

UNITED STATES PATENT OFFICE

2,373,688

FLOTATION OF ORES

Walter E. Keck, Hancock, Mich., assignor to
Sherwood Refining Company, Inc., Englewood,
N. J., a corporation of New Jersey

No Drawing. Application May 16, 1942,
Serial No. 443,282

14 Claims. (Cl. 209—166)

This invention relates to the froth flotation of ores and has particular reference to novel flotation agents and to processes for treating non-metallic mineral ores to more economically recover value-bearing minerals therefrom.

The non-metallic mineral ores have a tendency to slime badly and for that reason are difficult to float with the known types of flotation agents. The presence of slimes in the ore pulp often renders it impractical to use such materials as oleic acid, for the reason that oleic acid is a strong floating agent and a collector for nearly all slime minerals so that a dirty, tough and tenacious froth is formed which cannot be readily broken. Slimes are present in substantially all ore pulps and the amount of slimes is materially increased by the conventional methods of preparing ore for flotation.

Another difficulty which is encountered in the commercial flotation of non-metallic ores is the lack of flotation agents which permit an economical recovery of the valuable portion of the ore. Inasmuch as the finished products of such non-metallic ores are usually low priced, it is necessary to use inexpensive flotation agents in order to make recovery of the valuable portion of the ore economically feasible.

Thus, flotation of non-metallic mineral ores, from a practical standpoint, is complicated by the necessity of finding suitable, cheap flotation agents, which may be used in relatively small quantities and which are not affected by the presence of slimes.

An object of the present invention is to provide methods and flotation agents which have the necessary characteristics for the economical flotation of such ores.

Another object of the invention is to provide novel flotation agents which function effectively in the presence of slimes.

An additional object of the invention is to provide flotation agents which are selective in separating valuable non-metallic components of an ore from valueless non-metallic components.

Other objects of the invention will become apparent from a disclosure of typical flotation agents and processes embodying the present invention.

In its most general aspects, the invention involves the flotation of non-metallic mineral ores

with mahogany sulfonates and oil-soluble sulfonic acids derived from petroleum, either alone or in combination with other types of flotation agents.

5 The term "mahogany sulfonates," as used herein, refers to those crude, partially refined or completely refined sulfonates derived from petroleum stock which are oil-soluble, substantially insoluble in water, but dispersible in water. The refined mahogany sulfonates which are preferably
10 used in flotation operations are characterized by a wine color. These mahogany sulfonates form dispersions similar to colloidal gels when used with water in a concentration of about 12%, and
15 readily disperse upon agitation in hot water. Upon dilution of the dispersion, the viscosity decreases until the dispersion becomes very fluid. The mahogany sulfonates preferably are dispersed in hot water and then boiled for about ten
20 minutes. The dispersion, at any desired temperature, is added to the flotation system. The active principles of the mahogany sulfonates appear to be the sodium sulfonates or sulfonic acid groups.

25 The term "petroleum sulfonic acids" as used herein also refers to the oil-soluble, water-dispersible and substantially water-insoluble sulfonic acids obtained from the oil layer resulting from the sulphonation of petroleum fractions.

30 Mahogany sulfonates and petroleum sulfonic acids exert a strong collecting action not only on metallic minerals, but also on non-metallic minerals. It has been found that the collecting action of the mahogany sulfonates or petroleum sulfonic acids is materially enhanced by the presence of hydrocarbons such as, for example, fuel oil, which
35 apparently forms an additional coating on the surface of the already coated particle, and thus renders it more readily floatable. Fuel oil controls the quality of froth and prevents the inclusion of unwanted minerals in the froth inasmuch
40 as fuel oil is, in itself, an excellent collector. Many of the advantages of the mahogany sulfonates and the oil-soluble petroleum sulfonic acids arise from the fact that they are excellent emulsifiers
45 for fuel oil which is one of the most powerful and cheapest collectors known, but heretofore little used because of lack of a satisfactory emulsifier.

50 It has been found that mahogany sulfonates or petroleum sulfonic acids alone or in combination

with other classes of reagents, such as frothers, for example, pine oil, cresylic acid, conditioners, such as lime and soda ash, depressors, such as sodium silicate, strong acids, for example, nitric, sulfuric, hydrochloric, hydrofluoric and phosphoric acid, metallic salts, such as calcium chloride, ferrous or ferric sulfates, and aluminum sulfate, under proper conditions, improve flotation.

In addition to the characteristics noted above, mahogany sulfonates and the oil-soluble petroleum sulfonic acids are not strong frothers in the concentrations and under the conditions used, and may be used in flotation operations without being adversely affected by the presence of slimes. They, also, often act as froth conditioners inasmuch as they have a beneficial effect on the froth produced by other reagents.

The mahogany sulfonates and petroleum sulfonic acids form most economical flotation agents for the reason that they are by-products of petroleum refining operations and are available in quantity at relatively small cost under normal economic conditions.

In accordance with the present invention, mahogany sulfonates and oil-soluble petroleum sulfonic acids have been successfully used in the flotation of a great many of the non-metallic minerals such as, for example, epidote, gypsum, barite, fluorspar, calcite, limestone for the manufacture of Portland cement, and phosphate rock.

In the treatment of some of these ores, it has been determined that by proper control of conditions during flotation, the valuable portion of the ore may be floated or depressed as may be desired, therefore indicating the versatility of mahogany sulfonates in flotation operations.

Illustrative of the treatment of various types of non-metallic mineral ores with mahogany sulfonates, the following examples are given.

EXAMPLE 1—FLOTATION OF EPIDOTE

The epidote for this experiment was obtained from a pilot table in a mill operated on Michigan native copper ore. This pilot table product, consisting largely of epidote was ground in a rod mill until all of it was -65 mesh size. An aqueous mixture of the ground material containing about 35% solids was conditioned with 2 pounds of mahogany sulfonates for a period of five minutes. Thereafter, the conditioned pulp was diluted to about 23% solids and floated in a mechanical flotation machine for about five minutes. About 59% of the epidote was floated.

Other samples of the same material, treated under similar conditions, with the exception that sulphuric acid or metal salts were added to the pulp were conditioned for about one minute and further conditioned after the addition of 2 pounds of mahogany sulfonates. The results of these tests are shown in the following table:

Table A

Addition or activating reagent	Per cent epidote floated
0.42 pound CaCl_2	77.0
0.50 pound H_2SO_4	92.0
0.50 pound $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	88.0
0.50 pound $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	96.0

EXAMPLE 2—FLOTATION OF GYPSUM

The flotative properties of gypsum are of interest both from the standpoints of its beneficiation

for industrial use and of its elimination from iron ores where its sulphur content is extremely detrimental to the desired properties of iron and steel prepared from these same iron ores. As an example, in the Menominee range of Michigan there are large tonnages of otherwise useful ores which cannot be mined and smelted because of their excessively large sulphur content.

The gypsum material for this experiment was obtained from a gypsum producing property in Michigan. It was composed mainly of white gypsum with smaller quantities of dark colored minerals. The material was ground to -65 mesh size in a rod mill and was conditioned with 0.80 pound of mahogany sulfonates at about 35% solids content for five minutes. 0.1 pound of pine oil was added, the pulp was diluted to about 23% solids concentration and the pulp floated in a mechanical flotation machine for five minutes. Under these conditions the gypsum floated readily and 67% of the feed to flotation was collected in the froth.

When 1.5 pounds of fuel oil were added with the mahogany sulfonates, the quantity of material floated was reduced to about 23% of the weight of the feed. This floated material contained nearly all of the dark colored minerals, whereas the tailing was composed of white gypsum.

EXAMPLE 3—FLOTATION OF BARITE

The material for this experiment was composed almost entirely of barite. This material was crushed to pass 10 mesh and then was ground to a fineness such that nearly all of it passed through a 65 mesh screen. An aqueous pulp of the ground material was conditioned with 0.8 pound of mahogany sulfonate at a concentration of about 35% solids for five minutes and 0.1 pound pine oil was added. The pulp was diluted to about 23% solids and floated in a mechanical flotation machine for five minutes. Under these conditions, the barite floated readily, about 90% of the weight of the feed to flotation being collected in the froth.

EXAMPLE 4—FLOTATION OF FLUORSPAR

The fluorspar ore for this experiment was taken from the feed to a fluorspar milling operation in Illinois. This ore contained, in addition to fluorspar, considerable amounts of quartz, calcite and other gangue minerals.

The ore was crushed to -10 mesh and then ground in a rod mill to a fineness such that 48% of the ore passed through a 200 mesh screen. A pulp containing about 35% of the ground ore was conditioned with 2 pounds of mahogany sulfonates and 2 pounds of fuel oil for five minutes. 0.1 pound of pine oil was added to the pulp and the pulp was diluted to about 23% solids. The diluted pulp was floated in a mechanical flotation machine for four minutes. The fluorspar floated well under these conditions and considerable separation of this mineral from calcite was made. The froth or concentrate contained 4.4% calcite, whereas the tailing contained 9.9% of the same mineral. Likewise a good separation of fluorspar from quartz was obtained, as shown by the fact that the froth or concentrate contained 2.5% silica and the tailing contained 14% silica.

EXAMPLE 5—FLOTATION OF CALCITE

Calcite from an unknown source was crushed to -10 mesh and thereafter ground until it all passed through a 65 mesh screen. The ground

ore at about 35% solids concentration was conditioned with 0.40 pound of mahogany sulfonate for five minutes. 0.1 pound of pine oil was added to the conditioned pulp, the pulp diluted to about 23% solids and the pulp was floated in a mechanical flotation machine for five minutes. About 69% of the feed to flotation was collected in the froth.

Under the same conditions, except that one pound of mahogany sulfonates was added with 4 pounds of fuel oil, 95% of the feed to flotation was collected in the froth.

EXAMPLE 6—FLOTATION OF LIMESTONE

A limestone used in the manufacture of Portland cement was used for this experiment. The limestone was taken from the feed to a commercial flotation apparatus and contained, in addition to calcium carbonate, quartz and mica as well as other gangue materials.

The limestone was crushed to -10 mesh and then ground in a laboratory mill until 77% of the ore passed through a 200 mesh screen. A pulp of this ore containing 35% solids was conditioned with 2 pounds of mahogany sulfonates and 2 pounds of fuel oil for five minutes. The conditioned pulp was then diluted to about 23% solids concentration and floated in a flotation machine for eight minutes. With this flotation procedure the froth or concentrate contained 76% of lime in the flotation feed and the grade of this concentrate in respect to lime was 42%. The tailing contained 24% of the lime in the feed and the grade of the tailing was 26.7% lime.

When the limestone was crushed, ground and the reagents were added in small increments and flotation was accomplished after each addition of the reagents, a very high recovery of the calcium carbonate was made. The results of these tests are disclosed in the following table:

Table B

Per cent solids in pulp	Lb. mahog. sulf.	Lb. fuel oil	Lb. cresylic acid	Operation	Time, min.	Product	Per cent CaO in product	CaO distrib.
23-----	0.38			Condit-----	1			
		0.13		do-----	3			
	0.30	0.10	0.01	Flotat-----	2	1 conc-----	44.9	15.0
	0.23	0.08	0.01	do-----	2	2 conc-----	48.4	32.6
	0.23	0.08	0.01	do-----	2	3 conc-----	48.7	37.5
				do-----	2	4 conc-----	37.4	11.9
				do-----	2	Tail-----	7.5	3.0
								100.0

EXAMPLE 7—FLOTATION OF PHOSPHATE ROCK

The phosphate rock for this experiment was obtained from Florida. The phosphate rock in the form of a pulp containing about 60% solids was conditioned with 4 pounds of mahogany sulfonates for two minutes and then diluted to about 48% solids. Two pounds of sulphuric acid were added to the pulp and the pulp further conditioned for one-half minute. The pulp was diluted to 23% solids and floated in a mechanical flotation machine until flotation ceased. With this procedure, 55% of the phosphorus in the feed was obtained in the froth or concentrate. The grade of this concentrate with respect to phosphorus was 13.3%. The tailing from this operation carried 45% of the phosphorus in the feed and the grade of the tailing was 4.5% phosphorus.

When other acids were substituted for sulphuric acid and 0.1 pound of pine oil was added before flotation, the comparative results shown in the following table were obtained:

Table C

Quantity and kind of acid	Product	Per cent phos.	Phos. distrib.
1.5 lb. H ₃ PO ₄ -----	(Conc-----	16.0	58.1
	(Tail-----	4.8	41.9
			100.0
3.4 lb. HNO ₃ -----	(Conc-----	13.7	73.6
	(Tail-----	3.5	26.4
			100.0
3.8 lb. HCl-----	(Conc-----	13.2	78.9
	(Tail-----	2.8	21.1
			100.0
1.6 lb. HF-----	(Conc-----	15.4	51.8
	(Tail-----	4.7	48.2
			100.0
2.0 lb. H ₂ SO ₄ -----	(Conc-----	13.0	68.1
	(Tail-----	3.5	31.9
			100.0

It appears that the most desirable results were obtained through the use of hydrochloric acid, but satisfactory results were obtained in substantially all instances with the various acids indicated.

EXAMPLE 8—FLOTATION OF PHOSPHATE ROCK

In another experiment, the phosphate rock was conditioned with 3 pounds of fuel oil at a concentration of about 60% solids for fifteen seconds and then 4 pounds of mahogany sulfonates were added to the pulp and conditioning continued for an additional two minutes. The pulp was diluted to about 23% solids, 2 pounds of sulphuric acid were added and the pulp was floated for seven minutes. With this method of flotation, 82.4% of the phosphorus content of the feed was collected in the froth or concentrate and this concentrate had a grade of 12.7 in respect to phosphorus. The tailing from this flotation operation contained 17.6% of phosphorus in the feed and its grade was 2.2% phosphorus.

EXAMPLE 9—FLOTATION OF PHOSPHATE ROCK

In another test, the phosphate rock was ground in a mill charged with pebbles. The phosphate rock was separated into - and +325 mesh sizes. The +325 mesh phosphate rock was made into a pulp containing about 55% solids and was conditioned with 2 pounds of mahogany sulfonates for one minute. Two pounds of sulphuric acid were added to and mixed with the conditioned pulp. Thereafter the pulp was diluted to about 30% solids and floated in a mechanical flotation machine until flotation ceased. The results of these tests are recorded in the following table:

Table D

Product	Wt. distrib.	Per cent phos.	Phos. distrib.
-325 slimes-----	19.2	12.2	33.3
+325 conc-----	39.5	11.6	65.1
+325 tail-----	41.3	.3	1.6
	100.0		100.0

In the above tests with phosphate rock, the phosphate-bearing material was floated. This procedure is logical if the phosphate-bearing material or phosphate rock is relatively fine and the gangue minerals are relatively coarse. It has been found, however, that when the phosphate rock is relatively coarse, its flotation is handicapped and some of the coarser particles of phosphate rock remain in the tailing. If these coarse particles are floated under strong flotative conditions, much of the finer gangue may also be floated into the concentrate. With materials of this type, the better procedure is to float the gangue and depress the phosphate rock.

The following experiment discloses how this procedure can be carried out with mahogany sulfonates.

EXAMPLE 10

The phosphate rock obtained from Florida was formed into a pulp containing about 60% solids and conditioned with 1½ pounds of mahogany sulfonates for one minute. Aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$, in the amount of 0.8 pound was added to the conditioned pulp and the pulp was further conditioned for one minute. The pulp was diluted to about 38% solids, 0.2 pound of pine oil was added and the pulp floated in a flotation machine until flotation ceased.

With this procedure, the froth contained 41.8% of the phosphorus in the feed and the grade of this material was 4.9% phosphorus. The tailing from this same procedure contained 58.2% of the phosphorus in the feed and the grade of this material was 11.1% phosphorus.

Additional experiments involving the use of metal salts such as ferrous sulfate, ferric sulfate, copper sulfate and manganous sulfate indicated that these salts tend also to activate and float quartz in preference to phosphate rock.

The above examples of the flotation of non-metallic minerals show quite clearly that mahogany sulfonates are highly effective in the flotation of non-metallic minerals of widely varying type. Inasmuch as the mahogany sulfonates are inexpensive by-products, their use is commercially feasible in the flotation of these relatively low cost types of non-metallic mineral ores. Moreover, as shown in Example 6, the action of the mahogany sulfonates in the presence of slimes is not adversely affected inasmuch as all sizes of particles were floated together, a procedure not followed commercially. The usual procedure is to separate the coarse limestone from the slimes before the coarse particles are floated. Therefore, the mahogany sulfonates appear to fulfill all the requirements for flotation operations on these types of materials.

It will be understood that the proportions of flotation agents are susceptible to considerable variation in the treatment of the non-metallic mineral ores and, therefore, the proportions disclosed in the examples given above should be considered as illustrative of satisfactory concentrations and not as limiting the scope of the following claims.

I claim:

1. A froth flotation process comprising agitating and aerating an aqueous suspension of a non-metallic mineral ore in the presence of at least one of the group of flotation agents consisting of oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonates and oil-soluble, water-dispersible and substantially water-insoluble petroleum sulfonic acids to

coat and float a portion of said ore and form a tailing, and separating the tailing from the floated portion of the ore.

2. A froth flotation process comprising agitating and aerating an aqueous suspension of phosphate rock in the presence of a strong mineral acid and at least one of the group of flotation agents consisting of oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonates and oil-soluble, water-dispersible and substantially water-insoluble petroleum sulfonic acids to coat and float a portion of said ore and form a tailing, and separating the tailing from the floated portion of the ore.

3. A froth flotation process comprising agitating and aerating an aqueous suspension of limestone in the presence of at least one of the group of flotation agents consisting of oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonates and oil-soluble, water-dispersible and substantially water-insoluble petroleum sulfonic acids to coat and float a portion of said ore and form a tailing, and separating the tailing from the floated portion of the ore.

4. A froth flotation process comprising agitating and aerating an aqueous suspension of barite in the presence of at least one of the group of flotation agents consisting of oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonates and oil-soluble, water-dispersible and substantially water-insoluble petroleum sulfonic acids to coat and float a portion of said ore and form a tailing, and separating the tailing from the floated portion of the ore.

5. A froth flotation process comprising agitating and aerating an aqueous suspension of a non-metallic mineral ore in the presence of a frother of the class consisting of pine oil and cresylic acid, and at least one of the group of flotation agents consisting of oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonates and oil-soluble, water-dispersible and substantially water-insoluble petroleum sulfonic acids to coat and float a portion of said ore and form a tailing, and separating the tailing from the floated portion of the ore.

6. A froth flotation process comprising agitating and aerating an aqueous suspension of a non-metallic mineral ore in the presence of a strong acid and at least one of the group of flotation agents consisting of oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonates and oil-soluble, water-dispersible and substantially water-insoluble petroleum sulfonic acids to coat and float a portion of said ore and form a tailing, and separating the tailing from the floated portion of the ore.

7. A froth flotation process comprising agitating and aerating an aqueous suspension of a non-metallic mineral ore in the presence of a metal salt and at least one of the group of flotation agents consisting of oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonates and oil-soluble, water-dispersible and substantially water-insoluble petroleum sulfonic acids to coat and float a portion of said ore and form a tailing, and separating the tailing from the floated portion of the ore.

8. A froth flotation process comprising agitating and aerating an aqueous suspension of a non-metallic mineral ore in the presence of fuel oil and at least one of the group of flotation agents consisting of oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfo-

nates and oil-soluble, water-dispersible and substantially water-insoluble petroleum sulfonic acids to coat and float a portion of said ore and form a tailing, and separating the tailing from the floated portion of the ore.

9. A froth flotation process comprising agitating and aerating an aqueous suspension of phosphate rock in the presence of a strong acid and oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonates to concentrate the most valuable portion of the phosphate rock in the froth.

10. A froth flotation process comprising agitating and aerating an aqueous suspension of phosphate rock and containing coarse gangue in the presence of a strong acid and an oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonate to float a concentrate containing the most valuable portion of said phosphate rock

11. A froth flotation process comprising agitating and aerating an aqueous suspension of coarsely disintegrated phosphate rock containing gangue in the presence of a metallic salt and an oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonate to float said gangue and depress said valuable portion of said phosphate rock to form a tailing.

12. A froth flotation process comprising agitating and aerating an aqueous suspension of ground limestone containing gangue in the presence of fuel oil and an oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonate to float said limestone and cause said gangue to settle as tailing.

13. A froth flotation process comprising agitating and aerating an aqueous suspension of a calcium bearing ore in the presence of at least one of the group of collectors consisting of oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonates and oil-soluble, water-dispersible and substantially water-insoluble petroleum sulfonic acids, to coat and float a portion of said ore and form a tailing, and separating the tailing from the floated portion of the ore.

14. A froth flotation process comprising agitating and aerating an aqueous suspension of phosphate rock in the presence of fuel oil, a strong acid and oil-soluble, water-dispersible and substantially water-insoluble mahogany sulfonates to concentrate the most valuable portion of the phosphate rock in the froth.

WALTER E. KECK.