

- [54] **AMINE FLOTATION REAGENTS**
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 [22] Filed: **Nov. 6, 1972**
 [21] Appl. No.: **304,007**

2,569,417	9/1951	Pay et al.	260/404.5
2,737,509	3/1956	Jelling.....	260/97.5
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Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 467, Jan. 2, 1970,
 abandoned.

- [52] U.S. Cl..... **260/97.5**, 44/66, 209/166,
 260/18 R, 260/309.6, 260/404.5
 [51] Int. Cl. **C09f 7/00**
 [58] Field of Search 260/97.5, 309.6, 18, 404.5;
 167/38.7; 209/166; 44/66

References Cited

UNITED STATES PATENTS

- 2,494,132 1/1950 Jayne 209/166

Primary Examiner—Melvyn I. Marquis
Attorney, Agent, or Firm—Christie, Parker & Hale

[57]

ABSTRACT

A new class of useful reagents for ore beneficiation are obtained by the reaction of N,N-dialkyl alkylene diamines and N,N-dialkyl-N' -alkyl alkylene diamines with reconstituted tall oil. The reagents are particularly useful for the flotation separation of ore values from siliceous materials.

6 Claims, No Drawings

AMINE FLOTATION REAGENTS

This is a continuation in part of my application Ser. No. 467 filed January 2, 1970 now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates to a new family of amine flotation reagents in particular those based on the reaction product of reconstituted tall oil acid which are highly selective for the separation of ore values such as phosphate rock from siliceous materials.

Phosphate rock occurs widely in nature and contains as one valuable constituent impure calcium fluorophosphate. The deposits however, also contain siliceous materials, such as silica which are valueless constituents. Other valueless constituents such as calcium carbonate, some carbonaceous materials and heavy minerals may also be present.

Many methods have been used to beneficiate or concentrate the phosphatic constituents by flotation from the siliceous, carbonaceous and heavy mineral constituents. Commonly, partial concentration is first employed to remove slimes and the phosphate values are then extracted using two beneficiation separations.

The first involves a crude flotation of phosphate values through the use of a fatty acid and caustic in combination with a petroleum fraction, such as kerosene. These reagents are mixed with the aqueous suspension of phosphate rock and the mixture is agitated and aerated. The phosphate values tend to concentrate in the upper portion of the cell for separation.

The enriched fraction, typically known as the rough concentrate, still contains 8 to 20 percent siliceous matter which is attempted to be separated from the phosphate rock in a second flotation using a cationic reagent. The cationic reagents used have been long chain fatty acid amines or the salts, thereof.

One class of fatty acid amines used are those obtained by the reaction of fatty acids and ammonia in a two-stage reaction system. A nitrile is initially produced which is reduced to form the amines. The product usually contains a high concentration of free nitrile groups.

Another amine system, described in U.S. Pat. No. 2,927,692, has also been proposed. This reagent system is obtained by the condensation of fatty acid with an alkylene polyamine or a polyalkylene polyamine. The product is a mono- or diamine which contains a number of free amine groups depending on the molar ratios of materials employed in the reaction.

While both amine systems are utile, their selectivity for siliceous materials is somewhat limited and the degree of separation of the phosphate rock from siliceous materials has been less than that desired.

SUMMARY OF THE INVENTION

It has now been found that monofunctional N,N-dialkyl alkylene diamines and N,N-dialkyl-N'-alkyl alkylene diamines will react with saturated, unsaturated and hydroxy fatty acids particularly reconstituted tall oils by a condensation reaction to yield amines having free tertiary amine groups. These amines and the salts thereof have been found to be selective beneficiation reagents for the separation of mineral values, such as phosphate rock, from siliceous materials.

The preferred reconstituted tall oil acid-amines are obtained by reacting from about 0.9 to about 3.7 molar equivalents of reconstituted tall oil per active amine

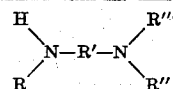
group in an amine system containing at least one N, N-dialkyl-alkylene diamine or a N,N-dialkyl-N'-alkyl alkylene diamine or a mixture thereof, at a temperature of from about 130°C to about 260°C for a time sufficient for the condensation reaction to occur.

The reconstituted tall oil amine reaction product formed and their salts are unusually selective reagents for the beneficiating separation of ore values, such as phosphate rock, from siliceous materials.

DESCRIPTION

According to the present invention, there is provided a new class of fatty acid amines which are highly selective beneficiation reagents for the removal of siliceous materials from mineral ores.

The amine reagents of this invention are prepared, in general, by reaction of saturated, unsaturated and hydroxylated fatty acids or mixtures thereof and in particular reconstituted tall oil with at least one monofunctional diamine having the general formula:



(1)

wherein R is hydrogen or an alkyl group and R'R'' and R''' are independently alkyl groups. The alkyl groups present may be straight chained or branched and preferably contain from about one to about four carbon atoms.

Illustrative but no wise limiting of the monofunctional N,N-dialkyl alkylene diamines and N,N-dialkyl-N'-alkylenediamines which may be used in accordance with the practice of this invention there may be mentioned N,N-diethylethylene diamine; N,N-diethyl-N'-methylethylene diamine; N,N-dimethyl-1,2-propane diamine; N,N-diethyl-1,3-propane diamine; N,N-dimethyl-1,3-propane-diamine; N,N-dimethylethylene diamine and the like.

In addition to at least one monofunctional N,N-dialkyl alkylene diamine or N,N-dialkyl-N'-alkyl alkylene diamine, there may be present in the reaction system, reactive polyfunctional amines such as alkylene diamines, polyalkylene diamines, polyalkylene polyamines and the like. The amounts which may be present, generally, range from about 0.6 to about 1.5 mol per mol of monofunctional diamine.

The fatty acids which are reacted with an amine system containing N,N-dialkyl alkylene diamines and N,N-dialkyl-N'-alkyl alkylene diamines to provide the most functional reagents of this invention are the reconstituted tall oils.

By "reconstituted tall oil" there is meant, in general, a reaction product containing on the average at most about 14 percent rosin acids, from about 72.0 to about 77.0 percent fatty acids and a minimum acid number of at least about 125. The preferred reconstituted tall oils contain by analysis from about 73 to about 76 percent fatty acids, from about 11 to about 16 percent rosin acids, from about 10 to about 13 percent unsaponifiables and having an acid number ranging from about 150 to about 165.

As will be shown, the reconstituted tall oil-amine reaction products of this invention are far superior to distilled tall oil-amine, tall oil heads-amine and oleic and-

amine reaction products with respect to their ability to separate acid insolubles (SiO_2) from P_2O_5 .

The amount of acid employed for the condensation reaction is an amount sufficient to provide from about 0.9 to about 3.7, preferably from about 1.0 to about 2.0 molar equivalent of reconstituted tall oil acid for each primary or secondary amine available in the reaction system.

Accordingly, each of the N,N-dialkyl alkyl diamines and N,N-dialkyl-N'-alkyl alkylene diamines provided in the reaction system in accordance with the practice of this invention provide one functional group for reaction with each molar equivalent of the reconstituted tall oil. Where polyfunctional amines, such as those set forth above, are present, a fatty acid equivalent, within the range prescribed above, should be provided for each amine group in the system having an active hydrogen, namely the primary and secondary amines.

Novel reagents provided in accordance with the practice of this invention are typically obtained by condensing the mixture of the fatty acid and amines at a temperature from about 130° to about 260°C for a period of time sufficient for the system to complete the reaction. Generally, depending on the mixture, condensation time from about 2 to about 6 hours or more will be required.

The properties of the condensation product obtained will vary somewhat depending upon the provided mol ratio of acid to amine. At lower mol ratios a condensation product will readily dissolve in water. At higher acid ratios, however, the product behaves generally more like the fatty acid used and shows a tendency to disperse rather than dissolve in solution.

The tertiary amine groups are present in the amine condensation products of this invention in combination with combined reconstituted tall oil acid and have been observed to provide reaction products with highly selective activity for separating of ore values, such as phosphate rock, from siliceous materials by froth flotation.

The tertiary amine groups also provide a functionality which allows the formation of salts by reaction with

acids such as formic acid, acetic acid, propionic and hydrochloric acid, hydrofluoric acid and the like, to provide salts in which the novel fatty acid amines of this invention serve as a cation and where the anion is provided by the acid. These salts are also active reagents for the beneficiation of ores and most particularly selective reagents for the flotation separation of ore values from siliceous materials.

Although they may be used alone in the beneficiation of mineral values, the activity of the amine reagents of this invention may be further promoted by the presence of certain acid like petroleum derivatives such as kerosene and the like in the system where flotation is carried out. They may also be used in conjunction with other beneficiating reagents for the separation of values from ores and the like.

The amount of the amines of this invention employed in the beneficiation of ores is not narrowly critical. Generally, amounts from about 0.1 to about 2.0 or more pounds per ton of ore beneficiated may be used.

While no wise limiting, the following are examples of the preparation of the novel fatty acid amines of this invention as well as their use as flotation reagents for the beneficiation of ores.

EXAMPLES 1 TO 15

A series of fatty acid-amine condensation reactions carried out using a reactor equipped with a stirrer, a condenser and a temperature indicator. In each instance, the amine and acid were added in specified amounts to the reactor and the mixture heated with agitation. An initial temperature increase was generally observed when the amine and the fatty acid were mixed. With additional heating, water began to distill off at a temperature from between 140°C and 150°C and continued to evolve until the temperature of the reaction mass reached about 220°C to 230°C . Reaction times varied from about 3 to about 6 hours. The nature of the amine fatty acids systems reacted and the mol ratios employed and general properties of the reaction mass obtained are shown in Table I.

Table I

Example	Fatty Acid Source	Wt. %	Amine	Wt. %	Mole Ratio Acid/Amine	Remarks
1.	Tall Oil ¹	84	N,N-dimethyl-1,3-propane diamine	16	1.82	Opaque solution — two layers in standing Clear Brown Solution
2.	Tall Oil	78	do.	22	1.20	
3.	Tall Oil	91.5	do.	8.5	3.68	
4.	Tall Oil	88	do.	12	2.50	
5.	Tall Oil	86.6	do.	13.4	2.25	Soluble at 40% Solids Separation on Standing
6.	Tall Oil	82.8	do.	17.2	1.54	Opaque Solution — no phase separation
7.	Oleic Acid	84	do.	16	1.9	Clear, light yellow solution
8.	Tall Oil Heads ²	84	do.	16	1.83	Opaque Solution
9.	Tall Oil Heads	77.8	do.	12.2	1.21	Insoluble
10.	Tall Oil Heads	91.4	do.	8.6	3.64	Opaque Brown Solution
11.	Distilled Tall Oil ³	84	do.	16	1.83	
12.	Tall Oil	77.7	N,N-dimethyl-1,3-propane diamine	11.1	1.21	
			Diethylene Triamine	11.2		
13.	Tall Oil	84.5	N,N-Dimethyl-1,3-propane diamine	6.2	1.92	
			Diethylene Triamine	9.3		
14.	Tall Oil	84.7	N,N-Dimethyl-1,3-propane diamine	9.7		
			Diethylene Triamine	6.2	1.92	
15.	Tall Oil Heads	84.5	N,N-Dimethyl-1,3-propane diamine	6.2	1.92	
			Diethylene Triamine	9.3		

1. Union Camp Corporation CX-1, a reconstituted tall oil acid containing from 72–77% by weight fatty acids, up to 14% by weight rosin acids and having an acid number of at least 125.

2. Arizona Chemical Company, Acintol H-2122

3. Arizona Chemical Company, Acintol D-29LR

EXAMPLE 16

To establish the utility of a reconstituted tall oil-amine reaction product to separate silica (SiO_2) by froth flotation there was employed a UnitolTM CX-1 having the following analysis:

Rosin Acids	16.3%
Fatty Acids	73.1%
Unsaponifiabiles	10.6%
Acid No.	164

The series of tests involved evaluation of the properties of the reaction product of a reconstituted tall oil known as "UNITOL" CS-1 with N,N-dimethyl-1,3-propane diamine as compared to the reaction product of the same amine with distilled tall oil, tall oil heads and oleic acid for their relative performance to separation by froth flotation of silica from P_2O_5 extracted from phosphate rock. The distilled tall oil and tall oil head were supplied by Arizona Chemical Company, the distilled tall oil having the product designation D296R and the tall oils heads having the product designation 2122. The oleic acid employed was a technical grade oleic acid supplied by Matheson, Coleman and Bell.

REAGENT PREPARATION PROCEDURE

To prepare the reaction product for use in flotation tests there was in each instance added to a stirred reaction vessel first 105 grams of the selected fatty acid and then 20 grams of the N,N-dimethyl-1,3-propane diamine. On mixing, there was an initial temperature increase of about 30°C . A condensation reaction was carried out over a period of about 6 hours during which time very little material distilled over as a condensate although the reaction temperatures reached were in excess of 200°C . The resultant end product was, in each instance, fluid on cooling to room temperature. The amine-acid reaction product was in each instance converted to its acetate salt for use as a flotation reagent.

REAGENT EVALUATION

To evaluate the prepared flotation reagents there was employed a standard Minerals Separation Gell. The objection was to determine the amount of Phosphorus (P) reported as P_2O_5 which could be extracted from phosphate rock as a function of the acid insolubles (SiO_2) remaining in the P_2O_5 . In each experiment there was employed a phosphate rock containing about 25 percent entrained free water. The rock was added to the cell with water to form a slurry of 20 percent solids density. A pH of the system in each instance was about 7.4. In each instance there was added with agitation the

candidate flotation reagent in an amount equivalent to 0.5 lb. per ton of rock and kerosene in an amount of 0.96 lb. per ton of rock. The reagent and kerosene were added with agitation to the slurry and air allowed to enter the cell. The froth which formed was collected in a basin over a period of about 1 minute. The solids in the float or tails and concentrate (P_2O_5) were filtered, dried and weighed. Both fractions were analyzed for P_2O_5 and acid insolubles (SiO_2). The results are shown in Table II.

Table II

Reagent Acid	P. as P_2O_5	Wt.%	Acid Insol.	(SiO_2) Wt.%
	Conc.	Tail	Conc.	Tail
Reconstituted Tall Oil	31.51	1.57	2.59	93.96
Distilled Tall Oil	32.24	1.39	4.2	93.7
Tall Oil Heads	32.18	1.34	6.44	94.25
Oleic Acid	33.2	1.66	4.10	94.96

Table III shows that using the reconstituted tall oil-N,N-dimethyl-1,3-propane diamine reaction product as the base the relative percent increase in the amount of acid insolubles (SiO_2) remaining with the P_2O_5 concentrate.

Table III

Reagent Acid	% Acid Insol. (SiO_2) in P_2O_5	% Increase
Reconstituted Tall Oil	7.8	—
Distilled Tall Oil	11.5	37.0
Tall Oil Heads	16.7	89.0
Oleic Acid	11.0	32.0

EXAMPLE 17

The amine reagent prepared in Example 2 was used as a beneficiation reagent for the cleaner float of a Florida phosphate rock containing 10 percent insolubles in a concentration of 0.3 lb. per ton of phosphate rock. Kerosene was present as a frother. The results of the froth flotation separation are shown in Table IV:

Table IV

Wt.%	Bone Phosphate of Lime Assay(% P_2O_5)		Distr.(%)	Insol. Assay, %
Concentrate	84.5	72.8	97.6	4.3
Tails	15.5	9.7	2.4	—
Head (Total)	100.0	63.0	100.0	—

EXAMPLE 18

The procedure of Example 17 was repeated except the amine was used at a concentration of 0.45 lb. per ton of ore process. The results are shown in Table V.

Table V

Wt.%	BPL		Insol. Assay%
	Assay(% P_2O_5)	Distr.(%)	
Concentrate	84.1	73.7	97.3
Tails	15.9	9.0	2.3
Heads	100.0	63.1	99.6

EXAMPLE 19

The amine reagent prepared in Example 9 was used in place of amine prepared in Example 2. Florida phosphate rock was treated using amine in the concentration of 0.45 lb. per ton of phosphate rock with kerosene as a frother. Results of this beneficiation separation are shown in Table VI:

Table VI

	Wt. %	BPL		Insol. Assay
		Assay	Distr.	
Concentrate	84.7	73.9	97.6	3.7
Tails	15.3	10.0	2.4	—
Heads	100.0	64.1	100.0	—

EXAMPLE 20

The amine prepared in Example 1 was used to treat a rougher phosphate rock containing about 10 percent insolubles in a concentration of 0.5 lb. per ton. The results are shown in Table VII:

Table VII

	BPL, Wt. %	Insol. Wt. %	Yield, BPL
Concentrate	69.2	2.6	98%
Tails	3.5	93.96	—

EXAMPLE 21 - 22

The amine prepared in Example 2 was used for the beneficiation of phosphate at a high slurry density (22% - 23%) and compared to a commercial amine (Control A) which was a reaction product of a tall oil acid and diethylene triamine. As shown in Table VIII, below, on a relative, comparative basis, phosphate loss in the tails was lower and insoluble retention by the float was also low.

Table VIII

	Example		Control A
	20	21	
Amine, lbs./ton	0.5	0.71	0.71
Kerosens, lbs./ton	0.96	0.96	0.96
Fraction, P ₂ O ₅ %			
Concentrate	29.35	31.48	31.87
Tails	2.83	1.98	2.43
Acid. Insol. Wt. %			
Concentrate	5.64	8.03	8.44
Tails	94.88	94.23	92.76

EXAMPLE 23

The performance of the amine of Example 2 was compared to the performance of an amine obtained by the condensation of tall oil acid with diethylene triamine at an acid to amine group ratio of approximately 1. The results are shown in Table IX wherein the amount

of siliceous insolubles in the concentrate was reduced by 50 percent:

Table IX

	Example 22	Control B
Kerosene, lbs./ton	1.2	1.2
Fraction, P ₂ O ₅ %		
Concentrate	32.65	31.58
Tails	2.27	1.92
Acid Insol., Wt. %		
Concentrate	3.54	6.70
Tails	91.04	92.99

What is claimed is:

1. The reaction product obtained by condensing a monofunctional diamine selected from the group consisting of N,N-dialkyl alkylene diamines and N,N-dialkyl-N'-alkyl alkylene diamines wherein each alkyl and alkylene group of said monofunctional diamine contains from 1 to about 4 carbon atoms, with about 0.9 to about 3.7 mols of a reconstituted tall oil per mole of said monofunctional diamine at a condensation temperature of from about 130°C to about 260°C for a period of time from about 2 to about 6 hours, said reconstituted tall oil containing from about 72 to about 77 percent fatty acids, from about 11 to about 16 percent rosin acids, from about 10 to about 13 percent unsaponifiables and having an acid number ranging from about 150 to about 165.

2. The salt obtained by contacting the reaction product obtained by condensing a monofunctional diamine selected from the group consisting of N,N-dialkyl alkylene diamines and N,N-dialkyl-N'-alkyl alkylene diamines wherein each alkyl and alkylene group of said monofunctional amine contains from about one to about four carbon atoms, with about 0.9 to about 3.7 mols of reconstituted tall oil, containing from about 72 to about 77 percent fatty acids, from about 11 to about 16 percent rosin acids, from about 10 to about 13 percent unsaponifiables and having an acid number ranging from about 150 to about 165, per mole of monofunctional diamine at a condensation temperature of from about 2 to 6 hours, with an acid selected from the group consisting of formic acid, acetic acid, propionic acid, hydrochloric acid and hydrofluoric acid.

3. The reaction product as claimed in claim 1 in which the monofunctional amine is N,N-dimethyl-1,3 propane diamine.

4. The salt obtained in claim 2 in which the monofunctional amine is N,N-dimethyl-1,3 propane diamine.

5. The reaction product as claimed in claim 1 in which the reconstituted tall oil is present in an amount from about 1.0 to about 2.0 mols per mol of primary and secondary amine groups in the reactive amine system.

6. The reaction product as claimed in claim 2 in which the reconstituted tall oil is present in an amount from about 1.0 to about 2.0 mols per mol of primary and secondary amine groups in the reactive amine system.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,817,972 Dated June 18, 1974

Inventor(s) Edward A. Grannen

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 61, after "16" insert therefor -- % --.

Column 8, Table IX reads as:

Table IX

	Example 22	Control B
Kerosene, lbs./ton	1.2	1.2
Fraction, P ₂ O ₅		
Concentrate	32.65	31.58
Tails	2.27	1.92
Acid Insol., Wt. %		
Concentrate	3.54	6.70
Tails	91.04	92.99

Table IX should read as follows:

PO-1050
(5/69)UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTIONPatent No. 3,817,972 Dated June 18, 1974Inventor(s) Edward A. Grannen

It is certified that error appears in the above-identified patent
and that said Letters Patent are hereby corrected as shown below:

Table IX

	Example 22	Control B
Amine lbs./ton	1.0	0.71
Kerosene, lbs./ton	1.2	1.2
Fraction, P ₂ O ₅		
Concentrate	32.65	31.58
Tails	2.27	1.92
Acid Insol., Wt. %		
Concentrate	3.54	6.70
Tails	91.04	92.99

Signed and sealed this 29th day of October 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents