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ORE DRESSING

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This invention relates to the separation of the mineral constituents of ores by flotation and related processes such as agglomeration and especially to improved reagents for such purpose.

The froth flotation of sulphide ores has reached a fairly high stage of development and is successfully practiced today with the use of various agents, particularly the xanthates. The non-sulphide ores are still a major problem so far as successful flotation is concerned although, in the past few years, some new flotation agents have been developed which are somewhat effective in the non-sulphide field.

My invention involves the utilization of new flotation agents which are highly effective in the froth flotation of both sulphide and non-sulphide ores and permit the production of relatively pure concentrates with a high percentage of recovery of desired mineral values.

My invention is also concerned with modifying the surface characteristics of the ore to permit the separation of constituents thereof by the well known agglomeration or granulation method wherein the ore particles are selectively oiled and wherein the separation is effected by tabling as, for example, on a Wilfley table.

One object of my invention is, accordingly, the provision of a new class of reagents which are highly effective in flotation and agglomeration processes.

Another object of my invention is the provision of novel procedures for effectively separating mineral values from gangue material associated therewith in ores and the like.

Still another and important object is concerned with froth flotation processes for floating away siliceous materials from ores and the like containing the same.

A further object is concerned with agglomerating processes for removal of silica and siliceous materials from ores and the like containing the same and wherein the silica or siliceous materials are agglomerated.

Still another object of the present invention relates to novel reagents for effecting the separation of soluble salts from each other by either froth flotation or agglomeration methods.

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

The chemical compounds which I have found unusually effective for my present purpose are condensation products of alkylolamines and higher organic acids, especially the higher fatty acids, or derivatives of such acids such as anhydrides, acyl halides and esters, as well as various derivatives of said condensation products, all as will hereinafter be set forth in detail. In general, these chemical compounds fall into three distinct classes: (1) those wherein the molal ratio of the alkylolamine to the higher organic acid is one to one or at least not greater than one to one, (2) those wherein the molal ratio of the alkylolamine to the higher organic acid is at least two to one or not substantially less than two to one, and (3) reaction products made from either of the above classes of condensation products with so-called alkylating, aralkylating or arylating agents. While all of these classes of compounds come within the general class of condensation products of alkylolamines and higher organic acid substances, still in many cases there is a wide difference in various of their properties and, in some instances, important distinctions in their efficacies in the separation of the mineral constituents of ores.

The term "condensation product" is employed herein to mean a reaction product between the reacting constituents, for example, alkylolamine and acid, wherein water or acid or the like is split out as the result of the union of the molecules of said reacting constituents. Similarly, the word "condensed" means a reaction involving the splitting out of water or acid or the like from the reacting constituents.

In preparing the chemical compounds which I employ herein, the condensation may be effected, where the free higher organic acids, anhydrides or esters thereof are employed, at temperatures as low as about 100 degrees C., but for appreciable results the temperature should preferably be somewhat above 100 degrees C., generally about 135 degrees C. Condensations have been successfully carried out as high as 250 degrees C. and even higher. It may be stated that the temperature range should be high enough to obtain appreciable speed of reaction but should not be high enough to cause decomposition of the resulting product. It has been found that, in general, for practical purposes, the best temperatures are between about 150 degrees C. and 175 degrees C. for most of the substances coming within the class of compounds of which I make use in my present invention. The time required for reaction may be as long as twenty hours or more at the lowest temperatures and as short as 15 minutes at the higher temperatures but this will also be influenced by the size of the batches of materials. Condensations may be made with or without the aid of condensing agents of either alkaline or acid character. The nature of the

condensing agent has an effect upon the speed of reaction and the temperature required. Although several different condensing agents have been employed, none has been found which offers sufficient advantage in a major number of cases to be worthwhile using in the practical preparation of these substances.

Considering initially the substances falling within the first subclass of the compounds which I may employ, I list hereinafter several illustrative examples for preparing the compounds:

Example 1

One mol of monoethanolamine is condensed with one mol of stearic acid for two to four hours at from 150 degrees C. to 175 degrees C., the mixture being stirred during condensation.

Example 2

One mol of triethanolamine is condensed with one mol of oleic acid at a temperature between 150 degrees C. and 180 degrees C. for two to four hours, the mixture being stirred during the condensation.

Example 3

One mol of oleic acid is condensed with one mol of diethanolamine at about 170 degrees C. for about three hours, the mixture being stirred during the condensation.

Example 4

One mol of triethanolamine and one mol of coconut oil mixed fatty acids are condensed at a temperature of 170 degrees C. to 180 degrees C. for two to four hours, the mixture being stirred during the condensation.

Example 5

One mol of abietic acid is condensed with one mol of monoethanolamine hydrochloride at a temperature of approximately 180 degrees C. for a period of four to five hours, the mixture being stirred during the condensation.

Example 6

One mol of toluol sulphochloride is condensed with one mol of monoethanolamine at a temperature of 140 degrees C. to 170 degrees C. for a period of between two and three hours, the mixture being stirred during the condensation.

Example 7

One mol of coconut oil mixed fatty acids is condensed with one mol of diethanolamine at a temperature of 160 degrees C. for a period of two to three hours, the mixture being stirred during condensation.

Example 8

One mol of stearic acid is condensed with one mol of diethanolamine at a temperature of 170 degrees C. to 180 degrees C. for a period of two to four hours, the mixture being stirred during condensation.

Example 9

One mol of stearic acid is condensed with one mol of triethanolamine at a temperature of 170 degrees C. to 180 degrees C. for a period of four to six hours, the mixture being stirred during condensation.

Example 10

One mol of diethanol propanolamine is condensed with one mol of oleic acid chloride at a temperature of approximately 80 degrees C. for about two hours, the mixture being stirred during the condensation.

Example 11

One mol of monoethanolamine and one mol of hexanoic acid are condensed at a temperature of approximately 150 degrees C. for about three hours, the mixture being stirred during the condensation.

Example 12

One mol of diethanolamine and one mol of octanoic acid are condensed at a temperature of 160 degrees C. to 180 degrees C. for two to four hours, the mixture being stirred during condensation.

Example 13

One mol of monoethanol-ethylene-diamine is condensed with one mol of stearic acid at a temperature of 150 degrees C. to 170 degrees C. for a period of three to five hours, the mixture being stirred during condensation.

Example 14

One mol of monoethanol-ethylene-tetra-amine and one mol of oleic acid are condensed at a temperature of 140 degrees C. to 160 degrees C. for a period of three to five hours, the mixture being stirred during condensation.

The products which have been described above are either soluble or readily dispersible in water, particularly in the presence of an acid. It will be understood, of course, that these properties will vary depending upon the particular alkylolamine and the particular higher organic acid substances which are condensed as well as upon the molal ratio of the alkylolamine to the higher organic acid substance.

The second sub-class of substances, which I have discussed above, and which, though condensation products, are sharply differentiated from the first sub-class in many of their properties, are those in which one mol of a higher organic acid, particularly higher fatty acid, or derivative thereof such as ester, anhydride or halide, is condensed with two mols or more of an alkylolamine, or not substantially less than two mols of alkylolamine. These condensation products are generally quite soluble or readily dispersible in water, are generally stable in the presence of both acid and alkali, and will not in most cases precipitate in the presence of calcium and/or magnesium salts. In other words, these seem to retain substantially all of their properties in most media met with in industrial operations.

For the benefit of those skilled in the art, I give hereinafter a number of representative examples which are by no means exhaustive, but are sufficient to teach those skilled in the art the manner in which this class of compounds which I employ in my invention may be produced.

Example 15

One mol of coconut oil mixed fatty acids is mixed with two mols of monoethanolamine and heated for two to four hours at a temperature of between 150 degrees C. and 175 degrees C.

Example 16

One mol of oleic acid is condensed with 2 mols of diethanolamine, the procedure being the same as in the first example. An oily product is obtained of excellent solubility and other valuable characteristics.

Example 17

One mol of stearic acid is condensed with two mols of diethanolamine at a temperature of 200 degrees—210 degrees C. for two to three hours. A solid fatty substance is obtained.

Example 18

One mol of coconut oil mixed fatty acids and two mols of diethanolamine are condensed for three hours at a temperature of 145 degrees C. to 155 degrees C. An oil-like substance is obtained which is soluble in water and stable in acid and alkali solution.

Example 18a

One mol of coconut oil mixed fatty acids and two mols of diethanolamine are condensed at a temperature of 170 degrees C. to 200 degrees C. for 3 hours. The resulting product is soluble in water.

Example 19

One mol of oleic acid and two mols of diethanolamine are condensed at a temperature of between 160 degrees and 180 degrees C. for 2 to 4 hours.

Example 20

One mol of stearic acid is condensed with two mols of monoethanolamine at 170 degrees—180 degrees C. for 2 to 3 hours. The resulting product has the same desirable kind of characteristics as the products produced in the above examples.

Example 21

One mol of stearic acid is condensed with two mols of triethanolamine at 180 degrees C. for 4 hours.

Example 22

One mol of abietic acid is condensed with three mols of diethanolamine at 160 degrees—180 degrees C. for 3 to 4 hours. The resulting product is a thick oily substance.

Example 23

One mol of castor oil is condensed with three mols of diethanolamine at 150 degrees—160 degrees C. for 2 to 3 hours. An oil-like product is obtained, completely soluble in water.

Example 24

One mol of sulphonated castor oil is condensed with one mol of diethanolamine and one mol of monoethanolamine at 140 degrees—160 degrees C. for 2 to 3 hours.

Example 25

One mol of oleic acid is condensed with two mols of triethanolamine, employing a temperature of about 165 degrees C. for 2 to 3 hours.

Example 26

One mol of stearic acid is mixed with four mols of monoethanolamine and the mixture heated to 180 degrees—200 degrees C. until no free stearic acid remains. The product has the same advantageous properties described in connection with the other examples.

Example 27

One mol of coconut oil mixed fatty acids is condensed with two mols of a mixture of ethanolamines representing the crude mixture obtained in the process of the manufacture of this product. The crude mixture is composed of mono-, di-, and tri-ethanolamines. The temperature of the condensation may be 160 degrees C. to 170 degrees C. and the time about 3 hours.

Example 28

One mol of sebacic acid is condensed with four mols of diethanolamine at a temperature of 150 degrees C. to 165 degrees C. for four or five hours.

Example 28a

One mol of mixed coconut oil fatty acids is condensed with two mols of triethanolamine at a temperature of 160–170 degrees C. for three hours.

The term "alkylol-amine" is employed in describing the compounds which may be utilized in my invention in a general sense to include substances like monoethanolamine, diethanolamine, triethanolamine including commercial triethanolamine which contains small proportions of monoethanolamine and diethanolamine, diethyl-alkylolamine, monoethyl-alkylolamine, propanolamines, iso-propanolamine, butanolamine, hexanolamine, cyclohexylethanolamine, the alkylolamines of glycerine, sugar, sugar alcohols such as sorbitol and mannitol, and other mono- and poly-valent alcohols. In addition, alkylol di- and poly-amines can satisfactorily be utilized.

By the term "higher organic acids" or "higher fatty acids", there are included acids having a chain of at least six carbon atoms. Fatty acids, derived from waxes, having as high as thirty-five carbon atoms or more may also be employed. Examples of suitable acids, as shown above, are the higher molecular weight saturated and unsaturated aliphatic and fatty acids including capric, caproic, caprylic, stearic acid, hydroxystearic acid, oleic acid, lauric acid, myristic acid, coconut oil mixed fatty acids, linoleic acid, ricinoleic acid, palmitic acid, melissic acid; and mixed higher fatty acids derived from animal and vegetable oils and fats, whether hydrogenated or not, such as cottonseed oil, corn oil, soya bean oil, sesame oil, fish oils, lard, oleo oil, and others, such as the fatty acids derived from waxes like beeswax and carnauba wax. It will also be understood that the acids which are condensed with the alkylolamines need not necessarily be mono-basic acids. Di-basic and poly-basic acids can also be used, such as sebasic acid and japanic acid. Cyclic acids, such as naphthenic acid, hydroaromatic acids such as abietic acid, and quinaldine-carboyxlic acid may also be employed as well as aromatic acids such as benzoic, naphthoic and the like. It is not necessary that the free acids, such as the free fatty acids, be employed, but it is also feasible and effective to use triglyceride oils or fats as a source of the higher fatty acids, in which case glycerine or other alcohols forming the fatty esters split off during the condensation. In place of the oils or fats, such as those referred to above as sources of higher fatty acid radicals, there may also be used sulphonated and phosphated derivatives of oils or fats as well as sulphuric acid esters of oils or fats, like sulphonated castor oil; also the substitution products thereof such as the halogenous and sulphur substitution products. The acid halides, such as stearyl chloride, may also be employed, as indicated above, but in this latter case relatively low temperatures must be used for the condensation. As a source of fatty acids, as has been stated, acid anhydrides may be employed. It is obvious to the skilled chemist that, when employing ordinary glyceride esters as a source of fatty acids, the number of equivalents of fatty acid must be taken into consideration in

calculating the molal ratio of the fatty acid with respect to that of the alkylolamine in connection with the preparation of products where molal ratios are important.

It is not necessary to use the same higher carboxylic acid or derivative thereof in the reaction but two or more varied acids can be used. Thus, for example, one may condense a mixture of stearic and oleic acids with diethanolamine, the mean molecular weight of these acids being determined so that the desired molal ratio of the diethanolamine to the higher fatty acid mixture is obtained. Similarly, mixtures of various alkylolamines may be employed as, for example, in the case of commercial triethanolamine.

It is also to be understood that, in connection with the second subclass of the compounds which I may employ for my present purposes, one mol of alkylolamine can, for certain purposes, be substituted by a straight or non-hydroxylated alkylamine. In other words, compositions satisfactory for many purposes can be made by condensing one mol of an alkylolamine with one mol of an alkylamine and one mol of a higher fatty acid or higher organic acid or derivative thereof.

With further regard to this second subclass of compounds, it will be understood that such covers condensation or reaction products which contain substantial proportions of condensation products of alkylolamines and higher fatty acids or the like in which the molal ratio of the alkylolamine to higher fatty acid is at least two to one or substantially more than one to one. Thus, for example, if one should condense a mixture of an alkylolamine and a higher fatty acid wherein the molal ratio of the alkylolamine to the higher fatty acid is, say, about 1.3, 1.5 or 1.8 to 1, such products would be within the scope of my second subclass since they would contain a substantial proportion of products corresponding to the condensation product of a mixture of an alkylolamine and a higher fatty acid whose molal ratio is 2 to 1.

The condensation may advantageously be carried out in either one or a plurality of stages. In the first method, the fatty acid or similar material is mixed with the alkylolamine and condensed at the proper temperature and for the proper length of time. In the second method, one mol of alkylolamine may be first condensed with a fatty acid or similar material and the resulting product then condensed with an additional mol or more of alkylolamine and so on. In some cases, by proceeding in accordance with this second method, products are obtained with improved properties over what would result if the same ingredients were condensed in the one stage process.

When a crude mixture of alkylolamines is used, mixtures of condensation products of the various types are obtained. In any usual process, when alkylolamines are synthesized, a mixture is formed. This mixture can be directly condensed with the higher fatty acids or similar organic acid substances to form products which are useful for the purposes of my invention. In this way, the necessity of expensive purifying processes is avoided.

In an earlier part of the present specification, reference has been made to temperatures at which the condensation reaction is carried out by stating that, in the case where a free higher carboxylic acid or ester or anhydride thereof is utilized temperatures as low as 100 degrees C. could be employed, but that a temperature high enough to cause decomposition of the final product should not be used. For practical purposes, any temperature between 120 degrees C. and 300 degrees C., generally speaking, can be used and the resulting products will serve admirably for my present purposes. While the difference in temperature employed is mainly one of speed of the reaction, some slight variations in the product may be noted if wide variations of temperatures are used. The temperature employed may be modified by the use of different pressure conditions. For example, if the condensation is carried out in a vacuum, lower temperatures in many cases can be employed and/or the heating time decreased.

A third subclass of the class of compounds remains to be considered. These comprise the reaction products of so-called alkylating, aralkylating and arylating agents with the compounds of the first and second subclasses discussed hereinabove. These latter two subclasses of compounds can be produced by reaction with the usual type of alkylating, aralkylating and arylating reagents, for example, dimethyl sulphate, alkyl halides such as methyl chloride, methyl iodide and ethyl iodide, ethylene chlorhydrin, benzyl chloride, paratoluene ethyl sulfonate, and the like. Unusually satisfactory results have been obtained by reacting dimethyl sulphate with certain of the compounds of the second subclass discussed above, as will be brought out hereinafter. The following examples are illustrative embodiments of the preparation of compounds falling within the third subclass and are given herein so that those skilled in the art will have no trouble in producing any desired compound in the subclass.

Example 29

One mol of stearic acid and two mols of diethanolamine are condensed for three hours at a temperature of 200–210 degrees C. The substance obtained is then treated with one molecule of dimethyl sulphate to obtain a viscous liquid easily soluble in water.

Example 30

One mol of oleic acid is treated with two mols of diethanolamine at 150–160 degrees C. for three hours. The oil-like substance obtained is treated with 1 mol of secondary amyl bromide at 100 degrees C. for two hours. The resulting solid is readily soluble in water and possesses relatively little frothing power.

Example 31

A compound prepared according to Example 18 above is heated for one hour at 100 degrees C. with one mol of normal octyl bromide. A heavy liquid is obtained soluble in water.

Example 32

A compound prepared according to Example 18 above is treated with one mol of dimethyl sulphate for each mol of fatty acid in the original compound. The resulting compound is a liquid readily soluble in water.

Example 33

A substance made in accordance with Example 1 is heated at 100 degrees C. for one hour with one mol of ethyl iodide. The result is a heavy oily substance soluble in water.

Example 34

One molecule of stearic acid is treated with two

mols of diethanolamine at 150–160 degrees C. for three hours. The resulting oil-like substance is treated with one mol of dichlorethyl ether at 100 degrees C. for one hour. The resulting product is a liquid soluble in water.

Example 35

About 462 pounds of a condensation product of coconut oil fatty acids and diethanolamine, the molal ratio of the diethanolamine to the acids being two to one, and resulting from heating together approximately equal weights of said reacting constituents at a temperature between 160 degrees C. and 170 degrees C. for from about 3 to 7½ hours (the length of time depending upon the temperature), are mixed, at room temperature, with 140 pounds of dimethyl sulphate. The dimethyl sulphate is added slowly to the condensation product at about room temperature. The reaction is exothermic and the temperature spontaneously rises. The addition of the dimethyl sulphate is regulated so that the temperature rises to between 80 degrees C. and 110 degrees C. After all of the dimethyl sulphate has been added, the mass may be heated, if desired, to maintain it between 100 degrees C. and 110 degrees C. to complete the reaction. It is advisable not to substantially exceed a temperature of about 130 degrees C. in order to obtain the best results. The reaction mass is kept at the desired temperature for about two hours.

Example 36

A condensation product of one mol of stearic acid and two mols of monoethanolamine is prepared by heating the mixture at about 200 degrees C. for approximately three hours. About 400 parts by weight of the resulting waxy product is treated with 140 parts by weight of benzyl chloride and the reaction mixture is kept at about 110 degrees C. to 125 degrees C., exercising the same general precautions as described in connection with Example 36. The reaction is permitted to proceed until the benzyl chloride odor disappears.

Example 37

One mol of abietic acid is condensed with three mols of diethanolamine at about 210 degrees C. to 220 degrees C. for approximately three hours. About 600 parts by weight of the resulting product, which is a thick oily substance, is reacted with 200 parts by weight of dimethyl sulphate, the same general precautions being observed as pointed out in connection with Example 36.

Example 38

One mol of japan wax and five mols of diethanolamine are condensed at a temperature between 160 degrees C. and 180 degrees C. for three to four hours. About 900 parts by weight of the resulting product are reacted with 200 parts by weight of dimethyl sulphate in a manner similar to that described hereinabove. The resulting product possesses saponaceous properties.

Example 39

One mol of oleic acid and two mols of diethanolamine are condensed at a temperature of between 160 degrees C. and 180 degrees C. for three to four hours. About 500 parts by weight of this reaction product, at room temperature, are reacted with about 150 parts by weight of methyl iodide. The reaction takes place with the evolution of heat and an oleaginous product results.

Example 40

One mol of coconut oil fatty acids is mixed with one mol of monoethanolamine and one mol of butylamine and the mixture is heated for from two to four hours at a temperature between 150 degrees C. and 175 degrees C. About 390 parts by weight of the resulting condensation product is reacted with 140 parts by weight of dimethyl sulphate, the same general precautions being exercised as in connection with Example 36.

Example 41

500 parts by weight of a condensation product of one mol of stearic acid and two mols of diethanolamine, produced by heating said materials at a temperature of about 200 degrees C. for three to four hours, is mixed, at room temperature, with 130 parts by weight of benzyl chloride. The mass is then heated for several hours at about 110 degrees C. to 125 degrees C. until the odor of the benzyl chloride disappears. The resulting product is oleaginous in character.

Example 42

400 parts by weight of a condensation product of coconut oil fatty acids and diethanolamine, made as described in Example 36 hereinabove, is reacted with 270 parts by weight of dimethyl sulphate for a few hours, the same general precautions being exercised as in connection with Example 36. An oleaginous product results.

Example 43

A condensation product is prepared by heating one mol of palmitic acid with two mols of diethanolamine at about 175 degrees C. for from two to four hours. After cooling down to room temperature, about 460 parts by weight of said condensation product is reacted with 220 parts by weight of phenyl iodide in accordance with the general procedure set forth above. An oleaginous product results.

These examples are by no means exhaustive and other means of producing reaction products of the condensation products with alkylating, aralkylating and arylating agents are known to those skilled in the art. Any of these may be employed with generally effective results.

The chemical compounds in the form of condensation products, as described hereinabove, may be reacted with sulphating and sulphonating agents such as sulphuric acid, fuming sulphuric acid, and chlorsulfonic acid or with phosphating agents such as phosphoric acids, P_2O_5, and the like, or with lower molecular weight halogeno-acids such as chloracetic acid, bromacetic acid, chlorpropionic acid and the like by general procedures well known in the art to produce modified products having utility in ore separating operations. Similarly, derivatives of the condensation products can be produced by reacting the same with SCl_2, S_2Cl_2, $SOCl_2$, SO_2Cl_2, P_2S_3, P_2S_5, thiodiglycol, thiodiglycerol and the like to introduce sulphur into the molecule. These complex compounds likewise are useful in the flotation and agglomeration treatments of ores.

I shall now describe the manner in which these compounds are used in the actual separation of mineral values from ores containing the same by flotation as well as agglomeration methods.

While flotation reagents may be classified in general into frothers and collectors, this classification is not particularly useful in describing my invention since I find that, under different conditions, these reagents may fall into one or

both classifications. In general, reagents of the classes fully described above possess frothing properties in at least some degree and I have found that, in many cases, certain of these compounds may be used as frothers with the exertion of a minimum of influence on the flotation circuit other than to provide the necessary volume of froth. For example, in the flotation of blende which has been activated with copper sulphate and for which either potassium ethyl xanthate or potassium amyl xanthate is used as a collector, I have found that recoveries are as good or slightly better than when using the usual frothers like pine oil or cresylic acid.

Thus, with a given blende ore from southwest Missouri, I have obtained the following results:

Assay of tails—percent zinc

Collector	Frother	
	Pine oil 0.08 lb/ton	Reagent prepared according to Example 18 above 0.08 lb/ton
Potassium ethyl xanthate 0.2 lb/ton	1.6	1.4
Potassium amyl xanthate 0.2 lb/ton	1.6	1.4

Similarly, I have found that, when it is desirable to remove a talcose gangue in a metal sulphide ore before adding sulphide collectors, reagents made in accordance with Examples 9, 12, 15, or 18 are especially useful in that they collect substantially no sulphides and leave the circuit in good condition for the addition of sulphide collectors. Reagents made in accordance with all of the examples from 1 through 26 are quite satisfactory as simple frothers.

On the other hand, I have found many instances where these reagents used as frothers made important improvements in both the grade of concentrate and the recovery. I am not prepared to state a definite theory concerning the mechanism of this action but I believe that the dispersing action of the reagents is important.

As an example, I shall give results which I have obtained on a chromite ore from Montana. This ore contained 23.86 percent Cr_2O_3 in a gangue essentially olivine. The charge used for floating it was NaOH 1.5 lb./ton; Na_2SiO_3 0.5 lb./ton; oleic acid 1.0 lb./ton. This charge gave an extraction of 85.3 per cent and a concentrate containing 40.8 Cr_2O_3. By the addition of 0.2 lb./ton of a reagent made in accordance with Example 18, the extraction was increased to 98.2 per cent and the grade of concentrate raised to 43.7 per cent Cr_2O_3.

As another example, I shall give my results on an iron ore from Minnesota containing 40 per cent Fe using an emulsion of crude oil as a collecting agent. Using as a frother an agent of the sodium higher molecular weight alkyl sulphate type, I obtained a concentrate assaying 60.0 per cent Fe and a recovery of only 40 per cent. By the use of a reagent made in accordance with Example 15, the recovery was increased to 85 per cent and the grade of concentrate to 63.5 per cent.

As another example, I have found that when a reagent prepared in accordance with Example 18 is added to a circuit for the flotation of copper ore from Utah, using cresylic acid as a frothing agent and potassium ethyl xanthate as a collector, the tailings are reduced in copper content from 0.11 to 0.06 per cent copper.

Since all of the reagents described also have good emulsifying and dispersing power, I have found that they may be advantageously used to prepare emulsions of petroleum oils, vegetable and animal oils and to prepare dispersions of lipophilic solids such as metallic soaps and xanthates. I have found that these emulsions and suspensions are useful collecting agents in the flotation and agglomeration art. The method of preparing such emulsions may be any of the several methods known in the art.

Preliminary emulsification of the higher aliphatic acids with any of the compounds described under subclasses 1 and 2 increases their efficiency and enables higher fatty acids to be used which are solid at room temperature.

Emulsification of the insoluble oils is readily accomplished by triturating the novel flotation and agglomerating agents of my present invention and oil with a small amount of water in a mortar. The aforesaid agents and water are added to the mortar first and mixed, then the oil is added in small increments with continued mixing until emulsification begins, after which the oil may be added more rapidly until the emulsion is completed.

Concentrated emulsions containing, for example, 80 percent of oil and 10 percent each of the aforesaid agents and water, were prepared and then diluted for subsequent use. The relative proportions of agent, water, and oil, the specific kind of agent and oil, the method of preparation, the pH, and the age of the emulsion affect the stability of the emulsion and the particle size of the dispersed phase. Care must be exercised in preparing the emulsion because an excess of agent may promote the formation of a water-in-oil emulsion rather than the oil-in-water type. The former emulsions have little or no advantage over straight oil in flotation. Although many of the water-in-oil emulsions will reverse on dilution, the reversal is often incomplete and the diluted emulsions are therefore unstable.

A typical test on a lead-zinc-iron ore, in which a paraffin oil emulsion, was used is given in Table 1. The ore was ground to 150-mesh and floated in a mechanical machine. Good froths were obtained and flotation was rapid. Lime would make possible a better rejection of pyrite in the zinc rougher concentrates. Control of the depressants is not critical when the oil emulsions are used as collectors, although a large excess, particularly of cyanide, should be avoided.

Table 1.—Flotation of a lead-zinc-iron ore with an emulsion

Product	Weight, percent	Assay, percent			Percent distribution		
		Lead	Zinc	Iron	Lead	Zinc	Iron
Lead concentrates	7.5	84.50	1.60	0.65	90.7	2.0	1.0
Lead middlings	3.9	12.31	8.83	6.70	6.9	5.9	5.3
Lead rougher concentrates	11.4	59.80	4.07	2.72	97.6	7.9	6.3
Zinc cleaner concentrates	6.8	.34	62.25	2.44	.3	72.1	3.4
Zinc middlings	8.3	.19	8.73	21.15	.2	12.3	35.9
Zinc rougher concentrates	15.1	.26	32.83	12.72	.5	84.4	39.3
Tailings	73.5	.18	.61	3.61	1.9	7.7	54.4
Composite	100.0	6.99	5.87	4.88	100.0	100.0	100.0

Table 1.—Flotation of a lead-zinc-iron ore with an emulsion—Continued

Reagents used	Pounds per ton of crude ore					
	Lead			Zinc		
	Conditioner	Roughter	Cleaner	Conditioner	Roughter	Cleaner
Zinc sulphate	1.9					
Sodium cyanide	.3		0.10			0.15
Soda ash		1.0				
Sodium silicate			.15			.15
Copper sulphate				1.5		
Compound prepared according to Ex. 18		1.5			2.0	
Time, minutes	5	5	3	10	10	5

The following examples are further illustrative of the scope of my present invention:

Chromite ore from Montana, 23.86% Cr_2O_3

Floated with the following charge:
NaOH—1.5 lb/ton
Na_2SO_3 .5 lb/ton
Oleic acid—1.0 lb/ton

Emulsion of 10% kerosene in reagent of Example 18*a* 0.2 lb/ton
Total extraction 98%.
Grade of concentrate 43.7% Cr_2O_3
Pure mineral 44.2% Cr_2O_3

Iron ore from Minnesota, 40.2% Fe

Floated with emulsion of 8 parts crude oil
1 part reagent of Example 18*a*
10 parts water 1 lb/ton.
Concentrate analyzed
63.5% Fe 5.91% Insol. Recovery 85%
For comparison the same ore was floated with a frother in the form of a higher alcohol sulphate.
Concentrate
60.0% Fe 8.5% Insol. Recovery 40%
The superiority of emulsions using the reagents of the present invention is evident.

Oxidized lead ore containing gold in quartz

The value of a reagent such as that of Example 18*a* as a carrier for insoluble oleaginous collecting agents may also be used to advantage over similar mixtures with emulsifiers such as the higher alcohol sulphates. Thus, in an oxidized lead ore containing gold in quartz, the gold bearing quartz may be completely removed by flotation with substantially no lead by floating with sodium sulphide and a suspension of lead-lauryl sulphate in the reagent of Example 18*a*. An attempt to do the same thing with a similar suspension in a higher alcohol sulphate reagent gives very unsatisfactory results, the lead minerals being, in fact, preferentially floated.

I have also found that emulsions of light oils such as kerosene with compounds made according to Examples 15, 17 and 23 can be used for highly selective flotation of talc from magnesite.

Oxidized ores like lead carbonate can also be advantageously floated by the use of dispersions of a sulphidizing medium in compounds of the class described. By warming lead ethyl xanthate with the product of Example 18 a dark colored dispersion of some complex compound of lead is obtained which is an excellent collector and frother for the flotation of oxidized lead ores.

Thus far, I have disclosed flotation results depending on frothing, dispersion or emulsification and, therefore, common in some measure to all the compounds of all three subclasses. Furthermore, I have indicated the particular compounds I have found most efficacious but those skilled in the art will have no difficulty in making other highly efficacious compounds with the aid of the examples.

I shall now describe my findings with regard to the collecting properties of these compounds. I have found that compounds of subclass 3 are especially efficacious as collectors for several minerals, particularly sulfides and silica or highly siliceous minerals. As an example of the collecting properties of reagents of this class for sulfides, activated blende in a southwest Missouri ore may be considered. For these tests I used compounds made in accordance with Example 30 and Example 35 respectively. The results using potassium ethyl xanthate and potassium amyl xanthate are given for comparison in the following table.

Reagent charge				Tailings	
Collector	Lb/ton	Frother	Lb/ton	Assay zinc	Percent loss
KEX	.24	Pine oil	.08	.22	1.6
KAX	.24	...do	.08	.21	1.6
Ex. 30	.24	...do	.08	.03	.2
Ex. 35	.24	...do	.08	.52	3.9

It will be seen that while the reagents made in accordance with both Examples 30 and 35 are collectors of activated blende, the material made in accordance with Example 30 is very much superior.

I have also found that reagents prepared by treating a substance made according to Examples 18 and 30 with P_2S_3 are excellent collectors for sulfides. With the substance from Example 18 treated with P_2S_3, used on the above ore, tailings have been produced with only .02% zinc and .17% lead. The material made by treating the substance made in accordance with Example 30 with P_2S_3 gave tailings assaying .023% zinc and .20% lead.

I have made experiments using many compounds of subclasses one and two and reacted with many alkylating agents and have found that compounds of subclass 3 made from the compounds of subclass 2 are, in general, much more effective collectors than those made from compounds of subclass 1 and that the total number of carbon atoms in the compound should be from about 26 to 30 for maximum collecting activity. The importance of the number of carbon atoms, so far as obtaining the best results is concerned, is well illustrated by comparing a compound prepared in accordance with Example 29 with that prepared according to Example 32. A compound prepared in accordance with Example 29 will presumably contain 28 carbon atoms while one prepared according to Example 32 will contain 22. To obtain a 90 per cent collection of silica from a certain barite ore required 0.20 pound per ton of the reagent of Example 29 and more than 0.75 pound per ton of the reagent of Example 32.

It does not of course follow that for every purpose maximum collecting action is desired. In certain instances, grade of concentrate may be more important. In floating a certain impure glass sand, I have found, for example, that, when enough reagent is used to collect substantially all of the silica, a reagent made according to Ex-

ample 30 gives a product 99.0 per cent SiO_2 while a product according to Example 35 which is a less active collector gives a product 99.85 per cent SiO_2.

In another test I have used a compound prepared in accordance with Example 34 to float silica from a magnetite iron ore. The results are given in the following table:

Table 2.—Flotation of silica from a magnetite ore

Products	Weight, percent	Assay, percent		Percent distribution	
		Fe	Insol.	Fe	Insol.
Cleaner concentrates	40.8	0.95	97.83	1.3	80.3
Cleaner middlings	10.0	20.80	68.82	5.5	13.6
Rougher concentrates	50.8	3.57	93.15	6.7	93.9
Rougher tailings	49.2	65.27	6.24	93.3	6.1
Composite (feed)	100.0	34.28	48.97	100.0	100.0

Reagents used	Pounds per ton of crude ore	
	Rougher	Cleaner
Sulphuric acid	0.5	
Example 34	0.25	
Pine oil	0.08	0.04

I have also found the compounds made in accordance with Example 29 especially efficacious in the flotation of silica from ilmenite ore from Virginia. In this ore I have used 0.2 pound per ton of the reagent of Example 29 and obtained a tailing containing 80 percent of the titanium and only 0.08 percent silica. A pH of 6.3 was used in the circuit.

Another example of the advantages to be gained by the use of the substances herein described in ore treatment is my method for concentrating tricalcium phosphate when it is admixed with silica as in the deposits near Mulberry, Florida and at certain points in Tennessee and elsewhere. In the heretofore known art, these mineral deposits have been concentrated by the flotation or agglomeration of the phosphate mineral by various oleaginous reagents, particularly soaps. By the use of the reagents described herein, the silica is floated away from the phosphate, which is particularly advantageous where the ratio of silica to phosphate is less than one to one. A specific example follows:

Assay of deslimed heads 53.6% tricalcium phosphate
pH of circuit 6.7
Reagents, substance made according to Example 29
pH=6.8 .3 lb/ton, pine oil .1 lb/ton

A concentrate containing 86.9% tricalcium phosphate remained in the rougher cell. The rougher lip overflow contained only 1.2% phosphate and could be discarded.

The same phosphate ore was also treated at a coarser size, 10—20 mesh, by agglomeration and tabling. Instead of agglomerating the phosphate and thus obtaining it over the front of the table as is the present practice, I have found it advantageous to agglomerate the silica and, for this purpose, I use preferably a reagent prepared according to Example 32 although other reagents of subclass 2 or 3 may be used. I have also obtained excellent results with a reagent made in accordance with Example 29. A specific example follows:

One ton of the phosphate material as deslimed and dewatered but not dried was mixed in a rotary mixer with .3 lb. of substance (Example 32) and 2 lbs. of fuel oil. The resulting mixture was diluted with 1 ton of water and fed onto a Wilfley table. This feed had a pH of 6.7. The product coming over the end of the table was taken as concentrate. It analyzed 91.2% tricalcium phosphate with a recovery of 87.6% of the total tricalcium phosphate.

Another example of the commercial utility of my invention is in the cement industry where an excess of silica and alumina are to be removed from lime rock to give the proper proportions for a cement mix. In current practice, the limestone is agglomerated or floated. I have floated and also agglomerated the much smaller proportion of silica and aluminiferous minerals which it is desired to remove. The following examples will illustrate my invention as applied to a certain lime rock from Pennsylvania.

By flotation

Reagents—substance according to Ex. 29 0.1 lb/ton pine oil .08 lb/ton. Analysis of lip overflow, silica 85.2% Al_2O_3 8.7%. Analysis of non-floated material

$CaCO_3$, Al_2O_3, SiO_2 } correct for Portland cement mix

By agglomeration

Reagents—substance according to Ex. 32 .2 lb/ton fuel oil 2 lb/ton. Mixing and tabling as described for phosphate. Analysis of product over end of table and from three last spigots on side

$CaCO_3$, Al_2O_3, SiO_2 } correct for Portland cement

In still another example I have separated mica from certain pegmatites and mica schists by flotation in a single operation using reagents made according to Examples 29 or 32. I have also found that the silica may be removed from North Carolina kyanite ore by agglomeration using fuel oil and the reagent made according to Example 32.

As a result of many tests on silica flotation I have found that the most effective collectors are those of subclass 3. I regard the flotation of silica as a very important phase of my present invention.

While silica is perhaps the most important non-sulphide mineral which is readily floated by the class of substance under discussion I have found that other acidic minerals, that is, those which, by hydration, form acid coatings such as zirkite, rutile and cassiterite and certain hydrous silicates are also floated by these reagents if sufficiently weathered.

Another example of the advantageous use of the reagents disclosed herein is in the fractionation of clays. Thus, for example, I have found that the kaolin minerals in a clay slip are readily floated by reagents prepared, for example, in accordance with Examples 29 and 32. I have also found that all zeolitic and similar base exchange minerals can be floated effectively with reagents of this type. The following example, illustrative of this phase of my invention, involves the treatment of a North Carolina clay. The clay was first blunged with 0.1 lb. of so-

dium silicate per ton of ore and then thickened by hydrochloric acid. It was then introduced into a mechanically agitated flotation machine and 0.15 lb. of the reagent of Example 29 and then 0.08 lb. of pine oil were added, for each ton of ore. About 35% by weight of the clay was removed as a typical loaded froth. This portion possessed greatly enhanced plasticity and burning properties.

Still another example of the advantageous use of these compounds is in the agglomeration treatment of iron ores. In iron ore from New Jersey, for example, the present practice is to separate magnetite by magnetic separators and martite by tabling. By the use of reagents made in accordance with Examples 16, 27, 28*a*, 29 or 32, for example, the silica in the tails from the magnetic separators is agglomerated and the capacity of the tables greatly increased without loss of recovery or grade of product. In a preferred form of this phase of the practice of my invention, the tails from the magnetic separators were dewatered by a drag and mixed with 0.2 lb. of the reagent made in accordance with Example 28*a* and 1 lb. of crude oil, the amounts of said agents referred to being per ton of ore. The mixing was satisfactorily carried out in a rotary mixing apparatus and the resulting mixture was then diluted with two parts of water for each part of the mixture and the final diluted mixture was fed to the tables. The end product was taken as concentrate and analyzed 68.2% Fe with a recovery of 95.8%.

I have also found that compounds of the types described hereinabove are very useful in effecting the separation of water-soluble salts by froth flotation as well as by agglomeration. I have found, for example, that, in a mixture of sodium chloride and potassium chloride crystals in their own brine (substantially saturated) or in an essentially saturated brine of either of the components, the sodium chloride can be floated very effectively by the use of relatively small proportions as, for example, 0.5 lb/ton of ore to 2.0 lb/ton of ore or more, of a compound such as that made in accordance with Example 32.

I have found further that, in such a mixture of water-soluble salts, the sodium chloride may be agglomerated by first adding about 0.5 lb. per ton of ore of a compound such as that made according to Example 18 and then adding 1 lb. per ton of ore of fuel oil. This mixture may be separated by tabling in brine, the sodium chloride coming over the front of the table. The addition of a small amount of a lead soap increases the efficacy of the process.

The unusual ability of these reagents to froth in saturated salt solutions makes them very valuable reagents for all water-soluble salt separations by froth flotation methods and I have used them successfuly in the separation of boric acid from potassium sulphate, ammonium chloride from sodium nitrate, and other water-soluble salt separations.

It will, of course, be understood, particularly in the light of the examples set forth hereinabove, that the novel flotation and agglomeration reagents of the present invention may be employed in conjunction 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 agents include, among others, mineral and vegetable oils, fuel oil, kerosene, mercaptans, xanthates, organic sulphides, hydrosulphides, carbamates, thiocarbamates, thioureas, dithiophosphates, 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, sulfonated oils and sulfonated higher fatty acids such as Turkey-red oil and sulfonated oleic acid, gelatin, glue, starch, copper sulphate and other salts of copper, mercury and lead, alkali metal sulfides such as sodium sulfide, alkalies such as sodium hydroxide, potassium hydroxide and sodium carbonate, alkali metal silicates such as sodium silicate, acids such as sulphuric acid, hydrochloric acid and the like, and other agents which are commonly employed in flotation and agglomeration processes. It will also be understood that the flotation circuit may be an acid or alkaline one depending upon the particular ore being separated, the nature of the reagents used and the character of the separation desired. In general, however, the agents described above function considerably better in a slightly acid circuit than in an alkaline circuit. Indeed, in the case of the flotation of silica, if the alkalinity is greatly increased the flotation is reversed so that the silica is depressed and other non-sulphides floated. This phenomenon also takes place in the case of agglomeration procedures. Thus, for example, in the agglomeration of cement rock, either the silica or the limestone can be agglomerated by control of the pH of the pulp. If the pulp is acid, the silica agglomerates when oil is added whereas, if the pulp is alkaline, the limestone agglomerates. In the light of the above facts, I prefer to operate, in general, in a slightly acid circuit.

It will be understood that the foregoing disclosure, while quite detailed, is to be considered as illustrative and in nowise 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.

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 condensation product of an alkylolamine and a higher organic acid substance.

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 condensation product of an alkylolamine and a higher fatty acid substance having between 12 and 18 carbon atoms.

3. The process of claim 2, wherein the molal ratio of the alkylolamine to the higher fatty acid substance is not more than one to one.

4. The process of claim 2, wherein the molal ratio of the alkylolamine to the higher fatty acid substance is substantially more than one to one.

5. A froth flotation process which comprises agitating and aerating an aqueous suspension of an ore in the presence of a relatively small proportion of a condensation product of a poly-

nitrogenous alkylolamine and a higher organic acid substance.

6. A froth flotation process which comprises agitating and aerating an aqueous suspension of an ore in the presence of a relatively small proportion of a condensation product of a polynitrogenous alkylolamine and a higher fatty acid substance having between 12 and 18 carbon atoms.

7. In the process of concentrating ores by froth flotation, the step of frothing the ore in an aqueous medium containing a fatty acid collecting agent and a small proportion of a condensation product of an alkylolamine and a higher fatty acid substance.

8. In the process of concentrating ores, the step of agitating the ore in an aqueous medium containing a mineral oil and a small proportion of a condensation product of an alkylolamine and a higher fatty acid substance.

9. A process for separating the mineral values from ores which includes the step of agitating an aqueous suspension of ore in the presence of a pre-emulsified oleaginous flotation agent and a condensation product of an alkylolamine and a higher fatty acid substance.

10. The process of claim 7, wherein the molal ratio of the alkylolamine to the higher fatty acid is not substantially less than two to one.

11. The process of claim 9, wherein the molal ratio of the alkylolamine to the higher fatty acid is not substantially less than two to one.

12. 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 condensation product of an alkylolamine and a higher organic acid substance.

13. 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 condensation product of an alkylolamine and a higher fatty acid substance.

14. 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 condensation product of an alkylolamine selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and a member selected from the group consisting of higher carboxylic acids, their esters, halides and anhydrides.

15. 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 the reaction product of an alkylating agent and a condensation product of an alkylolamine selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and a member selected from the group consisting of higher carboxylic acids, their esters, halides and anhydrides.

16. The process of claim 12, wherein the molal ratio of alkylolamine to higher organic acid substance present in the condensation product is not substantially less than two to one.

17. The process of claim 15, wherein the molal ratio of the alkylolamine to the higher carboxylic acid present in said condensation product is not substantially less than two to one.

18. The process of claim 14, wherein the separation is effected by an operation selected from the group consisting of froth flotation and agglomeration.

19. The process of claim 15, wherein the separation is effected by an operation selected from the group consisting of froth flotation and agglomeration.

20. 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 small proportion of the reaction product of an alkylating agent and a condensation product of diethanolamine and a fatty acid containing between 12 and 18 carbon atoms, the molal ratio of the diethanolamine to the fatty acid being not substantially less than two to one.

21. The process of claim 20, wherein the alkylating agent comprises dimethyl sulphate.

22. The process of separating silica from comminuted ores or the like containing the same which comprises agitating said comminuted ores or the like in an aqueous medium containing a small proportion of a condensation product of an alkylolamine and a higher organic acid substance.

23. The process of separating silica from comminuted ores or the like containing the same which comprises agitating said comminuted ores or the like in an aqueous medium containing a small proportion of a condensation product of an alkylolamine selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and a substance selected from the group consisting of fatty acids containing between 12 and 18 carbon atoms, their esters, halides and anhydrides, the molal ratio of the alkylolamine to the fatty acid present in the condensation product being not substantially less than two to one.

24. The process of separating silica from comminuted ores or the like containing the same which comprises agitating said comminuted ores or the like in an aqueous medium containing a relatively small proportion of the reaction product of an alkylating agent and a condensation product of an alkylolamine selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and a substance selected from the group consisting of fatty acids containing between 12 and 18 carbon atoms, their esters, halides and anhydrides, the molal ratio of the alkylolamine to the fatty acid present in the condensation product being not substantially less than two to one.

25. The process of separating silica from comminuted ores and the like containing the same which comprises subjecting said comminuted ores and the like to a froth flotation treatment in the presence of a small proportion of a reaction product of an alkylating agent and a condensation product of diethanolamine and stearic acid, the molal ratio of the diethanolamine to the stearic acid being not substantially less than two to one.

26. The process of separating mineral values from ores containing siliceous gangue which comprises selectively agglomerating said siliceous gangue and separating it from the remainder of the ore in the presence of a relatively small amount of a water-immiscible liquid material and a condensation product of an alkylolamine and a higher organic acid substance.

27. The process of separating mineral values

from ores containing siliceous gangue which comprises selectively agglomerating said siliceous gangue and separating it from the remainder of the ore in the presence of a relatively small amount of a fuel oil and a condensation product of an alkylolamine selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and a member selected from the group consisting of higher molecular weight carboxylic acids, their esters, halides and anhydrides, the molal ratio of the alkylolamine to the higher carboxylic acid present in said condensation product being not substantially less than two to one.

28. The process of separating mineral values from iron ores containing siliceous gangue which comprises selectively agglomerating said siliceous gangue and separating it from the remainder of the iron ore in the presence of a condensation product of triethanolamine and coconut oil mixed fatty acids, the molal ratio of the triethanolamine to the coconut oil mixed fatty acids being not substantially less than two to one.

29. The process of separating mineral values from ores containing siliceous gangue which comprises selectively agglomerating said siliceous gangue and separating it from the remainder of the ore in the presence of a relatively small amount of a water-insoluble oleaginous material and the reaction product of an alkylating agent and a condensation product of an alkylolamine selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof, and a member selected from the group consisting of higher carboxylic acids, their esters, halides and anhydrides.

30. The process of claim 29 wherein the higher carboxylic acids are fatty acids containing between 12 and 18 carbon atoms, and the molal ratio of the alkylolamine to the fatty acid present in the condensation product is not substantially less than two to one.

31. A froth flotation process for the separation of non-sulphide minerals which comprises agitating and aerating an aqueous suspension of ores containing said minerals in the presence of relatively small amounts of inorganic conditioning agents, a condensation product of an alkylolamine and a higher organic acid substance, and a material selected from the group consisting of higher fatty acids and salts thereof.

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