PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Processes of Concentrating Non-metallic Minerals from Ores containing Silicious Matter

We, PHOSPHATE RECOVERY CORPORATION, a Corporation organized under the Laws of the State of Delaware, United States of America, of 61, Broadway, City and State of New York, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to an improved process of concentrating non-silicon-bearing non-metallic minerals from ores containing them in association with silicious matter, the term " non-silicon-bearing non-metallic " being used herein to refer to those minerals which contain alkaline earth metals only. Among these minerals are included calcite, barite, fluorspar, and phosphate rock, the invention being herein described in connection with the examples given as applied to all four of these minerals.

In Specification No. 410,956 is described and claimed the use in flotation processes of certain high-molecular-weight quaternary amine salts, e.g., lauryl pyridinium sulphate. Such salts are stated to yield positively charged surface active ions in aqueous solutions and to be useful as collectors or foamers, as well as combined collector - foamers. Concerning the minerals to which their use may be applied, the flotation of coal and the clarifying of mineral sludges are specifically mentioned, an example being given dealing with the flotation of quartz.

In Specification No. 463,261 is described and claimed a flotation process of concentration employing various salts of the type yielding a positively charged surface active ion in aqueous solutions. Included in the various salts mentioned for use are those of high-molecular-weight quaternary amines with halogen acids, e.g., cetyl pyridinium bromide. In this instance the various salts disclosed are stated to be particularly useful in the flotation of acidic non-sulphide minerals, among which are mentioned various silicon-bearing minerals, e.g., the feldspars, the pyroxenes, the micas, and quartz.

The process of the present invention obviously effects a concentration of the silicious minerals present as gangue in the ores to which it appertains, but this is merely incidental to the desired concentration of the non-silicon-bearing non-metallic mineral values contained in such ores.

In accordance with the invention, this concentration is effected by the use of amine compounds of the class consisting of free amines containing a water-repellent hydrocarbon group, and the salts of said amines with acids substantially soluble in water, the water-repellent hydrocarbon group of such compounds being aliphatic except in the case of resin-amine compounds produced as free amines by condensation of an aldehyde with an aromatic amine, such as toluidine, in the presence of a reactive substance capable of yielding the water-repellent hydrocarbon group, or as amine salts by further reaction with an acid substantially soluble in water, in which case of resin amine compounds the water-repellent hydrocarbon group may be either aliphatic or aromatic. To the treated ore in the form of an aqueous pulp is added the proper proportion of a compound of this class as a collector for certain of its components. Thereafter, the ~~pulp~~ pulp is treated for separation of a material relatively rich in said components and relatively poor in the others, this separation being capable of being carried out in any manner known in the art.

Many advantages have been found to result from the use of the above-mentioned class of amine compounds in the process of the present invention, all of which advantages will become apparent hereinafter.

The process of the present invention is one according to which concentration is effected either by a selective separating action ~~of~~ upon the desired constituents of the ore or by a selective separating action upon the ~~desired~~ undesired constituents. In flotation, certain minerals are concentrated as a result of their being floated away from the silicious gangue, while in other cases

it is the silicious gangue which is caused to float, the non-floated material in the latter cases constituting the concentrate because of its retention therein of the greater proportion of the desired minerals. And in tabling, certain minerals are concentrated as a result of their being ejected at the side of the table, while in other cases it is the silicious gangue which is caused to be discharged at the side, the material delivered at the end of the table in the latter cases constituting the concentrate because of its retention therein of the greater proportion of the desired minerals.

Depending on the ore treated, the collectors of the present invention thus effect their collecting action either on the desired components or on the undesired components of the ore, it being possible in the case of ores containing more than one non-silicon-bearing non-metallic mineral in addition to the silicious matter to concentrate one of such minerals from another. According to the invention, silica may be floated away or otherwise separated from either phosphate rock or calcite. Either barite or fluorspar may be floated away or otherwise separated from silica, although it has been found possible in the case of certain ores to float away or otherwise separate silica from barite. For some ores fluorspar may be floated or otherwise separated from both silica and calcite, while for others both fluorspar and silica may be floated or otherwise separated from calcite.

Extensive researches on compounds that are collectors in effecting ore concentration have led to the establishment of the fact that two distinct portions entirely opposite to one another in characteristics are contained in such compounds which cause them to achieve collection. Fundamentally, these portions are as follows: (1) a water-avid chemically-active polar portion; and (2) a water-repellent chemically-inactive non-polar portion. That the two portions are both essential to make a compound a collector is true whether the compound is to exercise its collecting properties with reference to the mineral values or with reference to the gangue constituents. The function of the first-mentioned portion is to cause adherence of the compound to those particles of the ore on which collection is to take place, while that of the second-mentioned portion is to cause adherence of the compound with its attached ore particles to the air at the air-water interfaces. It is the polar portion which determines the preferential affinity of the compound for either the mineral values of the gangue constituents.

We have made the important discovery that extremely effective collectors for the desired or undesired constituents of non-silicon-bearing non-metallic mineral ores containing silicious matter are certain compounds of the type containing an amine radical as their effective polar portion and a water-repellent hydrocarbon group as their effective non-polar portion. More specifically stated, the basis of the invention is the discovery that amine radicals, when properly combined with certain water-repellent hydrocarbon groups, result in compounds which, when employed in the proper amount, have a high degree of selective separating action, upon one part or another of such ores, the separating action in any case effecting the desired concentration.

As a general rule, aromatic hydrocarbon groups are incapable of use as the effective non-polar portion of the collectors of the present invention. An exception to this rule, however, is a particular species of compounds to be hereinafter described, which is the only species included in such collectors which seems to permit effecting the requirement of water-repellency by the use of aromatic hydrocarbon nuclei. On the other hand, the effective non-polar portion of the collectors of the present invention can always be formed by an aliphatic radical, provided it is of such carbon content as to be characterized by water-repellency. As we have found, this radical should be a straight hydrocarbon chain of six or more carbon atoms, but preferably one of at least eight carbon atoms.

The collectors of the present invention may exist either in the form of free amines, i.e. amines unneutralized by acids, or in the form of amine salts, i.e., amines neutralized by acids. However, only those amine salts produced from acids characterized by substantial solubility in water can be used in the process of the present invention, such acids comprising sulphuric acid, hydrochloric acid, acetic acid, etc. In general, such salts are more stable than the corresponding amines.

The amines and amine salts capable of use in the process of the present invention are compounds in which the amine radical may be in direct or indirect chemical union with the hydrocarbon group required. Moreover, the amine radical may be a primary, secondary, tertiary, or quaternary amine radical, so that several useful hydrocarbon groups may be chemically combined therewith. In fact, several amine radicals may be present, each of such radicals being directly or indirectly attached to at least one useful hydrocarbon group.

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As a general rule, aromatic hydrocarbon groups are incapable of use as the effective non-polar portion of the collectors of the present invention. An exception to this rule, however, is a particular species of compounds to be hereinafter described, which is the only species included in such collectors which seems to permit effecting the requirement of water-repellency by the use of aromatic hydrocarbon nuclei. On the other hand, the effective non-polar portion of the collectors of the present invention can always be formed by an aliphatic radical, provided it is of such carbon content as to be characterized by water-repellency. As we have found, this radical should be a straight hydrocarbon chain of six or more carbon atoms, but preferably one of at least eight carbon atoms.

The collectors of the present invention may exist either in the form of free amines, i.e. amines unneutralized by acids, or in the form of amine salts, i.e., amines neutralized by acids. However, only those amine salts produced from acids characterized by substantial solubility in water can be used in the process of the present invention, such acids comprising sulphuric acid, hydrochloric acid, acetic acid, etc. In general, such salts are more stable than the corresponding amines.

The amines and amine salts capable of use in the process of the present invention are compounds in which the amine radical may be in direct or indirect chemical union with the hydrocarbon group required. Moreover, the amine radical may be a primary, secondary, tertiary, or quaternary amine radical, so that several useful hydrocarbon groups may be chemically combined therewith. In fact, several amine radicals may be present, each of such radicals being directly or indirectly attached to at least one useful hydrocarbon group.

The primary mono-amines included in the compounds above stated may be expressed by the general formula $R.NH_2$, while the salts of such amines may be expressed by the general formula $(R.NH_2.H)_nX$. In each of these formulæ the symbol R represents a group consisting of or containing the water-repellent hydrocarbon group, while the symbol X and multiplier n in the amine salt formula respectively appertain to the anion of an acid substantially soluble in water and to a whole number equal to the valence of the acid anion X.

From the foregoing description it is apparent that the process of the present invention may be successfully carried out with many species of amine compounds. Satisfactory results have thus not only been obtained with simple amines and amine salts in which an amine radical is directly attached to a water-repellent aliphatic hydrocarbon radical, but also with complex condensation products and their salts in which an amine radical is connected to a water-repellent aliphatic hydrocarbon radical through an esterified or otherwise altered carboxyl group.

The simple amine compounds characterized by direct attachment of amine and hydrocarbon radicals may be prepared in accordance with known chemical reactions. Their preparation therefore requires no description herein, it being understood that they should be caused to contain an alkyl or alkylene radical of the proper number of carbon atoms, as hereinbefore defined.

In the case of the compounds having amine and hydrocarbon radicals connected through an altered carboxyl group, a preferred method of preparation consists in condensing an organic acid having a straight hydrocarbon chain of the hereinbefore defined carbon content with an aminoalcohol. As another closely related method, however, an alcohol having a straight hydrocarbon chain of the hereinbefore defined carbon content is condensed with an aminoacid. In either of the ensuing reactions, the carboxyl group, a polar group commonly employed in collectors for non-silicon-bearing non-metallic minerals, is esterified or otherwise altered with the result that its properties adapting it as a polar group with reference to such minerals are destroyed. That is, the carboxyl group by reason of its alteration does not in any way interfere with the function of the amine radical, which is the effective polar portion of the complex compounds produced and becomes connected to the water-repellent straight-chain hydrocarbon radical through the altered carboxyl group. It is to be particularly noted, however, that amine soaps are conjointly produced by either of the two reactions yielding these compounds. These soaps have known collecting properties for non-silicon-bearing non-metallic minerals, because of which they should be removed from the reaction product where used to effect its collecting action upon silicious gangue.

It is understood that the condensation products ~~obtainable~~ obtained by either of the two methods above stated are free amines capable of being used as such or in a state of combination with acids hereinbefore defined.

The process of the present invention has also been successfully carried out with resin-amine compounds produced as free amines by condensation of an aldehyde with an aromatic amine such as toluidine in the presence of a reactive substance capable of yielding the water-repellent hydrocarbon group required, or as amine salts by further reaction with an acid substantially soluble in water. The free amines obtained in this manner are nothing more than synthetic resins of the well-known amine-aldehyde type, which accounts for the use of the term "resin-amine compounds" in referring to these amines and their salts. For this particular species of compounds, as we have found, their effective non-polar portion, constituted by the hydrocarbon group peculiar to the reactive substance employed with the aldehyde and aromatic reagents, may not only be an aliphatic hydrocarbon radical characterized by water-repellency; but, it may also consist of any one of various cyclic hydrocarbon groups. Satisfactory results have thus been obtained with resin-amine compounds containing as their effective non-polar portion such aromatic groups as naphthene and abietene nuclei. Resin-amine compounds containing the phenyl nucleus as their effective non-polar portion have also proved useful in the process of the present invention. It is not known, however, whether any cyclic hydrocarbon group can be used as the effective non-polar portion of the resin-amine compounds. Nor is it known ~~that~~ what criteria determine the water-repellency of such groups in such compounds.

Concerning the preparation of the resin-amine compounds, if they are to contain an aliphatic hydrocarbon radical as their effective non-polar portion, one of the starting substances required may be an unsaturated straight-chain hydrocarbon of the hereinbefore defined carbon content, or an ester of a fatty acid containing as a radical an unsaturated straight hydrocarbon chain of the hereinbefore defined

carbon content. One or more of such hydrocarbons or esters may be utilized, the use of fuel oil as a substance containing such hydrocarbons and of linseed oil as a substance containing such esters being thus possible. On the other hand, if the resin-amine compounds are to contain a cyclic hydrocarbon group as their effective non-polar portion, one of the starting substances may be a hydrocarbon of the class of naphthenes, abietenes, and analogous hydrocarbons; or a substance containing one or another of such hydrocarbons in the state of chemical combination, such as naphthenic acid and abietic acid. Still another substance which may be used is one containing the phenyl nucleus, such as benzaldehyde. Whether the effective non-polar portion of the resin-amine compounds is to consist of an aliphatic radical or of a cyclic group, their preparation involves the condensation of an aldehyde with an aromatic amine, such as a toluidine, the amine reagent being caused during this condensation to become joined to unsaturated carbon atoms of the substance employed to produce the water-repellent hydrocarbon group desired, with the amine radical free and capable of reaction. In the usual manner the condensation may be carried out in the presence of a mineral acid as a catalyst, in which case amine salts are produced.

The collectors of the present invention may contain aromatic groups in addition to the group constituting the effective non-polar portion. This is obviously true in the case of the resin-amine compounds. As another example, quaternary amine compounds may be employed having a water-repellent aliphatic hydrocarbon radical connected to the nitrogen atom contained in such nuclei as the pyridine ring.

It is also understood that the process of the present invention is not limited to the exclusive use of its amine compounds as agents. For example, a mineral oil may in certain cases be advantageously employed as a cooperating collector.

Some of the collectors of the present invention, particularly certain aliphatic amines and their salts, exhibit the peculiarity that they operate best when added to thin pulps and quickly distributed therein. Therefore, a material advantage provided by the invention resides in the fact that the usual preconditioning procedures of admixing into a thick pulp are made entirely unnecessary by these particular collectors. In froth flotation, for example, they may be added directly to the dilute pulp in the flotation machine, together with whatever additional agents it may be desired to employ, whereupon the float may be made immediately, without preliminary agitation. It is desired to have it understood, however, that practical results in all cases may be obtained by preconditioning the ore pulp in the usual manner. In practice, of course, simple experimental tests are necessary to determine the particular method of incorporating the reagents insuring best results in each individual case.

In so far as the actual step of concentration is concerned, the process of the present invention may be said to be identical in mechanical characteristics to the usual processes of concentration. Whether the desired constituents or the undesired constituents of the ore are floated, the collectors of the present invention give the same type of flotation froth, a thick mat float overflowing in a very short time.

The separating action as effected by the collectors of the present invention enables excellent results to be obtained. In general, concentrates of commercial grade are obtained in a single operation, no cleaning being required.

In those cases where the separating action takes place upon silicious gangue, it has been found that much improved concentration may be obtained by first producing a rough concentrate by a removal of silica, followed by a cleaning operation involving the usual separating action upon the mineral. For example, an appreciable portion of the silica may first be floated away from the valuable mineral, employing for this purpose an amine compound of the invention. Thereafter, the non-floated material, constituting a rough concentrate, may be subjected to a flotation operation by the use of such well-known agents as fatty acid soap and mineral oil, a finished concentrate being obtained by this operation. Such procedures are deemed to be an important feature of the invention, particularly in connection with phosphate ores. Fine sand is removed by the preliminary separation and the grade of feed employed in the subsequent separation is high, which factors represent increased efficiency of plant operation.

In preparing the ore for treatment by the process of the present invention, it is in general desirable that it be comminuted to a particle size most suitable for efficient operation and that it be largely deslimed, its desliming greatly minimizing the consuption of the reagents. Ordinarily, the crude ore is first subjected to a preliminary grinding operation and thereafter screened or classified to remove all particles other than those desired. The

undersize may then be deslimed, and the oversize reground, deslimed, and added to the deslimed undersize; or the oversize may be reground added to the undeslimed undersize, and the whole then deslimed.

The following examples describe certain tests which have been made in carrying the invention into effect, the reagent proportion in each being figured on the basis of the dry weight tonnage (2000 pounds) of the material treated.

EXAMPLE 1.

Deslimed phosphate feed to plant No. 4 of the Phosphate Recovery Corporation in Florida, consisting mainly of tricalcium phosphate, $Ca_3(PO_4)_2$ (phosphate rock), and silica, and of a particle size to pass 28-mesh was mixed with water in a laboratory-size Fagergren flotation machine, a thin pulp of about 20% solids being produced. To this pulp through the suction pipe was added 0.97 lb. per ton of a 10% kerosene solution of octadecylamine ($C_{18}H_{37}NH_2$), the added amount of octadecylamine being 0.09 lb. per ton. Incident to this addition, the machine was started and a froth produced, collection of the froth requiring about one minute.

It may here be noted that the Fagergren type of machine, because of its much higher running speed, visibly produces more violent agitation than the Minerals Separation subæration type, the former therefore effecting more rapid distribution of reagents than the latter.

The results obtained by the above procedures are indicated in the following table, it being observed that the larger portion of the phosphate values was obtained in the non-floated material:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	40.60		100.0
Floated	44.4	3.48		3.8
Non-floated	55.6	70.24	14.52	96.2

EXAMPLE 2.

The identical procedures of Example 1 were repeated on a sample of the same feed, but in this instance the solution of octadecylamine in kerosene was added to the machine in the increased proportion of 3.87 lbs. per ton, the proportion of octadecylamine being correspondingly increased to 0.35 lb. per ton. The tricalcium phosphate assay of the non-floated material was raised to 74.46%, but the tricalcium phosphate recovery lowered to 92.5%.

EXAMPLE 3.

Here the proportion of the solution of octadecylamine in kerosene was the same as in Example 2, but was added in conjunction with 0.14 lb. per ton of pine oil as a frother, all other conditions remaining the same. The non-floated material contained 77.17% tricalcium phosphate, the tricalcium phosphate recovered therein being 92.2%.

EXAMPLE 4.

For the purpose of this example a different phosphate feed was taken, namely, that to Florida plant No. 2 of the Phosphate Recovery Corporation, also largely consisting of tricalcium phosphate and silica and of a particle size to pass 28-mesh and largely deslimed, but of a lower grade in tricalcium phosphate, assaying on the average about 30% tricalcium phosphate. A sample of this feed was made into a dilute pulp in the Fagergren machine, and to it was added 0.7 lb. per ton of octadecylamine in solution with 7.04 lbs. per ton of kerosene, a simultaneous addition being made of 0.14 lb. per ton of pine oil. As in the preceding examples, frothing was carried out for about one minute, no preliminary agitation preceding the float. The tricalcium phosphate content of the non-floated material was 75.06%, the tricalcium phosphate recovered therein being 85.2%.

As a basis of comparison with Example 4, the following test was carried out:

COMPARATIVE TEST 1.

With a thick pulp of the same feed as in Example 4 were thoroughly admixed 1 lb. per ton of caustic soda, 1.99 lbs. per ton of fuel oil, 0.6 lb. per ton of fish acid, and 0.14 lb. per ton of a frothing agent consisting of three parts of crude rosin residue dissolved in one part of kerosene oil. The pulp was then diluted and frothed in a Minerals Separation flotation machine, the floated material being retreated in the same machine to separate a finished concentrate. This concentrate assayed 71.04% tricalcium phosphate, the tricalcium phosphate recovered therein being 79.4%.

EXAMPLE 5.

Here the collector was octadecylamine acetate, a compound having a comparatively high degree of solubility in water, as well as considerable frothing effect. To a thin pulp of the same feed as in

Example 4, formed in the Fagergren machine, was added 2 lbs. per ton of the said acetate, no other agent being employed. Immediately upon this addition the machine was started, the froth being removed over a period of about one minute. The non-floated material assayed 73.46% tricalcium phosphate, the tricalcium phosphate recovered therein being 91.4%.

EXAMPLE 6.

A sample of the same feed as in Example 1 was made into a thin pulp in the Fagergren machine, to which pulp was added 0.54 lb. per ton of kerosene and 0.1 lb. per ton of heptadecylamine ($C_{17}H_{35}NH_2$), the latter agent being used as a 5% solution in equal parts by volume of alcohol and benzene. Frothing was thereafter immediately carried out, the froth being collected over a period of approximately one minute. The results of this test were as follows:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	40.29		100.0
Floated	51.5	7.36		9.4
Non-floated	48.5	75.26	7.88	90.6

EXAMPLE 7.

A sample of the same feed as in Example 4 was made into a thin pulp in the Fagergren machine, to which pulp was added 0.24 lb. per ton of heptadecylamine in solution with slightly warmed kerosene, the added amount of this solvent being 0.96 lb. per ton. As before, frothing was carried out for about one minute, without preliminary agitation. The tricalcium phosphate content of the non-floated material was 70.03% and the tricalcium phosphate recovery therein 85.8%, the original feed analyzing 26.84% tricalcium phosphate.

As we have found, both heptadecylamine and octadecylamine are strongly affected by the material used as a solvent.

EXAMPLE 8.

The collector in this example was heptadecylamine sulphate ($(C_{17}H_{35}NH_2)_2H_2SO_4$), which was prepared by dissolving heptadecylamine in alcohol and neutralizing with dilute sulphuric acid, methyl orange being also added as an indicator. The precipitated sulphate was first thoroughly washed with distilled water and thereafter dissolved in a mixture of equal parts by volume of alcohol and benzene.

To a pulp of the same feed as in Example 1 was added 2.78 lbs. per ton of fuel oil and an amount of the above alcohol-benzene solution corresponding to 0.4 lb. per ton of the collector dissolved therein, the added amount of the alcohol being 3.03 lbs. per ton and that of the benzene 3.51 lbs. per ton. As before, the pulp was one of about 20% solids, but in this instance it was formed in a Minerals Separation flotation machine. Incident to the above addition, it was frothed in such machine, the silicious gangue being separated over a period of about one minute. The water which overflowed with the froth had a pH of 8.2.

The following table indicates the results of the test:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	48.08		100.0
Floated	33.8	7.64	88.84	5.4
Non-floated	66.2	68.73	15.74	94.6

EXAMPLE 9.

By doubling the proportion of the alcohol-benzene solution of Example 8 (i.e., by doubling the proportions of heptadecylamine sulphate and solvents), but otherwise following the identical procedures of that example, the following results were obtained, the overflow water in this instance having a pH of 8.0;

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	47.85		100.0
Floated	48.7	15.68	76.36	16.0
Nonfloated	51.3	78.38	4.43	84.0

Comparing Examples 8 and 9, it is seen that increasing the amount of heptadecylamine sulphate raises the tricalcium phosphate content of the non-floated material, but lowers the tricalcium phosphate recovery therein.

EXAMPLE 10.

A sample of the same deslimed phosphate feed as in Example 1 was made into a thin pulp in a Fagergren flotation machine, to which pulp was added 1.6 lbs. per ton of dodecylamine ($C_{12}H_{25}NH_2$), a liquid compound at normal temperatures, no other agent being used. Immediately after this addition, the machine was started, the froth being collected for about one minute. The following results were obtained:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	40.49		100.0
Floated	56.0	10.33		14.3
Non-floated	44.0	78.88	3.65	85.7

EXAMPLE 11.

With the added amount of dodecylamine of the preceding example employed in conjunction with 0.72 lb. per ton of concentrated sulphuric acid, an increased tricalcium phosphate recovery of 87.3% was obtained in the non-floated material, but the tricalcium phosphate assay of that material was decreased to 76.57%.

EXAMPLE 12.

A sample of the same feed as in Example 1 was formed with water into a thick pulp of about 70% solids. To this pulp were added, during agitation in an impeller-type mixer, 1.6 lbs. per ton of dodecylamine, agitation with this agent being continued for two minutes after its addition to the pulp. Thereafter, the pulp was transferred to a Fagergren flotation machine, where it was diluted and a float ~~conpected~~ collected in the usual manner. The results were as follows:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	40.00		100.0
Floated	57.3	16.88		24.1
Non-floated	42.7	71.04	12.72	75.9

EXAMPLE 13.

A 300 gram charge of deslimed minus 20-mesh phosphate ore was formed with water into a thick pulp, with which were thoroughly admixed 2 lbs. per ton of hexadecylamine hydrochloride ($C_{16}H_{33}NH_2$.HCl), added as a solution in about 10 cc. of alcohol. The pulp thus conditioned was transferred to a Minerals Separation machine, where it was diluted and frothed in the usual manner. The results were as follows:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate	% Recovery Insolubles
Feed	100.0	27.3	66.0	100.0	100.0
Floated	67.0	3.4	93.7	8.4	95.2
Non-floated	33.0	75.8	9.7	91.6	4.8

EXAMPLE 14.

Another charge of the same feed as in the preceding example was made up into a thick pulp with water, which pulp was conditioned with 1.33 lbs. per ton of laurylamine hydrochloride ($C_{12}H_{25}NH_2$.HCl), added as an alcohol solution. Subsequent treatment of the pulp in the flotation machine yielded the following results:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate	% Recovery Insolubles
Feed	100.0	28.1	65.1	100.0	100.0
Floated	67.4	8.4	87.8	20.3	90.9
Non-floated	32.6	68.6	16.2	79.7	9.1

EXAMPLE 15.

The conditions of this test were exactly the same as in Example 14, the only difference being that the laurylamine hydrochloride was used as a warm water solution. As shown by the following table, substantially the same results were obtained as in that example:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate	% Recovery Insolubles
Feed	100.0	29.0	63.9	100.0	100.0
Floated	66.9	6.7	87.4	20.0	91.6
Non-floated	33.1	70.2	16.4	80.0	8.4

EXAMPLE 16.

The collector used was decylamine hydrochloride ($C_{10}H_{21}NH_2.HCl$). A thick pulp of the same feed as in Example 13 was conditioned with 2 lbs. per ton of this collector, dissolved in alcohol. Subsequent treatment of the pulp in the flotation machine yielded the following results:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate	% Recovery Insolubles
Feed	100.0	29.1	64.0	100.0	100.0
Floated	54.9	1.6	96.3	3.1	82.6
Non-floated	45.1	62.6	24.6	96.9	17.4

In the following two examples greatly reduced quantities of amine chloride were permitted by their use in conjunction with fuel oil.

EXAMPLE 17.

With a thick pulp of the same feed as in Example 13 there was thoroughly admixed 6 lbs. per ton of fuel oil and 0.2 lb. per ton of hexadecylamine hydrochloride, the latter agent being added as a hot water solution. Subsequent treatment of the pulp in the flotation machine yielded the following results:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate	% Recovery Insolubles
Feed	100.0	29.6	62.8	100.0	100.0
Floated	63.1	8.9	86.6	18.9	87.0
Non-floated	36.9	65.0	22.1	81.1	13.0

EXAMPLE 18.

With a thick pulp of the same feed as in Example 13 there was thoroughly admixed 6 lbs. per ton of fuel oil and 0.66 lb. per ton of laurylamine hydrochloride, the latter agent being added as a warm water solution. Subsequent treatment of the pulp in the flotation machine yielded the following results:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate	% Recovery Insolubles
Feed	100.0	28.7	64.0	100.0	100.0
Floated	68.8	10.7	85.0	25.6	91.4
Non-floated	31.2	68.4	17.6	74.4	8.6

It is to be particularly noted that when such substances as fuel oil are mixed into a pulp of phosphate in the presence of the aliphatic amines or their salts, the oil is preferentially taken up by the silica. The phosphate particles do not absorb the oil unless an excess of both agents is used, in which case there is a tendency for both silica and phosphate to become oiled and flocculated. When fuel oil is used, a much smaller quantity of amine or amine salt is used than when such oil is absent.

The following example is intended to show the effect which may be produced, in floating silica away from phosphate, by the additional use of alkali:

EXAMPLE 19.

A thick pulp of the same feed as in Example 13 was conditioned with 2 lbs. per ton of caustic soda and 2 lbs. per ton of hexadecylamine hydrochloride, the latter agent being added as a solution in alcohol. Subsequent treatment of the pulp in the flotation machine yielded the following results, it being observed that the silica float was very clean, containing only 1.1% of phosphate:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate	% Recovery Insolubles
Feed	100.0	26.8	66.6	100.0	100.0
Floated	62.1	1.1	96.8	2.6	90.2
Non-floated	37.9	68.8	17.2	97.4	9.8

In each of the following three examples there was employed as a silica collector an amine compound having a non-polar group consisting of an unsaturated aliphatic hydrocarbon chain.

EXAMPLE 20.

A sample of the same deslimed phosphate feed as in Example 1 was made into a thin pulp in a Fagergren flotation machine, to which pulp was added 0.1 lb. per ton of nonadecyleneamine, dissolved in a small quantity of alcohol. Frothing was thereafter immediately carried out, the froth being collected over a period of approximately one minute. The tricalcium phosphate content of the non-floated material was 69.53% and the tricalcium phosphate recovery therein 92.4%.

EXAMPLE 21.

The same procedures as in Example 20 were repeated on a sample of the same feed, except that in this instance there was employed 0.3 lb. per ton of nonadecylamine sulphate, added as a 3.8% solution in equal parts by volume of alcohol and benzene. The non-floated material contained 69.73% tricalcium phosphate, the tricalcium phosphate recovery therein being 94.0%.

EXAMPLE 22.

The collector was octadecyleneamine ($C_{18}H_{35}NH_2$), the unsaturated analogue of octadecylamine and a liquid at normal temperatures. The procedures and feed were again the same as in Example 20, but here 0.18 lb. per ton of this collector was added to the pulp in the machine, no other agent being employed. The tricalcium phosphate content of the non-floated material was 67.23% and the tricalcium phosphate recovery therein 93.3%. By the following example the possible use in the process of condensation products having an amine radical connected to an aliphatic hydrocarbon radical through an altered carboxyl group is shown.

EXAMPLE 23.

One part by weight of commercial triethanolamine (a mixture composed in major part of triethanolamine and in part of secondary and primary amines) was refluxed with three parts by weight of U.S.P. oleic acid for eight hours. To remove any oleic acid combined as soap, the reaction product was thoroughly washed with absolute alcohol containing concentrated hydrochloric acid. The material thus obtained was a solution containing one or more amine compounds probably in the form of hydrochloric acid salt, and was used in the following test:

1000 grams, dry weight, of the same deslimed phosphate feed as in Example 4 was admixed with water into a pulp of about 70% solids. This pulp was agitated for three minutes in an impeller-type mixer with 3 cc. of the above solution. The pulp was then transferred to a Minerals Separation flotation machine, where it was diluted and a froth collected for about one minute.

The results of the test were as follows:

Product	% Weight	% Assay Tricalcium Phosphate	Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	23.76		100.0
Floated	67.3	1.71		4.8
Non-floated	32.7	69.13	13.17	95.2

The following six examples are illustrative of the use as collectors of resin-amine compounds, the first two having reference to compounds in which the effective non-polar portion is constituted by an aliphatic hydrocarbon radical, and the last four to compounds in which the effective non-polar portion is constituted by an aromatic hydrocarbon nucleus.

EXAMPLE 24.

To a mixture of 10.7 g. of ortho-toluidine and 8 g. of linseed oil was added a mixture of 10 g. of 40% formaldehyde and 4 cc. of 50% hydrochloric acid. A violent reaction took place, liberating heat. The material was cooled, liquid poured off, and the reaction product dried on a porous tile plate. This product (probably a mixture of resin-amine compounds) was dissolved in butanol, the resulting solution being used in the following test:

With a thick pulp of the same phosphate feed as in Example 1 was thoroughly admixed an amount of the butanol solution corresponding to 20 lbs. per ton of the material dissolved therein. The pulp was then diluted and a silica float separated.

The following results were obtained.

Product	% Weight	% Assay Tricalcium Phosphate	Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	41.90		100.0
Floated	50.5	8.12		9.8
Non-floated	49.5	76.37	6.23	90.2

EXAMPLE 25.

To 10.7 g. of orthotoluidine was added 5 g. of fuel oil and to the mixture was added 10 g. of 40% formaldehyde admixed with 4 cc. of concentrated hydrochloric acid. A reaction took place without heating. The reaction product, a black semi-solid, was dissolved in butanol.

This butanol solution was used in a flotation test identical in every respect to that of the preceding example, the same feed and the same quantity of collector being employed.

The results of this test were as follows:

Product	% Weight	% Assay Tricalcium Phosphate	% Recovery Tricalcium Phosphate
Feed	100.0	41.51	100.0
Floated	45.6	3.76	4.1
Non-floated	54.4	73.15	95.9

EXAMPLE 26.

To a mixture of 10.7 g. of ortho-toluidine and 7 g. of "impure" naphthenic acid was added 15 g. of 40% formaldehyde admixed with 4 cc. of concentrated hydrochloric acid. The material was heated for ten minutes and thereafter, while hot, dissolved in butanol in the proportion of 1 g. to 5 cc. of solvent, the resulting solution being used as follows:

A thick pulp of the same feed as in Example 1 was conditioned with 10.8 lbs. per ton of kerosene and an amount of the butanol solution corresponding to 20 lbs. per ton of the material dissolved therein. The pulp was then diluted and a silica float separated.

The following results were obtained:

Product	% Weight	% Assay Tricalcium Phosphate	Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	39.54		100.0
Floated	58.1	11.82		17.4
Non-floated	41.9	77.97	4.72	82.6

EXAMPLE 27.

To 10.7 g. of orthotoluidine was added 11 g. of an oil containing abietic acid and known as "Nelioresin" and to this mixture was added 15 g. of 40% formaldehyde admixed with 4cc. of concentrated hydrochloric acid. The material was heated for five minutes and thereafter, while hot, dissolved in butanol in the proportion of 1 g. to 5 cc. of solvent, the resulting solution being used as follows:

With a thick pulp of the same feed as in Example 1 were thoroughly admixed 18 lbs. per ton of kerosene and an amount of the butanol solution corresponding to 8 lbs. per ton of the material dissolved therein. The pulp was then diluted and a silica float separated.

The results were as follows:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	40.09		100.0
Floated	56.8	11.35		16.1
Non-floated	43.2	77.87	4.73	83.9

EXAMPLE 28.

Here retene, a hydrocarbon similar to abietene, was used to produce the water-repellent hydrocarbon group.

To 10.7 g. of orthotoluidine admixed with 15 g. of retene was added 15 g. of formaldehyde admixed with 4 cc. of concentrated hydrochloric acid. Heating was carried out for about thirteen minutes, the resulting material being used as a 25% solution in butanol in the following test:

A thick pulp of the same feed as in Example 1 was conditioned with 18 lbs. per ton of kerosene and an amount of the butanol solution corresponding to 6.4 lbs. per ton of the material dissolved therein. The pulp was then diluted and a silica float separated.

The results were as follows:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	40.60		100.0
Floated	35.3	9.85		8.6
Non-floated	64.7	57.37	29.05	91.4

EXAMPLE 29.

A mixture of 11 g. of benzaldehyde, 10.7 g. of orthotoluidine, 15 g. of formaldehyde, and 4 cc. of concentrated hydrochloric acid was heated for 10 minutes, the maximum temperature attained being 101° C. The resulting material was dissolved in butanol so as to produce a 21.8% solution, the following test being carried out with that solution:

To a thick pulp of the same feed as in Example 1 there was added, during agitation in an impeller-type mixer, 3.6 lbs. per ton of kerosene, 7.36 lbs. per ton of concentrated sulphuric acid, and an amount of the butanol solution corresponding to 8.72 lbs. per ton of the material dissolved therein. This addition required about one minute, subsequent to which agitation was continued for two more minutes. The pulp was then transferred to a Minerals Separation flotation machine, where it was diluted and a silica float separated for about one minute. Upon removal of the non-floated material (constituting the finished concentrate), the floated material was retreated in the machine, without further use of reagents. The non-floated material obtained by this second operation constituted a middling and is indicated as such in the following table:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	40.70		100.0
Refloated	43.1	1.36		1.5
Middling	5.9	14.69		2.1
Non-floated	51.0	76.95	5.72	96.4

EXAMPLE 30.

A sample of Valley Forge Cement Company's "Classifier Sands", which is a coarse product obtained by the Valley Forge Cement Company in its hydraulic treatment of limestone ore, was made into a very thick aqueous pulp in a beaker. With this pulp was mixed for about one minute 0.33 lb. per ton of hexadecylamine hydrochloride, dissolved in a small quantity of alcohol. The pulp was then transferred to a Minerals Separation flotation machine, where it was diluted and agitated in the usual manner, the froth being removed as long as it contained any solids. The results of the test were as follows:

Product	% Weight	% Assay $CaCO_3$	% Assay Insolubles	% Recovery $CaCO_3$	% Recovery Insolubles
Feed	100.0	69.3	22.3	100.0	100.0
Floated	23.3	25.2	66.6	8.5	69.5
Non-floated	76.7	82.6	8.9	91.5	30.5

EXAMPLE 31.

A thick pulp of the same limestone sands as in the preceding example was conditioned with 0.1 lb. per ton of laurylamine hydrochloride, dissolved in a small quantity of alcohol. It was then diluted in the Minerals Separation machine, its treatment therein yielding the following results:

Product	% Weight	% Assay $CaCO_3$	% Assay Insolubles	% Recovery $CaCO_3$	% Recovery Insolubles
Feed	100.0	69.61	22.48	100.0	100.0
Floated	32.0	29.9	62.6	13.8	89.1
Non-floated	68.0	87.7	3.6	86.2	10.9

EXAMPLE 32.

The conditions of this test were the same as in the preceding example, except that the added quantity of laurylamine hydrochloride was increased to 0.133 lb. per ton. Also, upon removal of the non-floated material, the floated material was again subjected to treatment in the machine, without further addition of reagent, the non-floated material obtained by this last operation being indicated as a middling in the following table:

Product	% Weight	% Assay $CaCO_3$	% Assay Insolubles	% Recovery $CaCO_3$	% Recovery Insolubles
Feed	100.0	68.7	22.4	100.0	100.0
Refloated	19.4	14.65	79.4	4.1	68.7
Middling	19.4	56.6	33.0	16.0	28.6
Non-floated	61.2	89.7	1.0	79.9	2.7

EXAMPLE 33.

Employing the same procedures as in Example 31, but with the added amount of laurylamine hydrochloride further increased to 0.2 lb. per ton, the results were as follows:

Product	% Weight	% Assay $CaCO_3$	% Assay Insolubles	% Recovery $CaCO_3$	% Recovery Insolubles
Feed	100.0	68.57	22.7	100.0	100.0
Floated	42.3	37.8	52.9	23.4	98.46
Non-floated	57.7	90.8	0.6	76.6	1.54

EXAMPLE 34.

A thick pulp of the same limestone sands as before was conditioned with 0.33 lb. per ton of decylamine hydrochloride, dissolved in a small quantity of alcohol. It was then diluted and a silica float separated, the following results being obtained:

Product	% Weight	% Assay $CaCO_3$	% Assay Insolubles	% Recovery $CaCO_3$	% Recovery Insolubles
Feed	100.0	69.52	22.3	100.0	100.0
Floated	33.5	29.3	62.8	14.1	94.34
Non-floated	66.5	89.7	1.9	85.9	5.66

From Examples 30 to 34 inclusive, it is apparent that silica may be effectively floated away from calcite with only a very small amount of amine hydrochloride, practically all of the silica being removed in Examples 32 and 33. Here again, with increasing amount of reagent, the grade of concentrate increases and the recovery decreases. It has been found, however, that both the silica and the calcite will float if too much reagent is used.

EXAMPLE 35.

A thick pulp of the same classifier sands as before was conditioned with 0.133 lb. per ton of laurylamine hydrochloride. Its subsequent treatment in a Minerals Separation flotation machine yielded the results shown in the following tables:

Product	% Weight	Insolubles	Analysis $CaCO_3$	Analysis $MgCO_3$	Analysis $FeCO_3$	Analysis $Fe_2O_3+Al_2O_3$
Feed	100.0	23.0	67.9	5.12	2.31	0.67
Floated	37.2	58.0	34.0	3.60	1.63	1.37
Non-floated	62.8	2.0	88.0	6.03	2.71	0.25

	Distribution Insolubles	Distribution $CaCO_3$	Distribution $MgCO_3$	Distribution $FeCO_3$	Distribution $Fe_2O_3+Al_2O_3$
In floated	94.3	18.6	26.2	26.4	76.1
In non-floated	5.7	81.4	73.8	73.6	23.9

From the latter tables it is observed that all carbonates concentrated together in the non-floated material while the oxides of iron and aluminium were in large part floated with the silica (insoluble).

EXAMPLE 36.

A sample of deslimed barite ore from Sweetwater, Tennessee, was made up with water into a thick pulp of about 70% solids, which pulp was conditioned for about fifteen seconds with 1.28 lbs. per ton of octadecyleneamine and 0.14 lb. per ton of pine oil. The pulp was then transferred to a Minerals Separation flotation machine, where after dilution concentrated sulphuric acid was added to it in the amount of 7.2 lbs. per ton. Thereafter, frothing was carried out in the usual manner, the addition of acid being found to assist in depressing both silica and iron oxide. The results of this test were as follows:—

Product	% Weight	% Assay $BaSO_4$	% Assay Fe_2O_3	% Assay SiO_2	% Recovery $BaSO_4$
Feed	100.0	76.53	4.73	14.63	100.0
Floated	60.0	94.61	1.08	1.48	74.2
Non-floated	40.0	49.40	10.20	34.36	25.8

EXAMPLE 37.

Another sample of the same barite ore was made up with water in a Fagergren machine into a thin pulp of 20% solids, to which pulp was added 1 lb. per ton of octadecylamine as a 10% solution in kerosene, a simultaneous addition being made of 0.14 lb. per ton of pine oil. Frothing was thereafter immediately carried out, no conditioning period preceding the float. The following table shows the results of the test:

Product	% Weight	% Assay $BaSO_4$	% Assay Fe_2O_3	% Assay SiO_2	% Recovery $BaSO_4$
Feed	100.0	75.52	5.11	15.17	100.0
Floated	64.4	95.45	0.67	0.33	81.4
Non-floated	35.6	39.46	13.16	42.02	18.6

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EXAMPLE 38.

Still another sample of the same barite ore was processed by admixing it in the form of a thick pulp with 1.6 lbs. per ton of octadecylamine as a 50% solution in warmed kerosene, also with 0.14 lb. per ton of pine oil, the conditioning period being about fifteen seconds. As in Example 36, with the pulp in a diluted state in a Minerals Separation flotation machine, 7.2 lbs. per ton of concentrated sulphuric acid was added thereto, this addition of acid being followed by the usual flotation treatment in that machine. Here, the material floated was twice retreated to yield a finished concentrate of barite, a further addition of 1.8 lbs. per ton of the same acid being made prior to the second retreatment. The results of the test are shown in the following table, wherein the non-floated materials obtained by the two cleaning operations are indicated as middlings:

Product	% Weight	% Assay $BaSO_4$	% Assay Fe_2O_3	% Assay SiO_2	% Recovery $BaSO_4$
Feed	100.0	76.53	4.90	15.09	100.0
Final Float	78.9	93.00	1.06	3.06	95.9
2nd Middling	2.2	27.96	14.80	51.05	0.8
1st Middling	4.7	13.80	19.14	61.20	0.8
Final residue	14.2	13.25	19.90	61.04	2.5

EXAMPLE 39.

In this test a high grade barite concentrate was produced by floating the silica away from the barite.

A minus 65-mesh barite ore, consisting mainly of barite and silica, but containing some brown oxide of iron, was deslimed, losing 40% of its weight, and then formed into a thick pulp with water. This pulp was conditioned with an alcoholic solution of laurylamine hydrochloride, the ratio of the hydrochloride to the ore being 0.35 lb. per ton. Thereafter, the pulp was transferred to a Minerals Separation flotation machine, where it was diluted and frothed in the usual manner, a rougher silica float being removed. This float was twice retreated in the machine, without additional reagent, the residue from the first retreatment being added to the residue from the first flotation operation. These two retreatments yielded a final silica float, a first barite middling being obtained as the residue from the second retreatment.

The aforestated combined residues were washed twice with hot hydrochloric acid (30% by volume) and then with water, whereupon they were conditioned in the form of a thick pulp with 0.275 lb. per ton of laurylamine hydrochloride. The conditioned residues were then diluted and frothed in the usual manner in the flotation machine, the material floated by this operation constituting a second barite middling.

The results of this test were as follows:—

Product	% Weight	% Assay $BaSO_4$	% Recovery $BaSO_4$
Feed (deslimed)	100.0	63.0	100.0
Final SiO_2 float	12.5	17.0	3.4
1st Middling	34.0	31.1	16.8
2nd Middling	18.8	85.5	25.7
Final $BaSO_4$ residue	34.7	98.3	54.1

EXAMPLE 40.

A sample of mine run fluorspar ore from the Hillside Fluorspar Company, of a particle size to pass 35-mesh and largely deslimed was made up with water into a thick pulp of 70% solids. This pulp was agitated in an impeller-type mixer with 0.18 lb. per ton of octadecylamine as a 50% solution in warmed kerosene and with 0.14 lb. per ton of pine oil, the period of agitation subsequent to addition of the reagents being two minutes. Thereafter, the pulp was transferred to a Minerals Separation flotation machine, where it was diluted and frothed in the usual manner, a rougher fluorspar float being separated. This float was twice retreated in the machine, without further addition of reagents, yielding a final fluorspar float and two middlings. The results of the test are shown in the following table, it being observed that the fluorspar was floated from both silica and calcite:

Product	% Weight	% Assay CaF_2	% Assay $CaCO_3$	% Assay SiO_2	% Recovery CaF_2
Feed	100.0	85.15	8.80	4.25	100.0
Final float	66.5	95.62	1.23	2.05	74.7
2nd Middling	7.3	67.42	11.98	18.85	5.8
1st Middling	10.7	88.82	3.61	4.68	11.1
Res. (1st flotation)	15.5	46.05	43.47	6.54	8.4

EXAMPLE 41.

The procedures of Example 40 were repeated on another sample of the same fluorspar ore, but with the reagents of that example replaced by 0.40 lb. per ton of octadecylamine acetate as the only reagent. Also, three retreatments were effected on the rougher fluorspar float, three middlings being obtained by these cleaning operations. The results in this instance were as follows:

Product	% Weight	% Assay CaF_2	% Assay $CaCO_3$	% Assay SiO_2	% Recovery CaF_2
Feed	100.0	86.93	8.53	3.33	100.0
Final float	81.7	94.59	1.98	2.70	88.9
3rd Middling	1.9	55.32	34.32	7.26	1.2
2nd Middling	2.9	50.91	41.05	5.35	1.7
1st Middling	4.9	56.22	36.28	4.20	3.2
Res. (1st flotation)	8.6	50.79	38.33	7.34	5.0

EXAMPLE 42.

Still another sample of the same fluorspar ore was formed into a thick pulp, as described in Example 40 and was conditioned for about fifteen seconds with 0.32 lb. of octadecyleneamine and 0.14 lb. of pine oil, both per ton. Thereafter, the pulp was diluted and frothed in the flotation machine in the usual manner, a rougher fluorspar float being obtained which was once retreated to produce a final fluorspar float and a middling. The following table shows the results of the test:

Product	% Weight	% Assay CaF_2	% Assay $CaCO_3$	% Assay SiO_2	% Recovery CaF_2
Feed	100.0	85.36	9.64	3.18	100.0
Final float	83.7	95.81	1.61	1.84	93.9
Middling	7.1	43.02	39.14	14.74	3.6
Res. (1st flotation)	9.2	23.02	65.24	7.98	2.5

In each of the following two examples, both silica and fluorspar were caused to float away from calcite.

EXAMPLE 43.

A sample of Hillside Fluorspar Company's "Slime Pond Tailing" was sized on a 35-mesh screen, the oversize was ground to pass through the same screen and added to the undersize, and the whole was then deslimed. To a thick pulp of the deslimed material was added, during agitation in an impeller-type mixer, 1.08 lbs. per tone of octadecylamine as a 50% solution in warmed kerosene, and 0.14 lb. per ton of pine oil, a two-minute period of agitation following said addition. The pulp was then diluted and frothed in a Minerals Separation flotation machine, the froth being removed over a period of about one minute. By this operation a rougher float of fluorspar and silica was produced which was three times re-treated in the machine, without further use of reagents. The results of the test are indicated in the following table, wherein the residues from the cleaning operations are indicated as middlings, it being observed that a relatively high grade calcite product was obtained as the residue from the first flotation operation:

Product	% Weight	% Assay CaF_2	% Assay $CaCO_3$	% Assay SiO_2	% Recovery CaF_2
Feed (deslimed)	100.0	45.18	37.02	16.87	100.0
Final float	47.3	74.28	3.11	21.71	77.8
3rd Middling	4.5	33.97	17.09	47.04	3.4
2nd Middling	6.3	32.94	28.20	36.96	4.6
1st Middling	8.2	33.61	48.29	16.64	6.1
Res. (1st flotation)	33.7	10.92	86.18	2.34	8.1

EXAMPLE 44.

Another sample of the same fluorspar-calcite ore as in Example 43 was processed in the same way, except that 1.31 lbs. per ton of octadecylamine acetate and 0.14 lb. per ton of pine oil were substituted for the reagents of that example. Also, the rougher fluorspar-silica concentrate was four times re-treated in the machine, the results in this instance being as follows:

Product	% Weight	% Assay CaF_2	% Assay $CaCO_3$	% Assay SiO_2	% Recovery CaF_2
Feed (deslimed)	100.0	42.11	40.34	16.48	100.0
Final float	56.3	67.79	11.08	20.08	90.6
4th Middling	3.5	23.12	51.78	23.90	1.9
3rd Middling	4.3	18.32	58.28	22.26	1.9
2nd Middling	6.3	14.09	64.85	20.03	2.1
1st Middling	9.4	8.18	77.53	13.15	1.8
Res. (1st flotation)	20.2	3.35	91.06	4.33	1.7

In each of the following two examples, a concentration of calcium phosphate was effected with exceptional efficiency by combining the usual process of floating that mineral by agents including fatty acid soap with a preliminary flotation of silica in accordance with this invention, the results attained in each instance surpassing anything that has hitherto been possible by that process alone.

EXAMPLE 45.

A sample of the same deslimed phosphate feed as in Example 1 was made into a thin pulp of about 25% solids in a Fagergren flotation machine, to which pulp was added 0.15 lb. per ton of nonadecyleneamine sulphate, dissolved in equal parts by volume of alcohol and benzene. Thereafter, without preliminary agitation, a sand float was separated for about one minute. The non-floated material obtained in this manner was used as the feed to the following flotation operation:

Dewatering of the non-floated material was carried out to a thick pulp of about 70% solids. To this pulp was added, during agitation in an impeller-type mixer, 0.8 lb. of caustic soda, 4.39 lbs. of fuel oil, 1.06 lbs. of fish acid, and 0.14 lb. of the kerosene-rosin solution described in comparative test 1, all per ton of the original feed prior to the preliminary operation of removing sand. Agitation with these agents was continued for two minutes following their addition, which required about one minute. The pulp thus conditioned was transferred to a Minerals Separation flotation machine, where it was diluted and a phosphate float separated for about one minute, the material remaining constituting a tailing. Upon removal of this tailing, the material floated was re-treated in the same machine for another one-minute period, yielding a finished concentrate and a middling, this cleaning being carried out without further addition of reagents.

The results of this test are indicated in the following table:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Original Feed	100.0	40.54		100.0
Sand Float	33.2	4.00		3.3
Phos. Flot. Feed	66.8	55.75		96.7
Concentrate	47.3	79.78	3.18	93.1
Middling	1.6	32.05		1.3
Tailing	17.9	5.45		2.3

EXAMPLE 46.

To a thin pulp of the same phosphate feed as in Example 1, formed in a Fagergren flotation machine, was added 0.09 lb. per ton of octadecylamine as a 10% solution in kerosene, simultaneously with 0.14 lb. per ton of pine oil. Incident to these additions, the machine was started and a sand float separated. The non-floated material thus obtained was dewatered to a thick pulp, with which was admixed 0.5 lb. of caustic soda, 2.5 lbs. of fuel oil, 0.5 lb. of fish acid, and 0.07 lb. of the kerosene-rosin solution previously described, all per ton of the original feed. The conditioned pulp was then diluted and frothed in the usual manner in a Minerals Separation machine, the collected froth being again treated in the same machine to separate a finished concentrate. The results were as follows:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Original Feed	100.0	39.95		100.0
Sand Float	44.4	3.09		3.4
Phos. Flot. Feed	55.6	69.39		96.6
Concentrate	46.0	80.59	2.05	92.8
Middling	1.0	53.66		1.4
Tailing	8.6	11.25		2.4
Conc. & Midd.	47.0	80.02		94.2

As a basis of comparison with Examples 45 and 46, the following two tests were carried out:

COMPARATIVE TEST 2.

A thick pulp of the same feed as in Example 1 was conditioned with 0.5 lb. per ton of caustic soda, 4.45 lbs. per ton of fuel oil, 0.47 lb. per ton of oleic acid, and 0.14 lb. per ton of the kerosene-rosin solution already described. Thereafter, it was treated in the usual manner in a Minerals Separation flotation machine, the rougher concentrate thus obtained being re-treated in the same machine to separate a finished concentrate. This concentrate assayed 80.18% tricalcium phosphate, but the tricalcium phosphate recovery was only 85.2%.

COMPARATIVE TEST 3.

The conditions of this test were the same as those of the preceding test, except that the added amount of oleic acid was increased to 1.18 lbs. per ton. The tricalcium phosphate recovery in the finished concentrate was 94.1%, but the tricalcium phosphate assay was only 76.67%.

The following two examples appertain to the use as collectors of quaternary amine compounds in which the nitrogen atom forms part of an aromatic nucleus.

EXAMPLE 47.

A one to one mixture of cetyl and oleyl alcohols, known commercially as "Stenol", was esterified with chloroacetic acid to form cetyl and stearyl chloroacetate. To 33.3 g. of this mixture was added 15.8 g. of pyridine, heating of the resulting material being thereafter carried out for fifteen minutes. This material began to darken as soon as the boiling point of pyridine was approached, considerable foaming also taking place. Upon cooling, the reaction product, containing both cetyl and stearyl pyridinium chloride acetate, was washed with alcohol and ether, whereupon it was dissolved in an amount of alcohol sufficient to produce a 6% solution, the following test being carried out with that solution:

A sample of the same feed as in Example 1 was made up with water into a thick pulp of about 70% solids. To this pulp was added, during agitation in an impeller-type mixer, an amount of the alcohol solution corresponding to 2 lbs. per ton of the compounds dissolved therein. This addition required about one minute, subsequent to which agitation was continued for two more minutes. The pulp was then transferred to a Minerals Separation flotation machine, where it was diluted and a silica float separated. A voluminous froth was produced, requiring from four to five minutes to collect. The results of the test were as follows:

Product	% Weight	% Assay Tricalcium Phosphate	% Recovery Tricalcium Phosphate
Feed	100.0	42.70	100.0
Floated	36.0	4.81	4.0
Non-floated	64.0	64.22	96.0

EXAMPLE 48.

The conditions of this test were identical to those of Example 47, except that the mixture of quaternary amine compounds was used as a 35% solution and in the increased amount of 12 lbs. per ton, the results in this instance being as follows:

Product	% Weight	% Assay Tricalcium Phosphate	% Recovery Tricalcium Phosphate
Feed	100.0	41.70	100.0
Floated	51.6	5.73	6.5
Non-floated	48.4	80.59	93.5

The applicability of the process of the present invention to tabling is shown by the following example:

EXAMPLE 49.

A sample of the same deslimed phosphate feed as in Example 1 was formed with water into a thin pulp of about 20% solids. To this pulp in a mixer was added 0.4 lb. per ton of octadecylamine in solution with 3.6 lbs. per ton of kerosene, agitation with these agents being carried out for a short period of about 15 seconds to insure their proper distribution in the pulp. Thereafter, the pulp was fed to a laboratory-size Wilfley table with the following results:

Product	% Weight	% Assay Tricalcium Phosphate	% Assay Insolubles	% Recovery Tricalcium Phosphate
Feed	100.0	42.44		100.0
Discharge Side	46.7	8.88		9.8
Discharge End	53.3	71.84	12.10	90.2

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. A process of concentrating non-silicon-bearing non-metallic minerals from ores containing silicious matter which comprises adding to an aqueous pulp of such an ore an amine compound included in the class consisting of free amines containing a water-repellent hydrocarbon group and the salts of said amines with acids substantially soluble in water, the water-repellent hydrocarbon group of such compounds being aliphatic except in the case of resin-amine compounds produced as free amines by condensation of an aldehyde with an aromatic amine, such as a toluidine, in the presence of a reactive substance capable of yielding the water-repellent hydrocarbon group, or as amine salts by further reaction with an acid substantially soluble in water, in which case of resin-amine compounds the water-repellent hydrocarbon group may be either aliphatic or aromatic, the amine compound used being added in suitable amount as a collector for certain components of the ore; and subsequently treating the pulp to separate a material relatively rich in said components and relatively poor in the others.

2. A process as claimed in Claim 1, in which the free amines used are those containing the water-repellent hydrocarbon group in the form of a straight-chain aliphatic hydrocarbon radical of more than five carbon atoms, but preferably of at least eight carbon atoms, the amine salts used being those of such amines with acids substantially soluble in water.

3. A process as claimed in Claim 2, in which the free amines and amine salts used are mono-amine compounds having their amine radical directly attached to the water-repellent aliphatic hydrocarbon radical.

4. A process as claimed in Claim 2, in which the free amines used are condensation products of an organic acid containing the water-repellent aliphatic hydrocarbon radical with an aminoalcohol, or of an alcohol containing the water-repellent aliphatic hydrocarbon radical with an amino acid, the amine salts used being those obtained by further reaction with an acid substantially soluble in water.

5. A process as claimed in Claim 4, in which the free amines used are those obtained by employing a fatty acid, such as oleic acid, for condensation with an amino alcohol, the amine salts used being those obtained by further reaction with an acid substantially soluble in water.

6. A process as claimed in Claim 1, in which the free amines used are resin amines obtained by employing as the substance yielding the water-repellent hydrocarbon group an unsaturated straight-chain hydrocarbon of more than five carbon atoms, but preferably of at least eight carbon atoms, or an ester of a fatty acid containing as a radical an unsaturated straight hydrocarbon chain of more than five carbon atoms, but preferably of at least eight carbon atoms, or a cyclic hydrocarbon of the class of naphthenes, abietenes, and analogous hydrocarbons, or a substance containing one or another of such cyclic hydrocarbons in the state of chemical combination, such as naphthenic acid and abietic acid, or a substance containing the phenyl nucleus, such as benzaldehyde, the amine salts used being those obtained by further reaction with an acid substantially soluble in water.

7. A process as claimed in any of Claims 1 to 6, in which the free amines and amine salts used are primary amine compounds.

8. A process as claimed in any of Claims

1 to 7, in which the step of separating the collected components of the ore is carried out by flotation.

9. A process as claimed in any of Claims 1 to 8, in which the ore treated is a phosphate ore and the collecting action is effected on the silicious matter.

10. A process as claimed in Claim 9, in which the concentrated phosphate is later treated with such known agents as fatty acid soap and mineral oil to separate a finished concentrate.

11. The improved process of concentrating non-silicon-bearing non-metallic minerals from ores containing silicious matter, substantially as hereinbefore described.

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