C_{14}, the C_{15} to C_{18}, C_{18} to C_{20} sec-alkylamines.

Specific 1-methylalkylamines found useful are 1-methyloctylamine, 1-methyldecylamine, 1-methyldodecylamine, 1-methyltetradecylamine, 1-methylhexadecylamine, and 1-methyloctadecylamine.

The amine is 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 is or by dissolving it in a 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.

The concentration of amine used is about 0.01 pound to about 2.0 pounds per ton of ore, the preferred range in most instances being about 0.05 pound to about 1.0 pound per ton.

The gilsonite material referred to 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, pyyroles, indoles, and quinolines, with some of the substituent carbon chains being olefinic. It also contains some unidentified nonnitrogeneous 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, semipurified or purified byproducts 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 byproducts 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 booiling 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: Extracted from a naphtha stream of approximately 283° F. volumetric average boiling point and 222° F.400° F. boiling range.

(2) Intermediate bases from PFB—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—Extracted from a gas-oil stream of about 520° F. volumetric average boiling point and 460° F. to 665° F. boiling range.

(4) Semipurified 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. at 760 mm.
   (c) Nitrogen compounds III—Boiling range 700° F. to 710° F. at 760 mm.
   (d) Nitrogen compounds IV—Boiling range 745° F. to 755° F. at 760 mm.
   (e) Bottoms V—Boiling range 755° F. and higher at 760 mm.

(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 nonnitrogenous compounds.

(6) Nitrogen bases concentrate oil: An extracted mixture of cyclic tertiary amines plus some nonbasic nitrogen compounds.

(7) Pyrrole polymer oil—An extracted mixture containing predominantly nonbasic nitrogen compounds and some cyclic basic nitrogen compounds.

In all reference to gilsonite, gilsonite material, heterocyclic nitrogen compound, nitrogen bases concentrate oil and the like herein, use of any, some or all of the various fractions above is intended. All are operable, although some may have more effectiveness for particular uses.

The preferred amount of gilsonite material utilized should be approximately about 0.01 pound to about 2.0 pounds per ton of ore, the preferred range in most instances being about 0.05 pound to about 1.0 pound per ton, the exact amount varying 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 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 makeup 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 makeup water, followed by addition to the makeup water of enough acetic or hydrochlorice 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 makeup water.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others thereof, and a composition of matter possessing the characteristics, properties, and the relation of components which will be exemplified in the composition hereinafter described, and the scope of the invention will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the drawings and the following detailed examples which refer to the figures in the drawings:

Example I

In this flotation, the effectiveness of a mixture of sec-alkyl primary amines, as compared to a mixture of normal alkyl primary amines as collectors for coarse phosphate ore separation, was determined. The alkyl group, in each instance, varied from C_{11} to C_{15} in carbon length. Special attention was given to the amines ability to float the +28 mesh silica selectively.

The ore utilized analyzed as follows:

TABLE I.—ORE ANALYSIS

Screening			Chemical Analysis					
Tyler Mesh	Weight		Assay, Percent		Units		Distribution, Percent	
	Gms.	Percent	Insol.[1]	BPL[2]	Insol.	BPL	Insol.	BPL
+12	9.7	1.93	7.39	72.62	0.14	1.40	0.33	3.11
12/20	101.1	20.10	8.89	70.89	1.79	14.25	4.16	31.69
20/28	141.7	28.18	27.97	58.32	7.88	16.44	18.30	36.57
Sub-Totals +28 Mesh	252.5	50.21	19.54	63.91	9.81	32.09	22.78	71.37
28/35	88.8	17.66	56.50	35.21	9.98	6.22	23.17	13.83
35/48	71.6	14.24	69.35	22.84	9.88	3.25	22.94	7.23
−48	90.0	17.90	74.86	18.98	13.40	3.40	31.11	7.56
Sub-Totals −28 Mesh	250.4	49.80	66.79	25.84	33.26	12.87	77.22	28.62
Grand Totals	520.9	100.01			43.07	44.96	100.01	99.99

[1] Insolubles. [2] Bone phosphate lime.

The ore was washed once, allowed to settle for 30 seconds, then deslimed and conditioned at 70% solids, and then floated in a Fagergren machine at 1600 r.p.m. as follows:

TABLE II

Sample No.	Conditioned Reagents[1] (lbs./ton)			Amine Collector (lbs./ton)		Flotation	
	Time in Min.	Pine Oil	Kerosene[2]	Name	Amount	Time in Min.	Percent Solids
1	.50	.1	1.6	$sC_{11}-C_{15}A$[3]	0.792	1.50	16
2	.50	.1	2.4	$sC_{11}-C_{15}A$[3]	1.188	1.50	16
3	.50	.1	4.0	$sC_{11}-C_{15}A$[3]	1.98	1.50	16
4	.25	.1	2.0	$sC_{11}-C_{15}A$[3]	1.98	1.50	16
5	.25	.1	2.0	$sC_{11}-C_{15}A$[3]	2.97	1.50	16
10	.25	.1	2.0	$sC_{11}-C_{15}A+ND$[4]	0.998	1.50	16
11	.25	.1	2.0	$sC_{11}-C_{15}A+ND$[4]	1.497	1.50	16
32	.25	.1	.8	TA[5]	.40	1.50	16
33	.25	.1	.7	TA[5]	.35	1.50	16
34	.25	.1	.9	TA[5]	.45	1.50	16

[1] The water used was Chicago tap water at 25° C.—pH 8.1 ± 0.1.

[2] The kerosene was added at various ratios with collector.

[3] Crude sec-alkyl primary amine wherein the alkyl group varies from C_{11} to C_{15} carbons.

[4] Sec-alkylamine plus nitrogen distillate, 2:1 ratio.

[5] Tallow amine such as Armeen T sold by Armour and Company, Chicago, Illinois, neutralized 45% with acetic acid and added as a 5% emulsion.

The flotation results were as follows:

TABLE III

Sample No.	Product	Weight		Assay				Distribution		
		Gms.	Percent	Percent Insol.	Percent BPL	Metallurgical Units Insol.	Metallurgical Units BPL	+28 M, gms.	Insol., percent	BPL
1	Rougher Float (Tailing)	148.9	30.12	94.07	1.28	28.33	0.39	16.49	33.42	0.87
	−28 Mesh Concentrate	121.3	24.53	31.09	55.36	7.63	13.58			30.18
	+28 Mesh Concentrate	224.2	45.35	14.65	68.40	6.64	31.02	32.85		68.95
		494.4	100.00			42.60	44.99			100.00
2	Rougher Float (Tailing)	157.9	81.56	96.82	2.45	30.56	0.77	8.72	17.67	1.75
	−28 Mesh Concentrate	114.6	22.91	24.70	59.60	5.66	13.65			30.97
	+28 Mesh Concentrate	227.8	45.53	17.83	65.13	8.12	29.65	40.62		67.28
		500.3	100.00			44.34	44.07			100.00
3	Rougher Float (Tailing)	188.4	37.70	95.92	2.61	36.16	0.98	23.73	48.09	2.19
	−28 Mesh Concentrate	91.6	18.33	9.38	71.37	1.72	13.08			29.28
	+28 Mesh Concentrate	219.8	43.98	11.65	69.60	5.12	30.61	25.61		68.52
		499.8	100.01			43.00	44.67			99.99
4	Rougher Float (Tailing)	193.2	38.71	96.12	2.02	37.21	0.78	25.43	51.54	1.78
	−28 Mesh Concentrate	93.7	18.77	10.09	69.87	1.89	13.11			29.86
	+28 Mesh Concentrate	212.2	42.52	11.27	70.59	4.79	30.01	23.91		68.36
		499.1	100.00			43.89	43.90			100.00
5	Rougher Float (Tailing)	193.1	38.84	97.15	2.20	37.73	0.85	27.72	56.18	1.90
	−28 Mesh Concentrate	88.4	17.73	7.10	73.27	1.26	12.99			29.11
	+28 Mesh Concentrate	216.6	43.43	9.98	70.89	4.33	30.79	21.62		68.99
		498.7	100.00			43.32	44.63			100.00
10	Rougher Float (Tailing)	175.4	35.03	96.00	3.10	33.63	1.09	17.25	34.96	2.52
	−28 Mesh Concentrate	108.5	21.67	21.05	60.80	4.56	13.18			30.42
	+28 Mesh Concentrate	216.8	43.30	14.80	67.11	6.44	29.06	32.09		67.07
		500.7	100.00			44.63	43.33			100.01
11	Rougher Float (Tailing)	190.4	38.16	96.38	3.45	36.78	1.32	23.91	48.46	2.90
	−28 Mesh Concentrate	93.9	18.82	12.46	72.03	2.35	13.56			29.79
	+28 Mesh Concentrate	214.6	43.01	11.85	71.24	5.10	30.64	25.43		67.31
		498.9	99.99			44.23	45.52			100.00
32	Rougher Float (Tailing)	235.3	47.18	69.86	22.71	32.96	10.72	25.97	52.63	25.47
	−28 Mesh Concentrate	75.4	15.12	42.89	44.55	6.49	6.74			16.01
	+28 Mesh Concentrate	188.0	37.70	12.43	65.32	4.69	24.63	23.37		58.52
		498.7	100.00			44.14	42.09			100.00
33	Rougher Float (Tailing)	238.4	47.11	69.70	22.93	32.84	10.80	25.87	52.43	25.32
	−28 Mesh Concentrate	81.2	16.05	45.70	43.20	7.34	6.93			16.25
	+28 Mesh Concentrate	186.4	36.84	12.59	67.64	4.64	24.92	23.47		58.43
		506.0	100.00			44.82	42.65			100.00
34	Rougher Float (Tailing)	257.8	51.20	67.77	24.35	34.70	12.47	28.27	57.30	28.39
	−28 Mesh Concentrate	63.6	12.63	40.85	45.36	5.16	5.73			13.04
	+28 Mesh Concentrate	182.1	36.17	11.57	71.13	4.19	25.73	21.07		58.57
		503.5	100.00			44.04	43.93			100.00

FIG. I summarizes the above data in a very succinct manner.

As is evident, the sec-alkyl primary amine collector alone or in admixture with a nitrogen distillate provides a substantially better selectivity of bone phosphate lime (BPL) providing equal grade and improved recovery of coarser phosphate ore (that retained on the 28 or lesser mesh screen) than the standard collector—tallow amine.

Example II

Another phosphate ore sample was floated but this time with special attention given to the influence of chain length of the amine collector.

The ore utilized had an average calculated head assay of 42.52% acid insolubles and a 44.33% bone phosphate lime content.

The ore was scrubbed for three minutes at 25% solids, then washed three times and allowed to settle for 60, 45 and 30 seconds respectively prior to desliming, and conditioned for 0.25 minute at 16% solids and then floated in a Fagergren machine at 1600 r.p.m. for two minutes at 16% solids as follows:

TABLE IV

Test No.	Condition Reagents [1]		Amine Collector (lbs./ton)	
	Pine Oil	Kerosene [2]	Name	Amount
1AR	.1	.88	TA [3]	.44
2R	.1	.72	TA	.34
3R	.1	.48	TA	.24
4R	.1	.86	AB [4]	.44
5R	.1	.64	AB	.34
6R	.1	1.04	AB	.52
16	.1	1.40	$sC_{12}A/ND$ [5]	.70
17	.1	1.60	$sC_{12}A/ND$ [5]	.82
18	.1	2.00	$sC_{12}A/ND$ [6]	1.00
19A	.1	1.4	$sC_{18}A/ND$ [6]	.70
20	.1	1.1	$sC_{18}A/ND$ [6]	.56
21	.1	.72	$sC_{18}A/ND$ [6]	.36

TABLE IV—Continued

Test No.	Condition Reagents [1]		Amine Collector (lbs./ton)	
	Pine Oil	Kerosene [2]	Name	Amount
22	.1	1.40	$sC_{18}A$ [7]	.70
23	.1	1.00	$sC_{18}A$ [7]	.48
24	.1	.48	$sC_{18}A$ [7]	.26
24A	.1	.24	$sC_{18}A$ [7]	.12
25A	.1	1.40	$sC_{12}A$ [8]	.70
25B	.1	.64	$sC_{12}A$ [8]	.34
26	.1	1.60	$sC_{12}A$ [8]	.82
27	.1	2.00	$sC_{12}A$ [8]	1.00
27A	.1	2.40	$sC_{12}A$ [8]	1.20
28AR	.1	1.68	sC_{11-15} [9]	.84
29R	.1	2.00	sC_{11-15} [9]	1.00
30R	.1	1.28	sC_{11-15} [9]	.64
31	.1	1.68	sC_{11-15}/ND [10]	.74
32	.1	2.00	sC_{11-15}/ND [10]	1.00
33	.1	1.28	sC_{11-15}/ND [10]	.64

[1] The water used was Chicago tap water at 25° C.—pH 8.1±0.1.

[2] The kerosene was added at a constant 2:1 ratio with collector.

[3] Tallow amine partially neutralized (45%) with acetic acid.

[4] Blend of nitrogen distillate, tallow amine and ethoxylated amine neutralized (45%) with acetic acid.

[5] Sec-dodecylamine and nitrogen distillate (2:1 ratio) partially neutralized (30%) with acetic acid.

[6] Sec-octadecylamine and nitrogen distillate (2:1 ratio), partially neutralized (30%) with acetic acid.

[7] Sec-octadecylamine partially neutralized (30%) with acetic acid.

[8] Sec-dodecylamine partially neutralized (30%) with acetic acid.

[9] Sec-alkylamine wherein the alkyl group varies from C_{11} to C_{15} carbons partially neutralized (30%) with acetic acid.

[10] Sec-alkylamine wherein the alkyl group varies from C_{11} to C_{15} carbons and nitrogen distillate (2:1 ratio) partially neutralized (30%) with acetic acid.

The flotation results were as follows:

TABLE V

Sample No.	Product	Assay of Product						
		Weight		Percent		Metallurgical Units		Distribution
		Gms.	Percent	Insol.	BPL	Insol.	BPL	BPL
1AR	Rougher Float (Tailing)	263.0	52.36	15.93	16.84	39.76	8.82	19.87
	Concentrate	239.3	47.64	4.42	74.65	2.11	35.56	80.13
2R	Rougher Float (Tailing)	225.1	44.64	87.01	8.80	38.84	3.93	8.96
	Concentrate	279.1	55.36	5.80	72.14	3.21	39.94	91.04
3R	Rougher Float (Tailing)	215.2	42.65	89.57	7.47	38.20	3.19	7.26
	Concentrate	289.4	57.35	6.35	71.00	3.64	40.72	92.74
4R	Rougher Float (Tailing)	225.1	45.04	89.17	7.34	40.16	3.31	8.05
	Concentrate	274.7	54.96	4.65	71.77	2.56	39.45	91.95
5R	Rougher Float (Tailing)	211.1	41.69	92.68	4.96	38.64	2.07	4.67
	Concentrate	295.3	58.31	5.92	72.38	3.45	42.21	95.33
6R	Rougher Float (Tailing)	238.6	47.04	85.55	10.40	40.24	4.89	11.15
	Concentrate	268.6	52.96	4.16	73.60	2.20	38.98	88.85
19A	Rougher Float (Tailing)	227.1	45.19	88.84	8.06	40.15	3.64	8.38
	Concentrate	275.5	54.81	4.24	68.62	2.32	39.82	91.62
20	Rougher Float (Tailing)	222.4	44.43	90.99	6.55	40.43	2.91	6.57
	Concentrate	278.2	55.57	4.32	74.52	2.40	41.41	93.43
21	Rougher Float (Tailing)	202.1	40.28	93.95	4.59	37.84	1.85	4.20
	Concentrate	299.6	59.72	7.64	70.74	4.56	42.25	95.80
22	Rougher Float (Tailing)	260.1	51.79	78.72	15.42	40.77	7.99	18.53
	Concentrate	242.1	48.21	3.77	72.88	1.82	35.14	81.47
23	Rougher Float (Tailing)	230.8	45.94	89.09	8.76	40.93	4.02	9.18
	Concentrate	271.6	54.06	4.71	73.60	2.55	39.79	90.82
24	Rougher Float (Tailing)	200.2	39.90	95.14	3.71	37.96	1.48	3.4
	Concentrate	301.5	60.10	7.00	70.06	4.21	42.11	96.60
24A	Rougher Float (Tailing)	154.1	30.91	95.30	3.65	29.46	1.13	2.41
	Concentrate	344.5	69.09	18.63	66.18	12.87	45.72	97.59
31	Rougher Float (Tailing)	211.2	42.00	87.50	5.15	36.75	2.16	5.01
	Concentrate	291.6	58.00	6.82	70.65	3.96	40.98	94.99
32	Rougher Float (Tailing)	213.8	42.53	90.54	7.27	38.51	43.14	7.03
	Concentrate	288.9	57.47	6.42	71.13	3.69	40.88	92.97
33	Rougher Float (Tailing)	206.4	41.13	91.89	6.16	37.79	2.53	5.94
	Concentrate	295.4	58.87	7.86	68.05	4.63	40.06	94.06
28	Rougher Float (Tailing)	215.6	43.05	91.15	6.25	39.24	2.69	6.17
	Concentrate	285.2	56.95	5.24	71.81	2.98	40.90	93.83
29	Rougher Float (Tailing)	217.0	43.10	91.69	5.79	39.52	2.50	5.60
	Concentrate	286.5	56.90	5.21	74.13	2.97	42.18	94.40
30	Rougher Float (Tailing)	212.2	42.14	92.16	5.85	38.84	2.47	5.63
	Concentrate	291.3	57.86	6.72	71.59	3.89	41.42	94.37
16	Rougher Float (Tailing)	202.0	40.40	91.89	6.25	37.12	2.53	5.60
	Concentrate	298.0	59.60	9.57	71.55	5.70	42.64	94.40
17	Rougher Float (Tailing)	209.0	41.62	91.01	6.81	37.88	2.83	6.26
	Concentrate	293.2	58.38	8.73	72.64	5.10	42.41	93.74
18	Rougher Float (Tailing)	209.0	41.63	90.74	7.19	37.78	2.99	6.55
	Concentrate	293.0	58.37	8.08	73.06	4.72	42.65	93.45
25A	Rougher Float (Tailing)	204.2	40.56	90.17	5.40	36.57	2.19	5.12
	Concentrate	299.2	59.44	9.06	70.25	5.25	40.58	94.88
25B	Rougher Float (Tailing)	188.3	37.83	92.46	5.92	34.97	2.24	4.83
	Concentrate	309.5	62.17	12.35	71.07	7.68	44.18	95.17
26	Rougher Float (Tailing)	207.6	41.31	90.73	7.62	37.48	3.15	7.17
	Concentrate	294.9	58.69	9.23	69.52	5.42	40.80	92.83
27	Rougher Float (Tailing)	206.4	41.19	92.27	6.49	38.01	2.69	5.84
	Concentrate	294.7	58.81	9.25	73.21	5.31	43.06	94.16
27A	Rougher Float (Tailing)	210.8	42.15	91.21	7.34	38.45	3.09	7.07
	Concentrate	289.3	57.85	7.68	70.17	4.44	40.59	92.93

FIG. II dramatically illustrates the above data.

As can be seen therein, the longer chain sec-alkyl primary amines are more selective by providing a cleaner separation of silica from phosphate (less percent insolubles in the concentrate), and especially in combination with nitrogen distillate, than the standard tallow amine (designated TA), and the standard amine blend (AB). The shorter chain sec-alkyl primary amines are less effective than the longer chain products.

Example III

Nonmagnetic taconite ore (hematite, goethite, etc.), chemically analyzed as containing 39% Fe and 38.8% insolubles, has the following screen analysis as indicated in Table VI:

TABLE VI

Size	Wt. percent	Percent Fe	Cumulative	
			Wt. percent	Percent Fe
+140 Mesh	0.3	33.2	0.3	33.2
+200 Mesh	0.8	27.4	1.1	29.0
+270 Mesh	3.4	26.8	4.5	27.3
+325 Mesh	8.0	33.4	12.5	31.2
+34 Microns	18.5	39.7	31.0	38.8
+25 Microns	7.6		38.6	
+16 Microns	30.8		69.4	
+9 Microns	26.9		96.3	
−9 Microns	3.7		100.0	

The ore was pulped, preconditioned and floated through three stages (or four, as noted) of rougher concentrate as follows:

TABLE VII

Stage	Condition (min.)	Float (min.)	Lbs./Ton Collector
1st Froth	½	2	See Table VIII.
2nd Froth	¼	2	Do.
3rd Froth	¼	2	Do.
4th Froth (if any)	¼	2	Do.

Flotation machine—Wemco at 1,600 r.p.m.
Flotation pH—7.9±0.1.
Pulp density—32% solids.
Frother—.056 lb./ton Pine oil.

The results were as follows:

TABLE VIII

Test		Collector		Assay of Product						Distribution	
		Name	Amount	Gm. Weight	Percent Weight	Percent Acid Insol.	Percent Fe	Metallurgical Units		Percent Insol.	Percent Fe
								Insol.	Fe		
12	1st Froth	CA [1]	.134	339.4	34.10	73.53	16.08	25.07	5.48	66.82	13.89
	2nd Froth	CA [1]	.134	243.5	24.46	38.41	39.25	9.40	9.60	25.05	24.33
	3rd Froth	CA [1]	.134	239.1	24.02	10.25	57.39	2.46	13.79	6.56	34.95
	Concentrate	CA [1]		173.3	17.41	3.41	60.81	0.59	10.59	1.57	26.84
				995.3	99.99			37.52	39.46	100.00	100.01
13	1st Froth	CA/ND [2]	.134	327.3	32.83	73.62	15.61	24.17	5.12	64.21	13.01
	2nd Froth	CA/ND [2]	.134	211.3	21.19	43.40	35.69	9.20	7.56	24.44	19.21
	3rd Froth	CA/ND [2]	.134	226.6	22.73	14.27	55.26	3.24	12.56	8.61	31.91
	Concentrate	CA/ND [2]		231.8	23.25	4.45	60.74	1.03	14.12	2.74	35.87
				997.0	100.00			37.64	39.36	100.00	100.00
15	1st Froth	$sC_{11-15}A$ [3]	.134	334.4	33.53	76.21	14.14	25.55	4.74		11.95
	2nd Froth	$sC_{11-15}A$ [3]	.134	179.8	18.03	48.26	33.62	8.70	6.06		15.28
	3rd Froth	$sC_{11-15}A$ [3]	.134	171.0	17.14	14.39	57.32	2.47	9.82		24.77
	Concentrate	$sC_{11-15}A$ [3]		312.2	31.30	3.30	60.80	1.03	19.03		47.99
				997.4	100.00			37.75	39.65		99.99
16	1st Froth	$sC_{11-15}A$/ND [4]	.112	220.0	22.07	80.14	12.27		2.71		6.89
	2nd Froth	$sC_{11-15}A$/ND [4]	.112	215.8	21.64	64.44	22.75		4.92		12.50
	3rd Froth	$sC_{11-15}A$/ND [4]	.112	143.5	14.39	31.05	45.27		6.51		16.54
	4th Froth	$sC_{11-15}A$/ND [4]	.112	125.1	12.55	9.90	58.35		7.32		18.60
	Concentrate	$sC_{11-15}A$/ND [4]		292.6	29.35	3.15	61.00		17.90		45.48
				997.0	100.00				39.36		100.00
17	1st Froth	$sC_{11-15}A$ [5]	.1188	256.8	25.75	79.08	12.75		3.28		8.33
	2nd Froth	$sC_{11-15}A$ [5]	.1188	217.7	21.83	60.23	25.08		5.47		13.90
	3rd Froth	$sC_{11-15}A$ [5]	.1188	111.3	11.16	22.52	50.37		5.62		14.28
	Concentrate	$sC_{11-15}A$ [5]		411.3	41.25	5.34	60.57		24.99		63.49
				997.1	99.99				39.36		100.00

[1] Coconut oil amine 40% neutralized with acetic acid and added as a 5% active solution.

[2] Coconut oil amine-nitrogen distillate mixture (3 to 1) 40% neutralized with acetic acid and added as a 5% active solution.

[3] Sec-alkylamine wherein alkyl group comprises mixture of C_{11} to C_{15} carbons 100% neutralized with acetic acid and added as a 5% active solution.

[4] Sec-alkylamine wherin alkyl group comprises mixture of C_{11} to C_{15} carbons—nitrogen distillate mixture (3 to 1) 100% neutralized with acetic acid and added "as is" to the float suspension.

[5] Sec-alkylamine wherein alkyl group comprises mixture of C_{11} to C_{15} carbons added "as is" to the float suspension.

As is evident from the data above, the sec-alkyl primary amine collectors of this invention, especially when admixed with nitrogen distillate as derived from gilsonite, effect a better iron separation when compared to the coconut amine. Also, more of the desired iron fraction is recovered on an overall basis. FIG. III illustrates this in a most dramatic way. It will be noted that the selectivity curves for the collectors of this invention are substantially better, than the amine collectors of the prior art. It is also to be noted that the sec-alkyl primary amine collectors may be applied in an unneutralized "as received" form while still providing superior results.

Example IV

Another iron ore flotation test series was run, but this time on a magnetite ore (magnetic concentrate) using the following chain lengths of sec-alkyl primary amines as the collector:

C_{6-7} sec-alkylamiens
C_{7-9} sec-alkylamines
C_{9-11} sec-alkylamines
C_{11-15} sec-alkylamines
C_{11-15} sec-alkylamines admixed with nitrogen distillate (2:1)
C_{18} sec-alkylamines

The ore utilized was a natural magnetic concentrate with an average calculated head assay of 8.63% insolubles and 64.63% Fe.

Stage additions of the collectors are utilized with 3 to 4 rougher floats as follows:

TABLE IX

Stage	Condition (min.)	Float (min.)	Lbs./Ton Collector	Frother (MIBC) [1]
1st Froth	¼	4	See Table XX	.03
2nd Froth	¼	4	do.	
3rd Froth	¼	4	do.	.03
4th Froth	¼	4	do.	

[1] Methylisobutyl carbinol.

Flotation machine—Denver at 1800 r.p.m.
Flotation pH—8.0±0.1.
Pulp Density—20% solids.

The results were as follows:

TABLE X

Test		Collector		Assay of Product						Distribution
		Name	Lb./Ton Amount	Gm. Weight	Percent Weight	Percent Acid Insol	Percent Fe	Metallurgical Units Insol.	Metallurgical Units Fe	Percent Fe
10	1st Froth	$sC_{6-7}A$[1]	.317	4.0	.78	35.75	68.24	.27	.30	.46
	2nd Froth	$sC_{6-7}A$[1]	.317	5.8	1.13	32.73	40.29	.37	.46	71
	3rd Froth	$sC_{6-7}A$[1]	.317	5.5	1.07	17.99	52.89	.19	.57	.88
	4th Froth	$sC_{6-7}A$[1]	.317	6.7	1.31	16.56	56.53	.22	.74	1.15
	Concentrate			490.5	95.72	8.14	65.35	7.79	62.55	96.80
11	1st Froth	$sC_{7-9}A$[2]	.302	12.5	2.50	30.98	43.90	.78	1.10	1.70
	2nd Froth	$sC_{7-9}A$[2]	.302	17.3	3.46	19.70	55.57	.68	1.92	2.96
	3rd Froth	$sC_{7-9}A$[2]	.302	15.1	3.02	13.31	61.23	.40	1.85	2.85
	4th Froth	$sC_{7-9}A$[2]	.302	11.0	2.20	12.18	61.91	.27	1.36	2.10
	Concentrate			444.4	88.83	7.25	65.93	6.44	58.57	90.39
12	1st Froth	$sC_{9-11}A$[3]	.291	37.0	7.40	27.80	49.22	2.06	3.64	5.60
	2nd Froth	$sC_{9-11}A$[3]	.291	91.3	18.25	14.53	59.79	2.65	10.91	16.79
	3rd Froth	$sC_{9-11}A$[3]	.291	69.3	13.85	8.62	65.28	1.19	9.04	13.91
	Concentrate			302.7	60.50	4.45	68.43	2.69	41.40	63.70
13	1st Froth	$sC_{11-15}A$[4]	.133	63.7	12.73	24.36	53.10	3.10	6.76	10.45
	2nd Froth	$sC_{11-15}A$[4]	.133	80.9	16.47	13.12	61.47	2.12	9.94	15.36
	3rd Froth	$sC_{11-15}A$[4]	.133	94.2	18.83	7.49	65.98	1.41	12.42	19.20
	Concentrate			261.4	52.26	4.16	68.08	2.17	35.58	54.91
15	1st Froth	$sC_{11-15}A$[5]	.135	46.6	9.31	26.22	51.18	2.49	4.77	7.40
	2nd Froth	$sC_{11-15}A$[5]	.135	77.4	15.46	15.35	59.57	2.37	9.21	14.29
	3rd Froth	$sC_{11-15}A$[5]	.135	72.4	14.47	8.63	64.55	1.25	9.34	14.49
	Concentrate			304.1	60.76	4.40	67.72	2.67	41.15	63.83
16	1st Froth	$sC_{18}A$[6]	.143	21.9	4.38	23.60	53.56	1.03	2.35	3.63
	2nd Froth	$sC_{18}A$[6]	.143	28.8	5.76	16.33	48.36	.94	3.36	5.18
	3rd Froth	$sC_{18}A$[6]	.143	49.0	9.80	17.12	57.77	1.68	5.66	8.73
	4th Froth	$sC_{18}A$[6]	.143	49.8	9.56	11.80	62.35	1.13	5.96	9.20
	Concentrate			352.7	70.51	5.76	67.35	4.06	47.49	73.26

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[1] Sec-alkylamine where the alkyl group has from 6 to 7 carbons added "as is" to the float suspension.

[2] Sec-alkylamine where the alkyl group has from 7 to 9 carbons added "as is" to the float suspension.

[3] Sec-alkylamine where the alkyl group has from 9 to 11 carbons added "as is" to the float suspension.

[4] Sec-alkylamine where the alkyl group has from 11 to 15 carbons added "as is" to the float suspension.

[5] Sec-alkylamie where the alkyl group has from 11 to 15 carbons and nitrogen distillate (see 5 under description of gilsonite material above) (2:11) added "as is" to the float suspension.

[6] Sec-alkylamine where the alkyl group has 18 carbons added "as is" to the float suspension.

FIG. IV illustrates the conclusion that may be reached from the test results above. As is evident from the curves on FIG. IV, the C_{11}–C_{15} sec-alkyl primary amine, with or without the nitrogen distillate additive, provides the best percent Fe recovery in the purest form (with the least amount of insolubles in the concentrate).

Example V

Another iron ore test series on magnetite ore (magnetic concentrate), with use of specific alkyl chain length of sec-alkyl primary amine, establishes the most effective amine of the group encompassed by this invention.

The ore utilized is a natural magnetic concentrate having an average calculated head assay of 8.5% insolubles and 63.57% Fe.

The same flotation testing conditions as in Example IV, (see particularly Table IX), are used. The collector utilized and the test results are indicated in Table XI which follows:

TABLE XI

Test		Collector		Assay of Product						Distribution
		Name	Lb./Ton Amount	Gm. Weight	Percent Weight	Percent Acid Insol.	Percent Fe	Metallurgical Units Insol.	Metallurgical Units Fe	Percent Fe
1	1st Froth	$sC_{11}A$	.120	40.6	8.12	29.02	47.44	2.36	3.85	6.08
	2nd Froth	$sC_{11}A$	.120	73.8	14.77	16.14	57.04	2.38	8.42	13.30
	3rd Froth	$sC_{11}A$	.072	43.1	8.63	9.51	62.68	0.82	5.41	8.54
	Concentrate	$sC_{11}A$		342.2	68.48	4.43	66.64	3.03	45.64	72.08
				499.7	100.00			8.59	63.32	100.00
2	1st Froth	$sC_{12}A$[2]	.125	67.3	13.49	24.11	52.60	3.25	7.10	11.11
	2nd Froth	$sC_{12}A$[2]	.125	110.0	22.05	11.47	61.95	2.53	13.66	21.38
	3rd Froth	$sC_{12}A$[2]	.075	60.0	12.03	6.52	65.21	0.78	7.84	12.27
	Concentrate	$sC_{12}A$[2]		261.6	52.44	3.62	67.31	1.90	35.30	55.24
				498.9	100.01			8.46	63.90	100.00
3	1st Froth	$sC_{13}A$	.128	75.7	15.16	23.33	52.53	3.54	7.96	12.50
	2nd Froth	$sC_{13}A$	.128	95.6	19.15	11.13	60.95	2.13	11.67	18.33
	3rd Froth	$sC_{13}A$	.0768	43.7	8.75	7.58	64.47	0.66	5.64	8.86
	Concentrate	$sC_{13}A$		284.2	56.93	3.87	67.47	2.20	38.41	60.32
				499.2	99.99			8.53	63.68	100.01
4	1st Froth	$sC_{14}A$	.128	64.0	12.83	24.52	52.14	3.15	6.69	10.46
	2nd Froth	$sC_{14}A$	.128	68.2	13.67	12.60	60.77	1.72	8.31	12.99
	3rd Froth	$sC_{14}A$	.0768	48.0	9.62	9.38	63.06	0.90	6.07	9.49
	Concentrate	$sC_{14}A$		318.6	63.87	4.32	67.19	2.76	42.91	67.07
				498.8	99.99			8.53	63.98	100.01

See footnotes at end of table.

TABLE XI—Continued

Test		Collector		Assay of Product						Distribution
		Name	Lbs./Ton Amount	Gm. Weight	Percent Weight	Percent Acid Insol.	Percent Fe	Metalurgical Units		Percent Fe
								Insol.	Fe	
5	1st Froth	$sC_{16}A$	.132	34.7	6.96	29.46	45.81	2.05	3.19	5.02
	2nd Froth	$sC_{16}A$	.132	43.4	8.70	19.03	55.41	1.66	4.82	7.58
	3rd Froth	$sC_{16}A$	.0792	68.6	13.76	12.30	60.68	1.69	8.35	13.14
	Concentrate	$sC_{16}A$		351.9	70.58	4.48	66.88	3.16	47.20	74.26
				498.6	100.00			8.56	63.56	100.00
6	1st Froth	$sC_{11-15}A$	.132	80.2	16.06	23.00	53.29	3.69	8.56	13.43
	2nd Froth	$sC_{11-15}A$	.132	90.8	18.18	11.00	61.95	2.00	11.26	17.66
	3rd Froth	$sC_{11-15}A$	.0792	57.3	11.47	6.90	64.87	0.79	7.44	11.67
	Concentrate	$sC_{11-15}A$		271.1	54.29	3.83	67.22	2.08	36.49	57.24
				499.4	100.00			8.56	63.75	100.00

[1] All collectors used are sec-alkylamines, the carbon length of the alkyl group indicated by the subscript of the C number. Each was added in the amount indicated at each froth "as is" without neutralization.

[2] The sec-dodecyl primary amine used comprised a mixture of the following isomers:

2-aminododecane, 27.4%
3-aminododecane. 22.7%
4-aminododecane, 22.7%
5-aminododecane, 27.2%

The above test results are portrayed graphically in FIG. V. As seen, the C_{12} sec-alkyl primary amine is the best of the group covered by this invention.

Example VI

In still another magnetite ore flotation test series (magnetic concentrate) to determine effectiveness in cold pulp (about 40° F.) which is the usual environment in iron ore country, such as Minnesota, a C_{11-15} sec-alkyl primary amine is compared to an amine blended with a nitrogen base concentrate oil, a standard flotation collector for iron recovery sold to the trade by Armour and Company, Chicago, Ill. Usually, collectors are much less effective in the cold.

The ore utilized was a natural magnetic concentrate having an average calculated head assay of 8.53% insolubles and 63.57% Fe.

The same flotation testing conditons as indicated in Table IX above (Example IV) were used. The flotation results were as follows:

TABLE XII

Test		Collector			Assay of Products						Distribution
		Name	Temp. Pulp	Lb./Ton Amount	Gm. Weight	Percent Weight	Percent Acid Insol.	Percent Fe	Metallurgical Units		Percent Fe
									Insol.	Fe	
14	1st Froth	$sC_{11-15}A$ [1]	38°–44°	.132	97.3	19.44	20.53	55.05	3.99	10.70	16.93
	2nd Froth	$sC_{11-15}A$ [1]	38°–44°	.132	106.9	21.35	9.69	62.21	2.07	13.28	21.01
	3rd Froth	$sC_{11-15}A$ [1]	38°–44°	.0792	57.1	11.41	5.75	65.34	0.66	7.46	11.80
	Concentrate	$sC_{11-15}A$ [1]	38°–44°		239.3	47.80	3.82	66.48	1.83	31.78	50.27
					500.6	100.00			8.55	63.22	100.01
16	1st Froth	AB [2]	40°–44°	.1	82.7	16.49	19.71	55.84	3.25	9.21	14.52
	2nd Froth	AB [2]	40°–44°	.1	131.2	26.17	10.22	62.01	2.68	16.23	25.59
	3rd Froth	AB [2]	40°–44°	.05	102.7	20.48	5.29	65.25	1.08	13.36	21.06
	Concentrate	AB [2]	40°–44°		184.3	36.86	3.85	66.82	1.42	24.63	38.83
					500.9	100.00			8.43	63.43	100.00

[1] Sec-alkylamine in which the alkyl group contains 11 to 15 carbon atoms, added "as is."

[2] Blend of coconut oil amine and 5% nitrogen bases concentrate oil neutralized 100% with acetic acid.

FIG. VI portrays the above results. As noted, the sec-alkylamine of this invention performs considerably better in cold uplp with respect to percent Fe recover with minimum percent insolubles in the concentrate.

The following Table XIII numerically summarizes data so that the improvement can be readily seen:

TABLE XIII

Ore Type	Collector	Lb./Ton	Lb./Ton Gilsonite	Grade of Concentrate, percent		Percent Recovery of Fe
				Insol.	Fe	
Iron	Coconut Oil Amine Acetate.	.268		7.36	58.85	61.79
Iron	$sC_{11-15}A$	.356		5.34	60.57	63.49
Iron	$sC_{11-15}A$	.252	.084	5.15	60.19	64.08

The C_{11-15} sec-alkyl primary amine ($sC_{11-15}A$) produces a higher percent Fe concentrate and higher recover of iron. The gilsonite material improves the recovery even further and lowers the amount of amine required to do so.

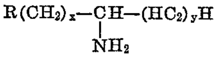
In summary, the above data and graphs verify the superiority of the sec-alkyl primary amines wherein the alkyl group ranges from C_6 to C_{24}, and especially when admixed with a nitrogen distillate derived from gilsonite, for froth flotation processes. They have better selectivity of bone phosphate lime, even if the ore is coarse. They provide a cleaner separation in uncontaminated form of phosphate ore. In iron ore recovery, they also have better selectivity and effect a cleaner iron recovery, even in cold pulp.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained, and since certain changes may be made in carrying out the above method and composition of matter without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and all statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Now that the invention has been described, what is claimed is:

1. A froth flotation process for separating phosphate from its crude ore, the improvement comprising utilization of about .01 to 2 lbs. per ton of ore of an amine falling within the following formula:



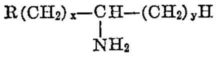
$$R(CH_2)_x-\underset{NH_2}{\underset{|}{C}}H-(HC_2)_yH$$

wherein

R is selected from the group consisting of hydrogen, an aliphatic radical, a carboxyaliphatic radical, an aminoaliphatic radical, and mixtures thereof,

x and y are positive integers having a sum from 9 to about 47, the total carbon atoms of the compound not exceeding 48.

2. A froth flotation process for separating iron ore concentrates from its crude ore, the improvement comprising utilization of about .01 to 2 lbs. per ton of ore of an amine falling with the following formula:



$$R(CH_2)_x\text{—}\underset{\displaystyle NH_2}{\underset{|}{CH}}\text{—}(CH_2)_yH$$

wherein

R is selected from group consisting of hydrogen, an aliphatic radical, a carboxyaliphatic radical, an aminoaliphatic radical, and mixtures thereof,

x and y are positive integers having a sum from 9 to about 47, the total carbon atoms of the compound not exceeding 48,

as the collector.

3. The process of claim **1** wherein the secondary-alkyl primary amine is a mixture of such amines wherein the alkyl group varies from C_{11} to C_{15} carbons.

4. The process of claim **2** wherein the secondary-alkyl primary amine is a mixture of such amines wherein the alkyl group varies from C_{11} to C_{15} carbons.

5. The process of claim **2** wherein the secondary-alkyl primary amine is a mixture of such amines wherein the alkyl group varies from C_9 to C_{11} carbons.

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