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2,442,455

CONCENTRATION OF NONMICACEOUS,
WATER-INSOLUBLE ALKALINE-EARTH
METAL SALT MINERALS

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This invention relates to the beneficiation of the mineral values of various ores. More particularly, the invention relates to an improved process of beneficiating ores containing salts of the alkaline earth metals.

Many of the common minerals occur as compounds which chemically may be considered salts of the alkaline earth metals. In concentrating these minerals or in the beneficiation of ores containing them, the alkaline earth metal compounds may constitute the desirable portions and in other cases constitute the gangue. In some cases the alkaline earth metal is the desired valuable constituent and in other cases the negative radical constitutes the important product.

In our copending application, now U. S. Letters Patent 2,410,770, an excellent procedure for beneficiating fluorite, a mineral of this type, has been shown. It now has been found that similar teachings are adaptable to other minerals. Typical members of the group of minerals with which the present invention are concerned are calcite, barite, pebble-phosphate, gypsum, celestite, magnesite, dolomite, scheelite, and the like. These minerals, so far as concentration by flotation is concerned, have one characteristic in common, other than being salts of alkaline earth metals. They react in general in the same way when subjected to flotation in the presence of anionic collectors of the fatty acid type, such as are commonly used in beneficiating non-metallic, non-sulfide minerals. This type of reagent includes material such as the fatty acids per se, talloel, naphthenic acids, resin acids, mixtures of these and also soaps thereof.

So far as the response of minerals in general to collecting agents of the anionic type is concerned, an exception should be noted. Some of the alkaline earth metal silicates, such as talc, are satisfactorily responsive to anionic type collectors. Most of the others, such as the micas, generally require reagents of the cationic type to obtain a satisfactory beneficiation. With this latter group, which require the use of cationic type reagents, the present invention is not concerned. Actually most of these materials are alkali rather than alkaline earth salts. The process is concerned only with those alkaline earth salts which are normally responsive to an anionic reagent, such as are commonly used in the flotation of non-metallics.

Many of these alkaline earth salts are commercially of great importance despite the fact that they occur in nature in deposits which are not as high-grade as is ordinarily desirable for

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commercial utility. Therefore, beneficiation of some type is very widely practiced on these ores. In general, a number of analogous problems are presented.

First, the ores in most cases are those of minerals such as calcite and pebble-phosphate, which must be handled in large quantities at the minimum expense. Unfortunately, most of the available low-cost anionic collectors are not as effective for the purpose as may be desired. Many of the reagents require the use of excessive quantities to obtain the desired result, the economic benefits being offset by the reagent consumption. Others are not sufficiently selective, so that when used in suitable amounts they do not produce a concentrate which is of sufficiently high-grade.

Secondly, many of these minerals occur in ores containing gangue which produces large quantities of slimes, or the valuable minerals may be sufficiently soft so as to produce considerable slimes during their preparation for flotation. Unfortunately, the ordinary anionic collectors such as the fatty acids, talloel, naphthenic acids and the like, or their sodium, potassium, and ammonium soaps have a certain tendency to become less effective in the presence of excessive slimes. Consequently, some corrective steps, either by addition of auxiliary reagents or by desliming the ore, must be taken. In many instances these latter, to be effective, require sufficient expenditure to offset any utility the process may otherwise possess.

There is, therefore, a demand for a suitable process of beneficiating minerals of the previously-described type which is of general utility, uses cheap and readily available reagents, does not require excessive reagent consumption and is not excessively sensitive to the presence of slimes. It is the principal object of the present invention to develop such a process, making use of a novel type of reagent which secures for the new process these desired advantages.

In general, the desired objects of the present invention are accomplished by carrying out a beneficiating operation dependent on surface conditions on the ore to separate the mineral values from the gangue while making use of a promoter comprising sulfonated petroleum hydrocarbons of the green acid type obtained in the refining of lubricating oils, or salts or soaps of such acids. Preferably, also the sulfonate is used in combination with an auxiliary reagent having a high degree of oiliness. The most common of such operations is froth flotation. How-

ever, other procedures dependent on surface phenomena such as agglomerate tabling, belt tabling, and the like, may be used to take advantage of the highly desirable properties of the reagents of the present invention.

Sulfonated petroleum hydrocarbons, such as those which constitute the principal reagent in carrying out the novel process of the present invention, are commercially available in a number of different forms. However, as shown, for example, in U. S. Patent 2,331,049, their principal source is as by-products from the refining of lubricating oil fractions in the course of treatment with fuming sulfuric acids or sulfuric acids. When so produced, these by-products are generally found to be salts of the sulfonated hydrocarbons. Most commonly, the metallic radical of the salt is sodium. However, salts of other metals such as the ammonium salts or salts of the alkaline earth metals, aluminum and the like, are encountered. In some cases, no attempt has been made to neutralize the acid product or only partially to neutralize the acid product.

So far as the present invention is concerned, it makes little difference whether the sulfonated petroleum hydrocarbon is used per se or as a salt; whether or not the sulfur is present in a sulfate or a sulfonate group, there usually being some of both present; or whether the compounds are used in acidic form, that is without neutralization or in partially neutralized form or as the ammonium salts or the salts of sodium, potassium, calcium, barium, aluminum, and the like. Nor need the materials be purified, since mixtures of these compounds produce wholly satisfactory results. As used in the present case, the term "sulfonated petroleum hydrocarbons" is, therefore, intended to include such mixtures as are found in the commercial products.

However, the commercially-available sulfonated petroleum hydrocarbons may be divided on a functional basis into two distinct groups. One of these is the group variously known as "mahogany" acids, "mahogany" soaps and the like. This group is characterized in that its constituents are generally oil-soluble but may be water-dispersible. Usually, but not necessarily, these compounds have a deep mahogany color which gives rise to the generic designation as "mahogany" compounds.

The other group is generally, but not necessarily, characterized by a green coloration. Hence, compounds of this group are usually referred to as "green" acids or "green" soaps. More important than the color distinction, however, is the fact that the so-called "green" compounds are characterized by being water-soluble. Despite their other similarities the two groups of compounds are by no means necessarily equivalents each to the other. Particularly is this true as in the present invention, when they are applied to ore dressing problems. The instant application is primarily concerned with the use of the water-soluble petroleum sulfonates, i. e., the green sulfuric acids and salts or soaps thereof, which require considerably different treatment than those of the mahogany or oil-soluble type.

In general, the process of the present invention comprises the steps of reducing the ore, if necessary, to a size suitable for feed to a froth flotation operation; desliming the ore, if necessary; making a pulp of the ore with water; adding the reagents thereto; subjecting the pulped ore to froth flotation and finally collecting the froth

concentrate in the usual manner. In many cases the flotation concentrate will contain the valuable constituents. In others, the flotation may be conducted to remove certain minerals from a valuable product which is retained as the flotation tailing.

Where it is desirable to use a desliming operation, it has been found well in some cases to carry out this operation in the presence of soda ash, sodium silicate, or some equivalent alkaline material or other dispersing agent to assist in freeing the slimes. If a modifier for the gangue is to be used in the subsequent operations, it may be well in some cases to add a small amount of the modifier during desliming. Where a modifier for the gangue minerals is to be used in carrying out the process of the present invention, quebracho was found to give excellent results. Other modifiers such as dextrin, particularly yellow corn dextrin, sodium and calcium lignin sulfonates and the alkali phosphates and polyphosphates may be used with highly satisfactory results.

It was also found desirable in certain cases to condition the ore-pulp with the flotation reagents prior to the actual flotation step. Pulp densities of about 60-65% solids were found to give excellent results and to be ordinarily preferable. However, if so desired, lower pulp densities even down to densities such as those commonly used in flotation operations per se may be used. The invention is not necessarily limited to any particular mode of admixture, and the reagents may be added directly to the flotation cell if so desired, and still obtain acceptable results.

The green type of petroleum sulfonates and/or their derivatives which are used in the present process are characterized, as noted above, by their solubility in water. While this solubility is not always complete, it is sufficiently high so that when used alone the reagent may not always produce the optimum concentration of certain minerals. These green compounds appear to lack certain water-repellant properties which are helpful in making successful concentration.

In the process of the present invention, this difficulty is readily overcome by the addition of an amount of a more hydrophobic material. This may be done by adding an oil in suitable quantity or by mixing a portion of oil-soluble petroleum sulfonates with the water-soluble type. Any of the commercially available oils of animal, vegetable or mineral origin may be used for this purpose. Unsulfonated petroleum derivatives such as crude oil, kerosene or fuel oil are very suitable. Saponifiable oils, such as coconut oil, cotton seed oil and other glyceride oils may be used. Anionic materials such as the fatty acids and the like may be used in certain cases. Talloel, in view of its low cost, is especially useful in such operations.

The use of fatty acids with a water-soluble petroleum sulfonate provides a very flexible reagent combination. It is suitable for the treatment of a wide variety of ores and minerals since it enables a wide control of the froth characteristics. For example, in certain flotation operations it is often desirable to use a strong promoter such as a fatty acid. Such a promoter is needed on many difficultly-floatable ores, yet it cannot be used because under the operating conditions a heavy, sticky froth is produced. The froth characteristics tend to entrap gangue particles, and, therefore, the concentrate obtained is too low in grade.

Such a difficulty is generally readily overcome by using the reagent compounds of the present invention. Even relatively small amounts of the water-soluble petroleum sulfonate may serve to modify the texture and volume of the froth. Such modification often so increases the selectivity of the operation that the same or increased amounts of the mineral value is collected as when the fatty acid is used alone. Yet, the rejection of the gangue particles is such as to produce a marked improvement in grade.

Similarly, the flotation reagent compounds of the present invention may be used to marked advantage under other conditions. For example, the concentration of scheelite by froth flotation ordinarily requires the use of highly alkaline dispersing agents. Their use often has a marked effect on the characteristics of the froth obtainable when using an anionic promoter of the fatty acid type such as oleic acid or talloel. On the other hand, the use of such reagents in conjunction with a water-soluble petroleum sulfonate enables the operator to control the froth characteristics so as to obtain the optimum benefit.

Amounts of the hydrophobic materials used will obviously vary with the particular circumstances. The most pronounced variations in demand are caused by the nature of the ore and the particular water-soluble petroleum sulfonates being used. No general rule can, therefore, be empirically established for all cases. In general, however, the amounts required have been found to fall within the range of about 0.1-2.5 pounds/ton of ore treated. Ordinarily, however, the amounts used will be between about 0.5 and 1.5 pounds/ton. Variations in the temperature at which the flotation is carried out have also been found to have an effect on the amount of these hydrophobic materials required.

Similarly, the nature of the ore, the pulp density, the type of water used, the amount of slimes present, the source of the water-soluble petroleum sulfonates have all been found to have a direct bearing on the amount of petroleum sulfonate required to bring about an effective concentration. Therefore, as in the case of the hydrophobic materials, no fixed rule applicable to all instances can be laid down as to the amount of collecting agent required. In general, however, it has been found that amounts of water-soluble petroleum hydrocarbons ranging from about 0.1 to 5.0 pounds/ton will take care of all but the most extraordinary cases. With the ores most commonly encountered, this range can be substantially halved, since most of the ores can be readily beneficiated using an amount of reagent in the range from about 0.2 to 3.0 pounds/ton.

The water-soluble petroleum sulfonates are frequently available as water solutions as well as in paste or dry forms. Frequently these products contain oil, sodium sulfate, caustic and other impurities. While it is unnecessary to remove these impurities before using the sulfonates in flotation, the amount of reagent used in any particular operation will depend frequently on the dilution and the amount of impurities present.

As has been shown, the water-soluble petroleum sulfonates have generally proved to be satisfactory when used as the principal promoter. However, as also has been shown, certain external circumstances may require that the actual froth flotation operation be carried out in the presence of other substances such as

oleic acid, talloel and the like, which are themselves well known anionic-type reagents. This condition may be brought about by the nature of the flow scheme employed, the presence of these additional agents being due to other operations which are being carried out in the same plant. For example, these reagents are frequently carried along in reusing process water. It has been found that the water-soluble petroleum sulfonates are perfectly effective in the presence of these extraneous reagents. In fact, as has been noted above, under some circumstances these agents may be added deliberately as corrective measures in certain parts of the flotation operation. Similarly, the presence of small amounts of the water-soluble petroleum sulfonates has been frequently found to increase the effectiveness of these additional reagents in their intended applications.

The invention will be more fully illustrated in combination with the following examples which are meant by way of illustration and not by way of limitation. All parts are by weight unless otherwise noted. Where tons are referred to, short tons are intended. In the following examples, the terms "reagents A, B, C, and D" have been used to designate water-soluble sulfonated petroleum hydrocarbons of the "green acid" type obtained in the refining of petroleum lubricating oil fractions. The principal distinction between these reagents is in the source of their origin.

EXAMPLE 1

A South-American gold-copper-barite ore was subjected to a froth flotation to remove a sulfide concentrate, using soda ash, sodium silicate, secondary butyl xanthate, and pine oil as reagents. The tailings from this flotation operation contained approximately 44% barium sulfate. These were conditioned without desliming with 1.0 pound/ton of reagent A and 1.0 pound/ton of fuel oil and then floated in a Fagergren flotation machine. The resulting concentrate was cleaned once without additional reagents. The concentrate assayed 95.6% barium sulfate and contained 86.6% of the barite in the feed. The water-soluble petroleum sulfonate used in this test was obtained from the manufacturer in the form of a dry solid.

EXAMPLE 2

A sample of Pennsylvania cement rock containing chiefly calcite, quartz, and mica was ground and conditioned for 30 seconds at about 22% solids with 0.5 pound/ton of reagent A and 1.0 pound/ton of fuel oil, followed by two additional conditioning flotation stages—each of which used 0.5 pound/ton of water-soluble petroleum sulfonate and 1.0 pound/ton fuel oil. The resultant concentrates were combined and cleaned. From a feed to flotation assaying about 72.9% CaCO_3 , a cleaned concentrate was obtained assaying 93.4% CaCO_3 , representing a recovery of 88.7% of the carbonate in the feed.

EXAMPLE 3

A sample of Pennsylvania cement rock containing calcite, quartz, mica, and carbonaceous material and assaying about 75.5% CaCO_3 was ground to 80% minus 325 mesh. Samples of this ground mixture were conditioned with 1.5 pound/ton of crude calcium lignin sulfonate in a Fagergren flotation machine. The reagents were varied. The metallurgical results and reagents are shown in the following table.

Table I

Reagents Used	Concentrate		
	Per Cent Weight	Per Cent CaCO ₃	
		Assay	Distribution
1.3 pounds/ton of 1:3:3 Reagent B, coconut oil and talloel.....	69.19	91.66	83.18
1.3 pounds/ton of 1:1:1 Reagent B, coconut oil and talloel.....	61.09	92.73	74.14
1.3 pounds/ton talloel.....	57.34	89.51	67.26
0.8 pound/ton saponified talloel.....	90.00	poor selectivity	

EXAMPLE 5

A number of samples of Florida pebble-phosphate ore assaying about 29.5% B. P. L. were deslimed, conditioned at high solids (60-65%) with various water-soluble petroleum sulfonates, and various oiling agents. After dilution to flotation density (20-22% solids), the pulp was subjected to flotation in a Fagergren machine and the concentrates given a single cleaning. In the fourth test the ore was deslimed, scrubbed and again deslimed; in other tests only a normal desliming by hydraulic classification was applied. The results are shown in the following table.

Table II

Sulfonate		Oiling Agent		Concentrate			B. P. L. Distribution	
Type	lb./ton	Type	lb./ton	B. P. L.		Insol. Assay	Middling	Tailing
				Assay	Distrib.			
				Per cent	Per cent	Per cent	Per cent	Per cent
A.....	2.0	Fuel Oil, No. 2.....	4.0	78.24	86.50	3.47	6.69	6.81
C.....	2.0	do.....	4.0	77.33	80.62	3.81	9.31	10.07
B.....	2.0	Coconut Oil.....	3.0	78.60	85.50	3.69	4.78	9.72
B.....	2.0	do.....	2.0	78.60	84.68		6.03	9.29
D.....	0.5	do.....	4.0	78.24	84.57	3.94	4.57	10.86
B.....	2.0	Talloel.....	0.5	78.96	78.95		10.45	10.60
B.....	2.0	do.....	1.0	74.96	90.58		3.38	6.04
B.....	1.0	do.....	1.0	77.33	84.42		6.26	9.32
B.....	2.0	Fuel Oil, No. 2.....	1.0	78.25	87.05	3.85	7.04	5.91
B.....	2.0	Talloel.....	1.0					
B.....	1.0	Fuel Oil, No. 2.....	1.0					
B.....	1.0	Talloel.....	1.0	77.69	87.78	4.23	5.10	7.12

From the foregoing results it will be apparent that the reagents used in the present invention gave superior results to those obtainable in similar tests using ordinary reagents such as talloel and saponified talloel.

EXAMPLE 4

A Texas ore containing celestite, dolomite and feldspars and having a SrSO₄-content of about 78% was crushed to minus 200 mesh, conditioned at 22% solids with 5 pounds/ton sodium silicate, 1 pound/ton of reagent A and 2 pounds/ton of fuel oil. On treatment by froth flotation in a Fagergren machine, a rougher concentrate was obtained which, after a single cleaning, gave a concentrate containing about 71% of the celestite in a 95.24% SrSO₄ grade.

It will be noted in the above tests that the ordinary procedure followed in treating Florida pebble phosphate in which caustic soda is used in the conditioning operation was not followed.

EXAMPLE 6

Samples of the Florida phosphate rock, described in Example 5 were deslimed and conditioned at high solids with reagent A and various auxiliary agents. The conditioned pulp was then floated and the resulting concentrate cleaned by refloating. The results of these tests are presented in the following table. 2.0 pounds/ton of the petroleum sulfonates was used in all tests except those using talloel and oleic acid and 1.0 pound/ton of the petroleum sulfonates was employed in these tests.

Table III

Auxiliary Agent		Cleaner Concentrate			B. P. L. Dist.	
Type	lb./ton	B. P. L.		Insol.	Cl. Tail.	Rgh. Tail.
		Assay	Dist.			
		Per cent	Per cent	Per cent	Per cent	Per cent
Bunker C Oil.....	3.0	75.69	94.57		1.46	3.97
Cottonseed Oil.....	3.0	77.69	86.21	3.52	5.77	8.02
Chlorinated Kerosene.....	4.0	77.33	90.22	4.13	3.60	6.18
Talloel-Methyl Ester.....	2.0	76.96	83.37		8.00	8.63
Fish Oil.....	2.0	76.78	89.80	5.03	4.40	5.80
Talloel.....	1.0	73.51	93.81		1.85	4.34
Naphthenic Acids.....	1.0	74.41	86.24		3.95	13.41
Naphthenic Acids.....	1.0					
Fuel Oil, No. 2.....	1.0	76.06	81.47	5.12	9.12	9.41
Oleic Acid.....	1.0	76.60	85.98	4.98	5.61	8.41

EXAMPLE 7

In order to show low sensitivity to slimes of the process of the present invention, samples of a Florida phosphate rock (about 30% B. P. L.), which in ordinary operation requires a high degree of desliming, were subjected to froth flotation using the ordinary reagent combination of talloel and fuel oil and also using a reduced amount of talloel which was replaced with reagent B. Only a very mild desliming was carried out. No caustic soda was used, the rougher concentrate was given a final cleaning. Illustrative results and the reagents used are shown in the following table.

Table IV

Pounds per Ton			Per Cent B. P. L.		Per Cent Insol. Assay	Per Cent B. P. L. Distrib.	
Reagent B	Fuel Oil No. 2	Talloel	Assay	Distrib.		Middling	Tailing
2.0	1.0	1.0	77.87	78.98	3.73	9.05	11.97
None	1.0	1.0	No flotation—0.24% weight recovery				
None	1.0	3.0	No useful flotation				

EXAMPLE 8

In certain cases caustic soda may be used to advantage in phosphate treatment as indicated in the following tests. A sample of Florida phosphate rock was deslimed hydraulically, conditioned with reagents at high solids, and floated in a Fagergren flotation machine. The flotation concentrate was cleaned twice. The feed to flotation assayed about 36.5% B. P. L. The results of several flotation tests follow. In all tests 2.4 pounds/ton of a neutralized water-soluble petroleum sulfonate from Sun Oil Company, 0.99 pound/ton talloel, and 5.0 pounds/ton 22° Bé. fuel oil were used and the caustic soda varied in amount as indicated.

Table V

lb./ton NaOH	Concentrate			B. P. L. Distribution	
	B. P. L.		Insol. Assay	Middling	Tailing
	Assay	Distribution			
None	Per cent 75.63	Per cent 82.80	Per cent 4.36	Per cent 2.11	Per cent 15.09
0.12	75.63	90.13	4.49	5.27	4.60
0.36	75.12	91.59	5.00	4.55	3.86
0.60	75.97	85.89	3.78	9.23	4.88

It will be noted that good results were obtained without the use of caustic. However, improvement was obtained when caustic was employed.

EXAMPLE 9

An Illinois fluorite ore, containing chiefly fluorite (about 72% CaF_2) and limestone (about 18.5% CaCO_3) were ground to minus 65 mesh, and deslimed using a 2 pounds/ton of soda ash and 0.1 pound/ton of quebracho. The deslimed pulp was then made up to 22% solids and conditioned for 1 minute with about 0.1 pound/ton of quebracho and varying amounts of green acids. In different tests the pulp was treated at different temperatures. The conditioned pulp was subjected to froth flotation in a Fagergren flotation machine. The concentrate was cleaned once using 0.25 pound/ton of quebracho. It was found that acceptable results could be obtained using green acids in amounts varying from 0.5–2.0 pounds/ton over a temperature range of from 32–100° F. At the lower temperatures it was

found that slightly more reagent was required, that the recovery was slightly less but that the concentrate in general was of higher grade and contained less objectionable non-metallic gangue. Illustrative results are shown in Table VI.

Table VI

Temperature °F.....	86	32
Pound/ton, Green Acids.....	1.00	1.50
Pound/ton, Fuel Oil.....	1.00	1.50
Cleaner Conc., per cent CaF_2 Assay.....	93.58	94.76
Cleaner Conc., per cent CaCO_3 Assay.....	4.84	3.96
Cleaner Conc., per cent CaF_2 Distribution.....	71.33	68.65
Cleaner Tailing, per cent CaF_2 Assay.....	67.58	73.24
Rough Tailing, per cent CaF_2 Assay.....	14.60	42.00

EXAMPLE 10

A table concentrate containing mainly scheelite, pyrite, and garnet were ground in the presence of 2.0 pounds/ton of soda ash, treated with 1.0 pound/ton sodium silicate, and deslimed. A sulfide concentrate was removed using 0.10 pound/ton sodium secondary butyl xanthate and 0.11 pound/ton of pine oil. The resulting tailings were conditioned with 1.0 pound/ton sodium silicate, 4.0 pounds/ton of a petroleum green acids and 1.0 pound/ton of fuel oil and a tungsten concentrate removed. This concentrate was cleaned once; 1.0 pound/ton of sodium silicate was added to the cleaning operation. 92.48% of the tungsten was thus recovered in the cleaner concentrate. The grade of this concentrate was 75.65% WO_3 .

EXAMPLE 11

A New York talc ore was ground, diluted to flotation density without desliming, conditioned with 6.0 pounds/ton of a water-soluble petroleum sulfonate, containing about 30% sulfonates. The sulfonate was added as an emulsion with 3.0 pounds/ton of fuel oil, a small amount of sulfuric acid being used as an emulsion stabilizer. The pulp was conditioned with the sulfonate-fuel oil combination for 1 minute and floated for 2 minutes in a Fagergren flotation machine. The resulting concentrate was cleaned twice, each cleaning operation being preceded by a 1-minute conditioning with 1.0 pound/ton sodium silicate. From a feed to flotation containing about 71% talc, a concentrate containing 96% talc and representing a recovery of 62% was obtained.

EXAMPLE 12

A 1:1 mixture of magnesite and quartz, ground to minus 100 mesh, was deslimed and conditioned with 4.0 pounds/ton of a water-soluble petroleum sulfonate containing about 43% water. The sulfonate was fed as a 2:1 emulsion with fuel oil, stabilized by the use of 1 part sulfuric acid. The conditioned pulp was floated to produce a magnesite concentrate which was cleaned once. 95.3% of the magnesite was thus recovered in the concentrate which assayed only 3.54% insoluble.

The preceding examples have been limited to froth flotation. As pointed out, however, the

process is by no means so limited. This will be more fully illustrated in the following example.

EXAMPLE 13

Samples of minus 8 mesh Florida phosphate ore, assaying about 55.9% B. P. L., were deslimed, conditioned with petroleum sulfonates and auxiliary agents and tumbled on a laboratory Wilfley table. In the first test the ore was conditioned with 4.6 pounds/ton of a water-soluble petroleum sulfonate and 13.9 pounds/ton of fuel oil. In the second test the procedure was the same except that 0.6 pound/ton of caustic soda was used with the sulfonate-oil combination. In the first test 90.3% of the B. P. L. was recovered in a concentrate assaying 70.0% B. P. L. In the second test 91.2% of the B. P. L. was recovered in a concentrate assaying 71.2% B. P. L.

We claim:

1. In separating ores containing a plurality of constituents by modifying surface conditions on at least one of the constituents with an agent having a selective affinity therefor, the improvement in beneficiating ores of a mineral selected from the group consisting of barite, calcite, celestite, dolomite, phosphate rock, gypsum, magnesite, scheelite and talc which comprises the steps of forming a pulp of the ore with water, treating the ore with an effective amount of a material selected from the group consisting of the water-soluble, sulfonated petroleum hydrocarbons of the green acid type obtained in the refining of lubricating oils, and soaps and water-soluble salts of such acids and subjecting the treated pulp to conditions under which the selectively-effected constituents are separated from the non-effected constituents.

2. A process according to claim 1 in which the action of the water-soluble, sulfonated petroleum hydrocarbon is enhanced by the conjoint use of a hydrophobic agent used in amounts sufficient to increase the lipophilic properties of the ore-promoter complex.

3. A process according to claim 1 in which the water-soluble, sulfonated petroleum hydrocarbon is used in amounts ranging from about 0.1 to about 5.0 pounds per ton of ore.

4. A process according to claim 1 in which the water-soluble, sulfonated petroleum hydrocarbon is used in amounts ranging from about 0.1 to 5.0 pounds per ton of ore and its efficiency is enhanced by the conjoint use of from about 0.1 to 3.0 pounds per ton of a hydrophobic agent.

5. In beneficiating ores of a mineral selected from the group consisting of barite, calcite, celestite, dolomite, phosphate rock, gypsum, magnesite, scheelite and talc by froth flotation, the steps

which comprise forming a pulp of the ore with water, treating the ore with an effective amount of a material selected from the group consisting of the water-soluble, sulfonated petroleum hydrocarbons of the green acid type obtained in the refining of lubricating oils, and soaps and water-soluble salts of such acids, and subjecting the treated pulp to conditions under which the selectively-effected constituents are floated away from the non-effected constituents.

6. In beneficiating ores of a mineral selected from the group consisting of barite, calcite, celestite, dolomite, phosphate rock, gypsum, magnesite, scheelite and talc by froth flotation, the steps which comprise forming a pulp of the ore with water, treating the ore with 0.1-5.0 pounds per ton of ore of a material selected from the group consisting of the water-soluble, sulfonated petroleum hydrocarbons of the green acid type obtained in the refining of lubricating oils, and soaps and water-soluble salts of such acids, and subjecting the treated pulp to conditions under which the selectively-effected constituents are floated away from the non-effected constituents.

7. A process according to claim 6 in which the efficacy of the water-soluble petroleum sulfonate is enhanced by the conjoint use of from about 0.1-3.0 pounds per ton of a hydrophobic material.

8. A process according to claim 6 in which the efficacy of the water-soluble petroleum sulfonate is enhanced by the conjoint use of from about 0.1-3.0 pounds per ton of a hydrophobic material selected from the group consisting of the animal, vegetable and mineral oils, fatty acids, talloel, water-insoluble sulfonated derivatives thereof, and the sodium, potassium and ammonium soaps of such oils, fatty acids and sulfonated derivatives thereof.

ROBERT BEN BOOTH.

JOSEPH EMMETT CARPENTER.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,170,665	Nutter	Feb. 8, 1916
1,996,035	Singleton	Mar. 26, 1935
2,105,827	Tartaron	Jan. 18, 1938
2,116,727	Lenher	May 10, 1938
2,163,701	Ried	June 27, 1939
2,216,992	Vogel-Jorgensen	Oct. 8, 1940
2,299,893	Greene	Oct. 27, 1942
2,303,931	Greene	Dec. 1, 1942
2,305,032	Reaol	Dec. 15, 1942
2,310,240	Keck	Feb. 9, 1943