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ORE DRESSING

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18 Claims. (Cl. 209—166)

My invention is concerned with the art of separating mineral constituents of ores and the like and is particularly concerned with froth flotation processes.

While the froth flotation process of separating the mineral values from gangue or undesired materials of ores has been quite highly successful in connection with sulphide ores, there is a large number of ores, particularly the non-sulphide ores, in connection with which the results thus far obtained leave much to be desired, not only from the standpoint of operative efficiency but also from the standpoint of reagent cost.

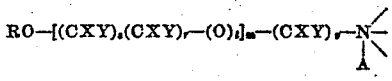
One object of my present invention is to overcome various of the disadvantages which have heretofore attended flotation processes, particularly as regards the processing of certain classes of ores.

Another object of my invention is the provision of novel flotation agents.

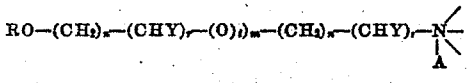
Another, and important, object of my invention is concerned with novel froth flotation processes for separating silica and siliceous materials from ores containing the same.

Other objects and features of the invention will become apparent as the description proceeds.

At least many of the novel flotation agents which I have found to be particularly suitable for my present purposes are organic nitrogenous substances which may, in general, be represented by the following formulae:

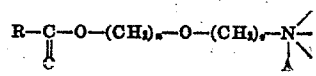


and



wherein R is a higher molecular weight organic radical such as an alkyl or acyl radical, X and Y are alkyl, hydrogen, or hydroxy or other anions such as halogen, sulphonic, sulphate, phosphate, borate or the like, A is an anion, preferably of a solubilizing character, s is a small whole number at least one, and preferably 2, 3 or 4, r is zero or a small whole number, m and n are whole numbers, preferably 1, 2, 3 or 4 although they may be much higher, t is zero or one, and at least one of the three indicated valence bonds attached to nitrogen is satisfied by a radical of the class consisting of alkyls, cycloalkyls, alkylols, aryls, aralkyls, aralkylols, and the radical of a heterocyclic ring of which the nitrogen is a member.

A subclass of the novel flotation agents which I have found to be unusually useful may be represented by the general formula

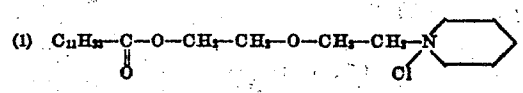


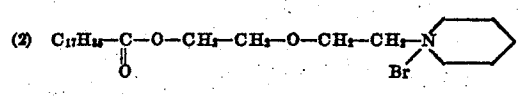
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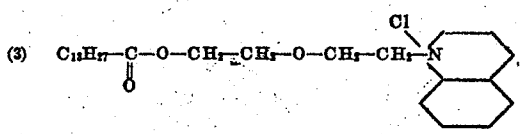


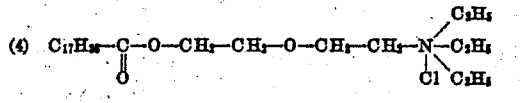
is a higher molecular weight acyl radical, n and v are small whole numbers, A is an anion, and at least one of the three indicated valence bonds attached to nitrogen is satisfied by radicals of the class consisting of alkyls, cycloalkyls, alkylols, aryls, aralkyls, aralkylols, and the radical of a heterocyclic ring of which the nitrogen is a member. Compounds of this group wherein R is an alkyl radical derived from a fatty acid, or mixture of fatty acids, containing between 8 and 18 carbon atoms, wherein n is 2, wherein A is halogen and N is part of a pyridine ring, have proven especially satisfactory. In both of the above formulae, it will be understood that n and v may be the same or dissimilar in particular compounds.

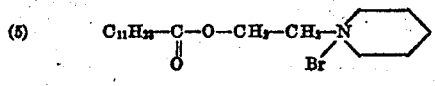
The following flotation agents are illustrative and representative of those which fall within the scope of my invention:

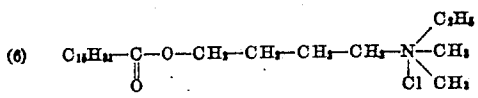
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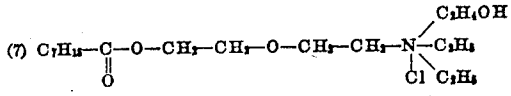
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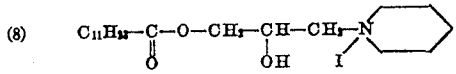
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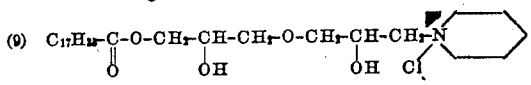
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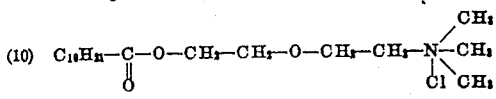
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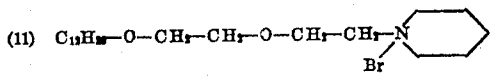
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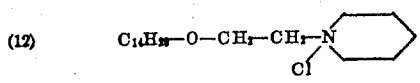
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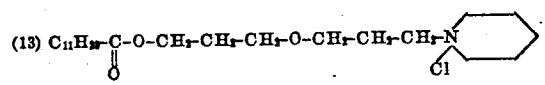
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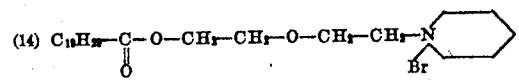
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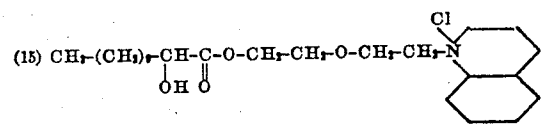
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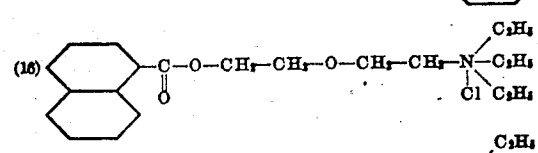
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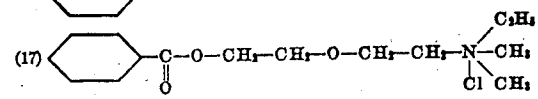
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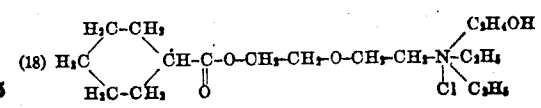
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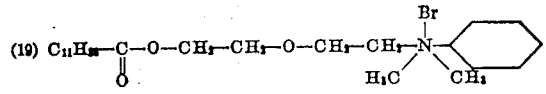
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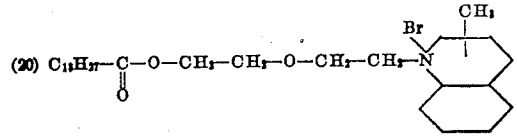
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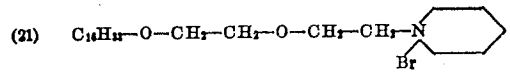
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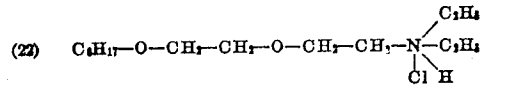
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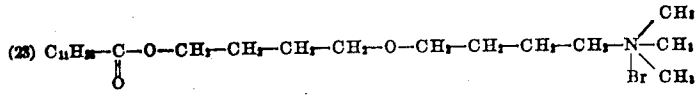
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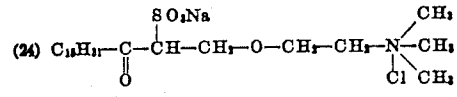
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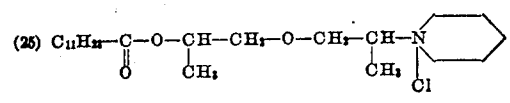
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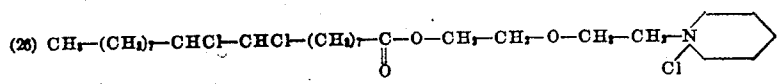
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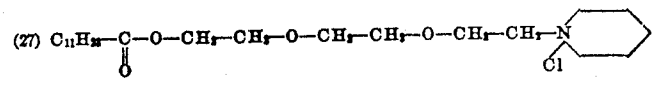
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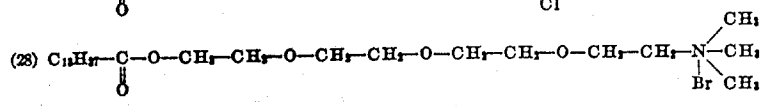
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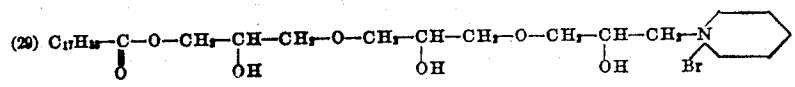
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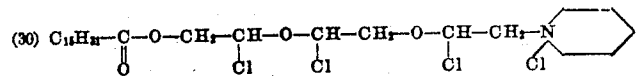
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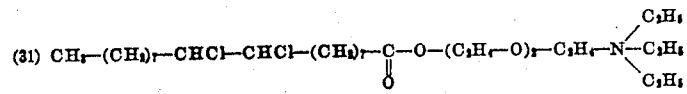
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My novel flotation agents have general utility in ore separation operations with respect to the types of ores the mineral values of which may be recovered by the employment thereof although, in particular, they tend to collect silica as well as silicate minerals under certain conditions. The agents function both as collectors and frothers although it may sometimes be of advantage to utilize auxiliary frothers such as pine oil, cresylic acid, and the like. It is advantageous to operate at certain pH values or within certain pH ranges, this being dependent upon the particular agent utilized, the ore being treated, the character of separation desired, and upon other factors. In general, an increase in the length of the hydrocarbon chain of the higher fatty acid radical or the like present in the agent decreases the pH range at which most satisfactory results are obtained, for example, in the separation of silica from ores containing the same. Thus, for example, in compound (1) which is the lauric acid derivative, the most satisfactory operating range is a pH from about 6½ to 8, whereas the stearic acid derivative of

the same compound is best utilized at a pH range of 4½ to 6½. It is evident, therefore, that agents having optimum activity at various pH ranges may be prepared through the simple expedient of selection of particular higher carboxylic or fatty acid derivatives.

In order that those skilled in the art may more fully understand the nature of the present invention, I shall first describe one illustrative manner which I have found to be especially satisfactory for producing some of the flotation agents which I employ herein, and I shall then disclose how such agents may effectively be utilized in ore separation procedures. With respect to the preparation of such flotation agents, it will be appreciated that other methods may be utilized, that the proportions of reacting ingredients, times of reaction, and temperatures may be varied and that supplementary processes of purification and the like may be resorted to wherever found desirable or convenient. These and other variations and modifications will be evident to those skilled in the art in the light of the guiding principles which I disclose herein.

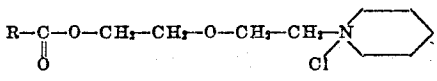
Example A

Mixed cocoanut oil fatty acid mono ester of diethylene glycol pyridinium chloride.

(A) 100 parts by weight of cocoanut oil mixed fatty acids were dissolved in 200 parts by weight of 95% ethyl alcohol and the solution was then neutralized to phenolphthalein with alcoholic potash. The alcohol was then removed by evaporating on a boiling water bath and the resulting soap was then dried for 72 hours in an oven at 110–150 degrees C.

(B) 50 parts by weight of the soap, as prepared in part (A), were mixed with 100 parts by weight of dichlorethyl ether and the mixture was refluxed for 2 to 3 hours at the boiling point of the solution. The soap gradually went into solution and a final precipitate comprising sodium chloride collected at the bottom of the vessel. The solution darkened considerably as soon as all of the soap had dissolved. When the reaction was completed, the solution was decanted from the sodium chloride precipitate and the excess dichlor ethyl ether was removed by distillation in vacuo at 150–170 degrees C. The resulting product was a clear brown liquid.

(C) 25 parts by weight of said clear brown liquid as produced in part (B) were dissolved in 25 parts by weight of pyridine and heated on an oil bath for about 5 hours at 170 degrees C. until the material in the reaction vessel became viscous. It was then heated for an additional 3 hours after which the excess pyridine was removed by distillation in vacuo at 125 degrees C. A dark product was obtained, at least the predominant portion of which corresponded to the following formula:



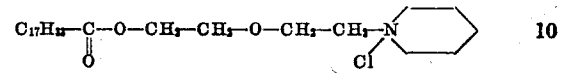
wherein RCO corresponds to the acyl radicals found in cocoanut oil mixed fatty acids.

Example B

Mono oleic acid ester of diethylene glycol pyridinium chloride.

(A) 20 parts by weight of dried sodium oleate were refluxed with 100 parts by weight of dichlor ethyl ether at the boiling point of the mixture for about 4 hours. When the reaction was completed, the solution was decanted from the sodium chloride which had precipitated and the excess dichlor ethyl ether was removed by distillation in vacuo at 160-170 degrees C.

(B) The resulting product was then reacted with an equal amount of pyridine as described in Example A. The final product consisted predominantly of a compound having the following formula:



Example C

Mono stearic acid ester of diethylene glycol pyridinium chloride.

This product was made in the same way as described hereinabove in Example B, employing the same proportions of reactants, using sodium stearate in place of sodium oleate.

Instead of preparing the soaps as described in part (A) of Example A, an alternative procedure has proved highly satisfactory. In accordance with this latter procedure, higher fatty acids, such as lauric acid or cocoanut oil mixed fatty acids, are melted and introduced into a hot aqueous solution of alkali such as potassium hydroxide or sodium hydroxide, the mass being stirred until combination of the fatty acids with the alkali has taken place to form soap. The alkali should preferably be used in stoichiometric amounts to form the soap. To the hot, aqueous soap solution, common salt is added until the soap separates out, the salt solution then being separated from the soap. The soap solidifies at room temperature to a crumbly mass which loses its water easily by drying in air. To facilitate the drying, the air may be heated slightly. This soap product may then be reacted with dichlorethyl ether and then with pyridine, as described in parts (B) and (C) of Example A.

In use, it will be understood that my reagents may be employed in pure, impure or commercial form and that mixtures of any two or more may be utilized.

Satisfactory separations of silica may be effected by means of my agents, with or without addition reagents, by floating the silica from silicate minerals such as kyanite, garnet, tourmaline, beryl, spodumene, dumortierite and the like. This may be effectively accomplished by means of the agent of Example A at a pH of 4½ to 6½, approximately 0.1 pound of the agent per ton of ore being satisfactory, no special precautions being required to be observed. If the ore contains a substantial micaceous fraction, such may be removed ahead of the silica by employing about .01 pound of said reagent per ton of ore and sufficient pine oil to form a froth.

Feldspar may be separated from quartz in a circuit at a pH of about 4½, about 0.12 pound of the agent of Example A and 2.0 pounds of sodium fluoride per ton of ore being satisfactory. The conditioning of the ore pulp with the sodium fluoride should be continued for about five minutes. The feldspar floats and is recovered in the form of a 96% feldspar concentrate, with a recovery of better than 95%. A slightly lower pH may be utilized but at a slight sacrifice of the collecting efficiency of the agent.

Since my reagents have the ability to wet coal, they have utility in processes whereby silica can be floated away from the coal. While the exact pH at which this separation is optimum varies, among other things, with the particular material being treated and the particular flotation agent

selected, I have obtained good results with the reagent of Example A at a pH of about 5.3.

Since many flotation circuits contain calcium carbonate, it is substantially impossible to maintain such circuits at a pH lower than about 7.5. My reagents may be adapted to use therein with effective results, the agent of Example 1 having been found to have particular efficacy in such a circuit for separating silica from cement rock. From 0.1 pound to 0.5 pound of the reagent per ton of ore has proven satisfactory.

Another separation which may be effected in an alkaline circuit with highly satisfactory results involves the separation of silica from phosphate rock. The phosphate rock was ground to pass a 65 mesh screen and treated in a circuit having a pH of 8. The silica content was reduced from 38.2% to 2.6% with a recovery of the phosphate of 96.1%.

Still another separation which may be made with advantage in an alkaline circuit, preferably at a pH of about 7.5 to about 8.0, is that of quartz and feldspar. Under these conditions, the quartz is preferentially floated, and by the addition of 0.1 pound per ton of the agent of Example 1, a rougher concentrate can be made containing approximately 90% free silica, and this can readily be cleaned to produce a practically pure silica and a small amount of feldspar-quartz middling. The rougher tails in this separation are substantially pure feldspar. By the addition of more agent, the feldspar can be floated away from other silicate or carbonate minerals which may be present. This preferential flotation of feldspar and other aluminiferous minerals ahead of carbonates is frequently advantageous in the treatment of cement rock, where it is desirable to obtain a lower ratio of alumina to lime than is contained in the original rock. In the separation just discussed, most of the alumina is contained in the second, third and further concentrates. Hence, by mixing the first concentrate with the tails, a recovery of 75% of lime can be obtained in a form having a ratio of approximately 10 parts of lime to 1 part of alumina, this being suitable for cement mixtures.

Again, effective separations at a pH of about 7 to 8 can be made with, for example, the reagent of Example 1 in the separation of silica from iron ore. Since my reagents are somewhat sensitive to the presence of soluble iron salts, it is desirable to condition the ore pulp with a small amount of sodium fluoride, for example, about 2 lbs. per ton. With an iron ore containing 20.2% SiO_2, the silica content was reduced to 4.2% by the use of 0.15 lb. of the agent of Example 1 per ton of ore, the iron recovery being 89.5%.

Many of the agents of my invention are highly effective collectors of sulphides and may be substituted for xanthates in flotation processes. If the gangue material is silica, the agents such as those of Example A give satisfactory results when used at a pH of approximately 7.5. At this pH, the silica collecting power is very low and a high grade sulphide concentrate may be obtained. For preferential flotation of sulphides, the same addition reagents may be used as when using xanthates in accordance with known practice.

Still other separations may be effected with facility by the use of the flotation agents of my invention. Thus, for example, chromite may be separated from olivine, the gangue material with which it is usually associated, by froth flotation in a neutral circuit by reagents such as those of Examples 1 and A hereinabove, the former being preferred for this particular separation because of its greater efficiency as a collector at a pH corresponding to neutrality. The chromite flotation takes place readily, leaving olivine in the cell. Similar separations can be made for ilmenite and magnetite from black sands. If desired, the ore pulp may be conditioned with a small amount of potassium ferrocyanide.

When the gangue is silica, as in the case of certain magnetites, both the quartz and the feldspar which constitute the gangue can be floated away from the magnetite by the use of agents such as those of Example 1 in a neutral circuit. Conditioning with potassium ferrocyanide or sodium fluoride is sometimes preferable.

Separations of various other minerals may be effected by the use of my agents such as, for example, graphite and mica, it being preferred to carry out such separations in a slightly alkaline circuit when using reagents such as those of Example A, the collecting power for silica being quite low in such circuits. Again, my reagents are useful in the treatment of clay-like substances, including tungsten ore and scheelite type of ore and many slimy gold ores. These ores can be conveniently fractionated, using several of my reagents at various pH ranges and in such a manner a variety of fractions containing these minerals may be obtained.

Another use for the reagents of my invention is in the flotation of silica from soluble salts. In many places, for example, it is desirable to mine old lake beds which contain considerable silica in addition to the soluble salts. By carrying out the flotation in saturated brine, for example, a brine prepared from the ore itself, the silica can readily be removed, leaving the soluble salts for further treatment either by flotation or otherwise. Still another separation which may be made with my reagents is the flotation of silica from carbonate minerals such as smithsonite or rhodochrosite.

It will, of course, be appreciated that the ores mentioned are referred to only by way of illustration and it is obvious that my reagents may be employed with advantage in the separation of various other ores, as, for example, flints, pyroxenes, iron oxides, for example, hematite, limonite and siderite; micas, such as biotite and muscovite; spinels such as picotite and magnetite; and the like.

While I have described hereinabove the use of my reagents in froth flotation processes, it will be understood that my reagents may also be employed for separations involving agglomeration and tabling. In this connection, it should be understood that wherever the term "flotation" is employed in the claims it is intended to cover both froth flotation as well as granulation and agglomeration processes. In the granulation and agglomeration processes, the material, generally of a size which passes through approximately a ten mesh sieve, is treated in a highly concentrated pulp with one or more of my reagents and an ordinary petroleum oil is added to produce a filming on the mineral. When such a mixture is tabled, the filmed mineral passes rapidly over the front of the table and is thereby separated from the mineral not filmed. At least most of the separations which have been described above can be made in the coarser sizes by agglomeration and tabling. Thus, for example, the use of 0.2 lb. of a reagent such as that of Example 1 and 1 lb. of heavy petroleum oil per ton of an iron ore consisting principally of martite, in a gangue of

quartz and feldspar, gave excellent results. In this case, the heavy metal salts were initially removed and, after thorough mixing with the reagent, the ore pulp was tabled, resulting in a much more rapid and complete separation of the quartz and feldspar than may be accomplished by the present practice of tabling without agglomeration. Again, phosphate ore was treated with 0.05 lb. of the reagent of Example 1 and 1.0 lb. of heavy petroleum oil per ton of ore, the pulp having a pH of 7.8. After thorough mixing, the silica was readily separated from the phosphate rock by tabling, the silica in this case passing over the front of the table.

My agents, described hereinabove, are also useful in separating certain water-soluble salts from each other by froth flotation as well as agglomeration or tabling methods, this being carried out in a substantially saturated brine or solution of the ore itself or in a substantially saturated brine of any of the salts to be separated. In the event that the agglomeration or tabling method is employed, fuel oils or similar filming agents are added to the brine.

In carrying out all of the separations described above and others not specifically mentioned, it is preferable to size the ore or the minerals to be separated since the fine material appears to have a preferential affinity for the flotation reagent and seems to withdraw the same from the coarse material.

It will be understood, particularly in view of the examples set forth hereinabove, that my novel agents may be utilized together with one or more already known agents such as collecting agents, frothing agents, depressing agents, emulsifying agents, dispersing agents, activating agents, deactivating agents, inhibitors, in general, organic and inorganic conditioning agents, and the like. These include, among others, mineral and vegetable oils, fuel oil, kerosene, mercaptans, xanthates, organic sulphides, hydro sulphides, carbamates, thio-carbamates, thio-ureas, di-thio-ureas, azo and diazo compounds, amines such as triethanolamine, higher molecular weight alkyl sulphates such as octyl sulphate, lauryl sulphate, oleyl sulphate, cetyl sulphate, stearyl sulphate, said higher alkyl sulphates being used preferably in the form of their salts such as sodium and the like, alkali metal and heavy metal soaps, higher fatty acids such as oleic acid and palmitic acid, sulphonated oils and sulphonated higher fatty acids such as Turkey red oil and sulphonated oleic acid, gelatin, glue, starch, copper sulphate and other salts of copper, mercury and lead, alkali metal sulphides and fluorides, such as sodium sulphide and sodium fluoride, alkalies such as sodium hydroxide, potassium hydroxide, and sodium carbonate, alkali metal silicates such as sodium silicates, acids such as sulphuric acid, hydrochloric acid and the like, salts such as potassium ferrocyanide and other agents which are commonly employed in flotation and agglomeration processes. In this general connection, it should be noted that the presence of heavy metal ions, particularly trivalent ions such as iron, chromium, and aluminum, tends to reduce the collecting power of my reagents. Hence, should these ions be present, they should be removed by washing or their effect counteracted by appropriate addition agents. Sodium fluoride and potassium ferrocyanide, previously mentioned, are representative as addition agents effective for this purpose. When using potassium ferrocyanide, it is preferred to condition the ore pulp therewith and then wash out the excess. However, when this is not feasible, conditioning may be effected with a smaller amount of potassium ferrocyanide, which is allowed to remain in the pulp, and the results are satisfactory.

It will be understood that the foregoing disclosure, although in considerable detail, is to be considered only as illustrative and in no wise limitative of the full scope of my invention. Those skilled in the art will, in the light of my teachings, readily understand the full scope thereof which, in general, is indicated in the appended claims.

As Examples 11, 12, 21 and 22 show, my reagents may also comprise higher molecular weight ether derivatives. These may be prepared, for example, by reacting a compound containing a reactive halogen, for example, dichlorethyl ether ($ClCH_2—CH_2—O—CH_2—CH_2Cl$) with an alkali metal alcoholate such as sodium laurylate ($C_{12}H_{25}—ONa$) in accordance with general methods known in the art. The resulting compound may then be treated with pyridine or other desired nitrogenous base to produce agents suitable for my present purposes.

The higher molecular weight organic radical represented by R in the general formulae may be derived from various sources. Among such sources may be mentioned straight chain and branched chain, saturated and unsaturated, carboxylic, aliphatic, cycloaliphatic, fatty, aromatic, hydroaromatic, and araliphatic acids including caprylic acid, butyric acid, heptylic acid, caproic acid, capric acid, pimelic acid, sebacic acid, behenic acid, arachidic acid, cerotic acid, erucic acid, saturated and unsaturated higher molecular weight aliphatic acids such as the higher fatty acids containing at least eight carbon atoms and including, in addition to those mentioned, melissic acid, stearic acid, oleic acid, richinoleic acid, risinelaidic acid, ricinostearolic acid, linoleic acid, linolenic acid, lauric acid, myristic acid, palmitic acid, mixtures of any two or more of the above mentioned acids or other acids, mixed higher fatty acids derived from animal or vegetable sources, for example, lard, coconut oil, rapeseed oil, sesame oil, palm kernel oil, palm oil, olive oil, corn oil, cottonseed oil, sardine oil, tallow, soya bean oil, peanut oil, castor oil, seal oils, whale oil, shark oil and other fish oils, partially or completely hydrogenated animal and vegetable oils such as those mentioned; hydroxy and alpha-hydroxy higher carboxylic, aliphatic and fatty acids such as i-hydroxy stearic acid, dihydroxy-palmitic acid, dihydroxystearic acid, dihydroxybehenic acid, alphahydroxy capric acid, alpha-hydroxy stearic acid, alpha-hydroxy palmitic acid, alpha-hydroxy lauric acid, alpha-hydroxy myristic acid, alpha-hydroxy coconut oil mixed fatty acids, alpha-hydroxy margaric acid, alpha-hydroxy arachidic acid, and the like; fatty and similar acids derived from various waxes such as beeswax, spermacetic, montan wax, coccerin, and carnauba wax and higher molecular weight carboxylic acids derived, by oxidation and other methods, from paraffin wax, petroleum and similar hydrocarbons; resinic and hydroaromatic acids such as hexahydro-benzoic acid, naphthenic acid and abietic acid; araliphatic and aromatic acids such as phthalic acid, benzoic acid, Twitchell fatty acids, naphthoic acid, pyridine carboxylic acid; hydroxy aromatic acids such as salicyclic acid, hydroxy benzoic and naphthoic acids, and the like. It will be understood that mixtures of any two or more of said acids may be employed if desired and it will also be appreciated that said acids may

contain substituent groups such as sulphate, sulphonic, halogen, ketone and other groups.

In those cases where the higher molecular weight organic radical is derived from alcohols, such alcohols include those corresponding to the higher molecular weight acids referred to hereinabove as well as others as, for example, aliphatic straight chain and branched chain alcohols such as hexyl alcohol, heptyl alcohol, octyl alcohol, nonyl alcohol, decyl alcohol, undecyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, oleyl alcohol, linoleyl alcohol, stearyl alcohol, ricinoleyl alcohol, palmitoleyl alcohol, melissyl alcohol, ceryl alcohol, carnaubyl acohol, myricyl alcohol, branched chain octyl, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl aliphatic alcohols as, for example, 2-ethyl hexanol-1, 2-n butyl octanol-1, 2-butyl tetradecanol-1, and, in general, the higher molecular weight saturated and unsaturated aliphatic straight chain and branched chain alcohols. Preferably, the alcohols which are utilized are those corresponding to the fatty acid occurring in triglyceride oils and fats of vegetable or animal origin, natural or hydrogenated, such as corn oil, cottonseed oil, sesame oil, coconut oil, palm kernel oil, sunflower seed oil, lard, tallow, soya bean oil and the like, those alcohols containing from 12 to 18 carbon atoms being preferred. Other alcohols which may be employed are the cyclo-aliphatic or alicyclic alcohols such as the sterols, as, for example, cholesterol, isocholesterol, phytosterol, sitosterol, hydroaromatic alcohols such as abietol, and such unsaturated alcohols as linalool, citronellol, geraniol and the like. Also included within the class of alcohols which may be employed are such compounds as the hydroxy and alpha-hydroxy higher aliphatic and fatty acids as, for example, ricinoleic acid, alpha-hydroxy stearic acid, alpha-hydroxy lauric acid, dihydroxy stearic acid, 1 hydroxy-stearic acid, alpha-hydroxy palmitic acid, and the like, as well as esters of hydroxy-fatty acids, such as ethyl ricinoleate, castor oil, butyl alpha-hydroxystearate, cetyl hydroxystearate, and the like.

The term "alcohols", as employed herein, is intended to include alcohols which may or may not contain other groups such as carboxylic, halogen, sulphonic, sulphate, or other radicals. The alcohols obtainable by substituting alkyl or acyl radicals, preferably of high molecular weight, in place of the hydrogen of one or more hydroxy groups of polyhydroxy substances or polyhydric alcohols, it being understood that at least one hydroxy group attached to the nucleus of the polyhydroxy substance or polyhydric alcohol remains, are also within the scope of the alcohols from which my reagents may be produced. As examples of such alcohols may be mentioned, partially esterified or partially etherified mono-, di-, and poly-saccharides, and sugar alcohols such as monolauric acid ester of sucrose, monostearic acid ester of dextrose, mono-palmitic acid ester of mannitol, dicaproic acid ester of maltose, mono-octyl ether of sorbitol, monolauryl ether of pentaerythritol, monolauric acid ester of penta erythritol, and the like; the monoglycerides and diglcerides, preferably of the higher fatty acids, as, for example, monolaurin, monomyristin, monostearin, distearin, diolein, dicaproin, mono-lauryl ether of glycerol, di-cetyl ether of glycerol, monostearic acid ester of diethylene glycol, monolauric acid ester of ethylene glycol, and the like.

It is, of course, obvious that the alcohols may be prepared in accordance with any desired method. For example, many of these alcohols may be prepared by the so-called Bouveault and Blanc method or, alternatively, by the reduction or catalytic reduction with hydrogen of natural or hydrogenated animal or vegetable fats and oils, or mixtures thereof, in accordance with well known practices. Again the alcohols may be derived from synthetic processes such as by the oxidation of hydrocarbons or may be prepared by saponification of waxes and the like. Alternatively, they may be prepared by reduction of aldehydes or by the Grignard reaction.

It is likewise apparent that mixtures of the foregoing or other alcohols may be utilized in the preparation of the reagents of my invention as, for example, the mixture of alcohols resulting from the hydrogenation of coconut oil or the free fatty acids of coconut oil. Lauryl alcohol comprises about 45% of the total alcohol mixture, the remaining alcohols running from C_8 to C_{18}. Again, mixtures of alcohols such as are present in the so-called sperm oil alcohols, as well as those present in wool-fat, may equally efficaciously be utilized. Indeed, these higher molecular weight alcohols are generally offered on the market in the form of mixtures of different alcohols. If desired for any specific purpose, special fractions which predominate in a certain particular higher molecular weight alcohol may be utilized or, if so desired, the products may be prepared from a single, substantially pure alcohol.

I have previously indicated that the anion represented by the letter A in the general formulae illustrating the flotation agents which I may employ herein is a halogen such as chlorine, bromine or iodine. Other anions may be substituted therefor as, for example,

$$OH^-,\ HSO_4^-,\ RSO_4^-,\ C_6H_5SO_3^-,\ NO_3^-,$$

acetate, borate, phosphate or some other organic or inorganic anion. As a general rule, I find the halogen derivatives to be particularly satisfactory.

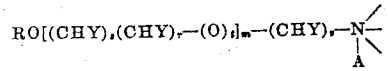
The pentavalent nitrogen present in my flotation reagents may be introduced into the molecule by means of various organic nitrogenous bases as, for example, primary, secondary and tertiary amines including alcohol-, alkylol-, and aralkylol-amines, including monoethanolamine, diethanolamine, triethanolamine, propanolamines, butanolamines, pentanolamines, hexanolamines, glycerolamines, sugar alkylolamines and sugar alcohol alkylolamines such as those of dextrose, sucrose, sorbitol, mannitol and the like; dimethyl monoethanolamine, diethyl monoethanolamine, dibutyl mono-ethanolamine, diethanol methyl amine, diethanol ethyl amine, diethyl butanoul amine, cyclohexyl ethanolamine, diethanol cyclohexylamine, ethanol aniline, alkylol polyamines such as alkylol derivatives of ethylene diamine, mono-methyl monoethanolamine, dipropyl mono-ethanolamine, 1-amino-2, 3-propanediol, 1,2-diamino-propanol; alkylamines such as ethylamine, propylamine, laurylamine, cetylamine, butylamine, hexylamine, cyclohexylamine, aniline, toluidines, dimethylamine, diethylamine, N-methyl-N-ethylamine, triethylamine, trimethylamine, ethylene diamine, diethylene triamine, triethylene tetraamine, betaine, monomethyl ethylene diamine, monoethyl diethylene tetra-amine, mono-allyl amine, hydrazine and substituted hydrazine,

aromatic and heterocyclic bases and cyclic nitrogenous substances such as benzylamine, cyclohexylethyl aniline, morpholine, pyridine, dimethylaniline, N-methyl-N-benzyl amine, N-ethyl-N-naphthyl amine, quinoline, quinaldine, piperidine, alkyl pyridines such as methylpyridine, pyrrolidines, nicotine, and homologues and derivatives or substitution products thereof, and, in general, primary, secondary and tertiary amines substitued or not with other radicals, such as hydroxy, alkyl, aryl, cyclo-alkyl groups and the like; and mixtures of any two or more of said bases as, for example, in the case of commercial triethanolamine which contains minor proportions of mono- and di-ethanolamine. It will be understood that these organic nitrogenous bases may be utilized in pure, impure, or commercial form.

The term "higher", as used herein and in the claims to describe carboxylic and fatty acids and the like, will be understood to mean at least four carbon atoms unless otherwise specifically stated.

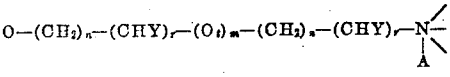
What I claim as new and desire to protect by Letters Patent of the United States is:

1. A froth flotation process for the treatment of ores which comprises frothing the ore in the presence of an aqueous medium containing a relatively small proportion of a chemical compound corresponding to the formula



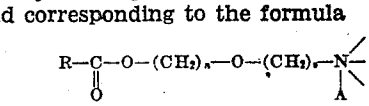
wherein R is higher molecular weight organic radical, Y is alkyl, hydrogen, or hydroxy or other anion, A is an anion, s, m and v are whole numbers, r is zero or a small whole number, t is zero or one, and at least one of the three indicated valence bonds attached to nitrogen is satisfied by a radical of the class consisting of alkyls, cycloalkyls, alkylols, aryls, aralkyls, aralkylols, and the radical of a heteorcyclic ring of which the nitrogen is a member.

2. A froth flotation process for the treatment of ores which comprises frothing the ore in the presence of an aqueous medium containing a relatively small proportion of a chemical compound corresponding to the formula



wherein R is an acyl radical containing between 8 and 18 carbon atoms, Y is hydrogen, alkyl, hydroxy, sulphate or halogen, n and m are small whole numbers, t and r are zero or one, A is an anion, and at least one of the three indicated valence bonds attached to nitrogen is satisfied by a radical of the class consisting of alkyls, cycloalkyls, alkylols, aryls, aralkyls, aralkylols, and the radical of a heterocyclic ring of which the nitrogen is a member.

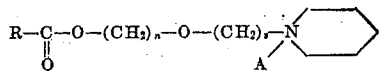
3. A froth flotation process for the treatment of ores which comprises frothing the ore in the presence of an aqueous medium containing a relatively small proportion of a chemical compound corresponding to the formula



wherein R is a higher molecular weight alkyl radical, A is an anion, n and v are small whole numbers, and the three indicated valence bonds attached to nitrogen are satisfied by radicals of the class consisting of alkyls, cycloalkyls, alkylols, aryls, aralkyls, aralkylols, and the radical of a heterocyclic ring of which the nitrogen is a member.

4. The process of claim 1 wherein R is a fatty acid acyl radical containing from 8 to 18 carbon atoms and A is halogen.

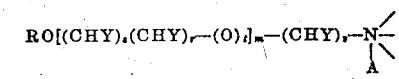
5. The froth flotation process for the treatment of ores which comprises frothing the ore in the presence of an aqueous medium containing a relatively small proportion of a chemical compound corresponding to the formula



wherein R is a higher molecular weight alkyl radical, n and v are small whole numbers, and A is halogen.

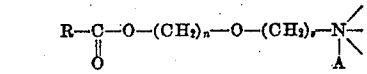
6. The process of claim 5 wherein R is a higher fatty acid alkyl radical containing from 12 to 18 carbon atoms, n and v are each 2, and A is chlorine.

7. The process of separating mineral values from comminuted ores containing the same which comprises effecting the separation thereof in the presence of a chemical compound corresponding to the formula



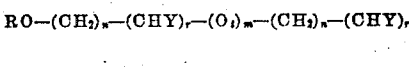
wherein R is higher molecular weight organic radical, Y is alkyl, hydrogen, or hydroxy or other anion, A is an anion, s, m and v are whole numbers, t is zero or one, and at least one of the three indicated valence bonds attached to nitrogen is satisfied by a radical of the class consisting of alkyls, cycloalkyls, alkylols, aryls, aralkyls, aralkylols, and the radical of a heterocyclic ring of which the nitrogen is a member.

8. The process of separating mineral values from comminuted ores containing the same which comprises effecting the separation thereof in the presence of an aqueous medium containing a relatively small proportion of a chemical compound corresponding to the formula



wherein R is a higher molecular weight alkyl radical, A is an anion, n and v are small whole numbers, and at least one of the three indicated valence bonds attached to nitrogen is satisfied by a radical of the class consisting of alkyls, cycloalkyls, alkylols, aryls, aralkyls, aralkylols, and the radical of a heterocyclic ring of which the nitrogen is a member.

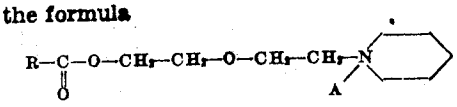
9. The process of separating silica from other mineral matter or the like which comprises frothing said mineral matter or the like in the presence of an aqueous medium containing a chemical compound corresponding to the formula



wherein is a higher molecular weight organic radical, Y is hydrogen, alkyl, hydroxy, sulphate or halogen, n and m are small whole numbers, t and r are zero or one, A is an anion, and at least one of the three indicated valence bonds attached to nitrogen is satisfied by a radical of the class consisting of alkyls, cycloalkyls, alkylols, aryls, aralkyls, aralkylols, and the radical

of a heterocyclic ring of which the nitrogen is a member.

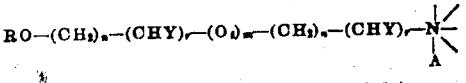
10. The process of separating silica from comminuted ores or the like containing the same which comprises agitating said comminuted ores in an aqueous medium containing a small proportion of a chemical compound corresponding to the formula



wherein R is a higher molecular weight alkyl radical and A is an anion.

11. The process of claim 10 wherein R is a fatty acid alkyl radical containing between 12 and 18 carbon atoms and A is halogen.

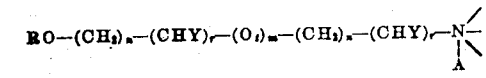
12. A froth flotation process for the treatment of ores which comprises frothing the ore in the presence of an aqueous medium containing at least one flotation agent and a relatively small proportion of a chemical compound corresponding to the formula



wherein R is a higher molecular weight organic radical, Y is hydrogen, alkyl, hydroxy, sulphate or halogen, n and m are small whole numbers, t and r are zero or one, A is an anion, and at least one of the three indicated valence bonds attached to nitrogen is satisfied by a radical of the class consisting of alkyls, cycloalkyls, alkylols, aryls, aralkyls, aralkylols, and the radical of a heterocyclic ring of which the nitrogen is a member.

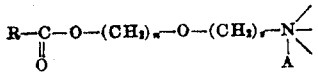
13. The process of claim 10 wherein the agitation is carried out in the presence of an additional flotation agent selected from the class consisting of frothers and collectors.

14. As new flotation agents, chemical compounds corresponding to the formula



wherein R is a higher molecular weight organic radical, Y is hydrogen, alkyl, hydroxy, sulphate or halogen, n and m are small whole numbers, t and r are zero or one, A is an anion, and at least one of the three indicated valence bonds attached to nitrogen is satisfied by a radical of the class consisting of alkyls, cycloalkyls, alkylols, aryls, aralkyls, aralkylols, and the radical of a heterocyclic ring of which the nitrogen is a member.

15. As flotation agents, chemical compounds corresponding to the formula



wherein R is a higher molecular weight alkyl radical, n and v are small whole numbers, and A is an anion.

16. Flotation agents in accordance with claim 15 wherein R is an alkyl radical derived from fatty acids containing between 12 and 18 carbon atoms, n and v are each 2, and A is halogen.

17. Flotation agents in accordance with claim 15 wherein R is the radical $C_{11}H_{23}$—, n and v are each 2, and A is a member selected from the group consisting of chlorine, bromine and iodine.

18. Flotation agents in accordance with claim 15 wherein R comprises the radical $C_{17}H_{35}$—, n and v are each 2, and A is a member selected from the group consisting of chlorine, bromine and iodine.

BENJAMIN R. HARRIS.