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CONCENTRATION OF SYLVITE FROM ITS ORES

Louis T. Monson, Puente, Calif., assignor to Petrolite Corporation, Wilmington, Del., a corporation of Delaware

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This invention relates to processes for concentrating sylvite (KCl) from its ores and naturally-occurring solutions, and principally from sylvinite. The latter mineral is a mechanical mixture of sylvite and halite (NaCl), which occurs importantly in the Carlsbad district of New Mexico, in Texas, and elsewhere. Brines containing sylvite, and from which it may be recovered after evaporation, occur, for example, near Bonneville, Utah.

Various procedures have been proposed for concentrating the valuable sylvite from such mixtures; and a number of processes are in commercial use today, to that end. In some of these, the halite is removed from the sylvite. More commonly, the sylvite is separated from the other constituents of the mixtures.

For example, the following patents relate to processes for recovering sylvite from such mixtures: U. S. 2,088,325, to Kirby; U. S. 2,288,497, to Tartaron and Duke; U. S. 2,330,158, to Tartaron; U. S. 2,355,365, to Cole; U. S. 2,364,520, to Cole and Houston; U. S. 2,365,805, to Cole; U. S. 2,420,476, to Greene, Sherertz, and Cole; U. S. 2,569,672, to Jackson; U. S. 2,672,236, to Weinig; U. S. 2,689,649, to Atwood; U. S. 2,695,100, to Barr and Bunge; U. S. 2,699,255, to Brown and Cecil; U. S. 2,706,559, to Duke; U. S. 2,721,657, to Smith, Mattson, and Meyer; U. S. 2,733,809, to Wrege and Adams.

Such processes relate to procedures involving wet stratification, such as froth flotation, skin flotation, and agglomeration tabling. In each of them, a certain class of reagents, the long-chain aliphatic amines and their salts, are disclosed as collectors for sylvite. (Additionally, auxiliary reagents like fuel oil, and frothers like pine oil are disclosed in such patents.)

My present invention relates only to such collector element of such processes. It does not relate specifically to such auxiliary agents or such frothers; although my class of reagents may exhibit collateral effects similar to those exhibited by such auxiliary agents or such frothers, and may even make the use of such other agents unnecessary.

My invention resides in the use of a particular class of reagents for collecting sylvite from its mixtures; the other procedural details of conventional processes for this purpose may be practised as before. For instance, it is immaterial whether a sylvinite ore be fine-ground before de-sliming; or whether the ore be ground only to about 10-mesh size, then de-slimed, and then ground further to furnish a flotation-cell feed of acceptable particle size. My reagents may be employed in the presence of auxiliary agents, or of frothers. They may be employed in froth-flotation, skin-flotation, agglomeration-tabling or other processes in which such long-chain aliphatic amines and their salts have been proposed for use.

Because the operating procedures of such processes are

well-known and many of them are conventionally employed in the industry, it is unnecessary to describe them in detail here. Rather, attention will be devoted to a description of the class of reagents to be used in the practice of my invention.

My reagents are liquids, in contrast to the solid or paste-like character of the conventionally employed aliphatic amine acetate reagents. They are therefore much easier to handle and to feed. They may be transported in conventional steel drums and removed therefrom by simply removing one of the bungs. They flow readily at all temperatures likely to be encountered in their transportation and use. They may be made into dilute aqueous dispersions by simply filling a solution tank part-full of solution water, starting an agitator, and pouring in the desired amount of reagent from the drum. A few minutes' agitation produces a homogeneous dispersion which does not separate after stirring is stopped.

My reagents possess good tolerance for slimes. Sylvinite characteristically includes several percent of clay and other insoluble matter; and it is necessary to use a de-sliming step in any beneficiation procedure proposed to recover sylvite therefrom. It is of course highly desirable that a reagent used to collect sylvite shall be capable of doing so in the presence of considerable slime material. Further, the presence of slimes should not materially increase the proportion of reagent required to be used as a sylvite collector. My reagents meet these requirements well.

My reagents are capable of collecting sylvite particles of different sizes, which is obviously an important characteristic of a satisfactory collector, because of the unavoidable variations in particle size range of the feed.

My reagents operate satisfactorily on feeds of different grade. It is substantially impossible to operate a mill on a feed of constant composition. Some reagents, capable of producing satisfactory concentrates on high-grade feed, are incapable of doing so when relatively low-grade feed is required to be used. My reagents produce high-grade concentrates in either case.

My reagents are selective in their action. When they are fed in proportions required to produce high-grade concentrates, they do not do so at the expense of recovery. In other words, there is no excessive loss of potash values in the tailings or rejected fraction of the feed.

The performance of my reagents reflects quickly and markedly the proportion of reagent fed at any time. With some reagents, a considerable proportion must be fed before there is evidence of substantial collection of potash. Thereafter, one can increase the feed rate appreciably without improving greatly this first level of performance. Finally, one may be unable to remove the last traces of potash, to achieve a high-grade concentrate, regardless of the proportion of reagent that is fed. Prompt response of the operation to changes in reagent feed rate, i. e., sensitivity of the reagent to changes in the amounts used, is an important characteristic of my reagents. This is an obviously desirable characteristic of a collector.

Dispersibility in the system is an extremely important characteristic of a collector, although it is at times difficult to describe clearly. If the reagent is not sufficiently dispersible in the pulp, it is present in relatively large aggregates or globules or particles. One such particle of reagent can lift only one mineral particle, even though the lifting of that particle could have been accomplished using only a fraction of the particle of reagent. On the

contrary, if a reagent is too dispersible in the pulp, it may have relatively weak collecting power, because it has relatively less tendency to concentrate at the solid-air-liquid interface.

Dispersibility may be controlled in a number of ways. First, the inherent dispersibility characteristics of the individual reagents will vary. Second, the degree of neutralization of the reagents with an acid, such as acetic acid, will usually affect their dispersibility. In addition, there may be fluctuations in the pH of the system which will affect reagent dispersibility.

My reagents have appreciable inherent dispersibility in water, even in the un-neutralized state; and their performance is sometimes improved by using them in partial salt form.

My reagents are unneutralized or partially neutralized mixtures of a petroleum distillate, particularly a high-boiling aromatic petroleum solvent, and a co-generic mixture of organic compounds which may be best described in terms of its method of manufacture because of the number and complexity of its components.

The manufacturing procedure used to produce the co-generic mixture involves several separate and distinct steps. I have found that such steps must be performed separately and in the sequence recited below, if reagents of high effectiveness are to be produced.

To prepare my reagents, I first react a polyethylene-polyamine with tall oil, under closely controlled conditions of reactant proportions and reaction conditions. In a second and separate step, I then subject the product, so prepared, to reaction with dichloroethylether. Such second reaction product is mixed with an appreciable proportion of a petroleum distillate, preferably a high-boiling aromatic petroleum solvent, to produce a homogeneous liquid. This liquid, as such or in partially neutralized form, is my finished reagent. As will be shown later, it is extremely important from a performance standpoint that the finished product include such petroleum material.

The polyethylenepolyamines are well-known articles of commerce. They include diethylenetriamine, triethylenetetramine, tretraethylenepentamine, and binary and ternary mixtures of these in various proportions. For example, an 80/20 mixture of the first two of these is offered as a commercial product. So is a 40/60 mixture of the last two; and 80/12/8 mixture of the three; and also a ternary mixture of the three in approximately equal weight proportions.

These are synthetic products, made by a reaction that produces varying proportions of these homologs, which are separated from the reaction mass by fractional distillation. Such distillation leaves a still residue comprising a mixture of polyethylenepolyamines. Such still residue, which includes minor proportions of the above-recited three polyamines, also is believed to include the higher polyamines such as pentaethylenehexamine, hexaethyleneheptamine, and the like. Such still residue is likewise a useful reactant for preparing my reagents, and may be so used either alone or admixed with one or more of the individual polyethylene polyamines mentioned.

I have prepared my reagents from various of the polyamines and mixtures thereof. I prefer to use the lower members of the series or mixtures rich in such lower members. My preferred reactant of this class is a mixture comprising about 80% by weight diethylenetriamine and 20% triethylenetetramine, although I have also prepared a very satisfactory reagent of the present kind using triethylenetetramine and tetraethylenepentamine.

I use tall oil as the second reactant in the production of my first intermediate reaction product. A mixture of fatty and rosin acids, this product arises in the pulp and paper industry. It is of unique composition, is available in large quantities on the open market, and is inexpensive. Either crude or refined grades of tall oil may be used to produce my reagents. I prefer to use crude tall oil for economic reasons.

The polyamine and the tall oil must be reacted in carefully controlled proportions if a flotation reagent of desirably high effectiveness is to be produced. Others have in the past reacted these two classes of reactants in either equimolar proportions or using an excess of polyamine; but the reagents prepared using such proportions are definitely inferior to those produced using my proportions.

A clearly superior finished reagent is obtained if there is present in this reaction mixture appreciably less than an equimolar proportion of the polyamine reactant. As one reduces the molar proportion, polyamine-to-tall oil, from 1:1 down to 0.9:1 and then to 0.8:1, the effectiveness of the finished reagent obtained from such intermediate reaction product increases materially. As the proportion is reduced further, the improvement in finished-product quality continues.

While there is no sharp break-point in the effectiveness curve, I prefer to employ a ratio, polyamine-to-tall oil, of from about 0.6:1 to about 0.8:1. The intermediates made using reactant proportions within this last-recited range produce finished reagents whose effectiveness is clearly better than others made with ratios much outside this range. I therefore limit myself herein to reagents made from intermediates whose reactant ratio lies within this narrow range. My preferred molal ratio, polyamine-to-tall oil, is about 0.63:1.

The polyamine and the tall oil are reacted by heating together, with stirring, at a temperature range of quite narrow limits, as I shall next explain.

When one reacts tall oil and a polyamine, by heating and stirring, water is evolved as the temperature of the reaction mass rises. Evolution of water first occurs in the neighborhood of 150° C.; and from one-half to two-thirds of all the water that will eventually be evolved has come over by the time the temperature has reached 200° C. Finished reagents made from intermediates prepared by heating these two reactants at temperatures not exceeding 200° C. have poor effectiveness in my process.

As the temperature of the reaction mass is increased to about 250 C., more water and a small portion of non-aqueous distillate are evolved. (The 250° C. point is mentioned here because it has been the reaction temperature specified in numerous descriptions of procedures for preparing amides from polyamines of the present kind.) Products prepared from intermediates made at 250° C. do not have acceptable effectiveness in my process, however.

In fact, to prepare my desired intermediate the reaction temperature must be held at between 270° and 300° C. for at least part of the reaction period. Usual practice is to mix the reactants and start heating and stirring the reaction mass at atmospheric temperature, or slightly above. (Mixing the tall oil and the polyamine produces a salt, in a slightly exothermic reaction.) The reaction vessel and contents are then brought to the desired reaction temperature prudently, and the reaction is continued as long as required, at that temperature. Prudence in heating is required because appreciable foaming accompanies the reaction and the liberation of water from such reaction mass.

In commercial steel processing vessels, my desired intermediate can be so produced in about 12 hours, of which about 9–10 hours are consumed in reaching a temperature of 285°–290° C.; and about 2–3 hours are consumed in completing the reaction at this temperature. Below about 270° C., the final and critical portion of the reaction does not occur. It is not necessary to raise the temperature much above my preferred range of about 285°–290° C. to complete the desired reaction in a relatively few hours, as stated.

It is also practicable to prepare this first intermediate

reaction product by heating the tall oil to a temperature somewhat above that at which foaming usually occurs in such reaction. For example, if the tall oil is heated to 200–260° C. and the polyamine is then introduced in small increments, foaming is substantially eliminated and an acceptable intermediate is produced.

In a second and separate step of preparing my finished flotation reagents, the intermediate reaction product prepared as just described is subjected to reaction with dichloroethylether. While this second reaction may be conducted in the same reaction vessel as was employed to prepare the above intermediate, and without removing that first reaction mass from the vessel, it must be emphasized that the second reaction, using dichloroethylether, is separately conducted and is distinct from the first reaction.

The reaction using dichloroethylether is quite exothermic in character. Care must therefore be exercised to prevent a run-away reaction, especially when larger proportions of this halogenated reactant are used. I prefer to start the reaction at about 100°–105° C.; under usual conditions, the temperature may thereafter be expected to rise to about 130° C. without application of additional heat.

The foregoing preferred reaction temperature is not limiting, however. I have prepared my reagents using reaction temperatures appreciably higher than these. For example, I have started the dichloroethylether reaction at 100° C. as above; but thereafter have raised the reaction mass to 150° C. Again, I have added the dichloroethylether at 150° C. and have thereafter raised the temperature of the reaction mass to 200° C. In each case, the reagent so prepared is effective for the present purpose.

This reaction converts a portion of the organically-bound chlorine atoms to chloride ions. The degree of conversion of chlorine to chloride ion will importantly influence the characteristics of the finished reagent. I prefer to achieve conversion of at least 35% of the total chlorine, as a minimum; and I ordinarily convert from about 40% to about 70% of such organically-bound chlorine atoms to chloride ions. The amount of chlorine converted can of course be measured by conventional titration of the chloride ion produced.

As un-ionized organically-bound chlorine atoms are converted into chloride ions, the inherent dispersibility of the product in water increases. Water-dispersibility of a basic material can usually be increased by neutralizing it with a low-molal acid, such as acetic, as is well-known in this and other arts. I have coined the term "inherent dispersibility" to distinguish from the conventional neutralization-derived dispersibility; it means the tendency of my basic material itself to disperse in water.

Such tendency may be concealed in some instances because of the presence in the molecule of large hydrophobic elements; and two such materials may appear to be equally not dispersible in water. However, one may be much more readily converted into water-dispersible form, as by neutralization, because of its relatively greater inherent dispersibility. Conversely, two materials may appear to be equally dispersible in water in, say, 5% concentration. Both may produce dispersions which appear alike; yet one dispersion may be considerably more stable and comprise smaller, more completely hydrated particles. Such inherent dispersibility in water may usually be augmented by neutralization of the material with an acid, like acetic acid; but it is not destroyed by the addition of dilute alkali to a dispersion of such neutralized product.

Such inherent dispersibility in water, although difficult to explain, is believed by me to be responsible in part for the improved effectiveness of my reagents, as compared with conventional aliphatic amine acetate reagents.

To achieve it, I have found it necessary to employ an appreciable proportion of dichloroethylether in preparing my reagents. I prefer to employ at least 0.5 equivalent (0.25 mol) of dichloroethylether for every 1 equivalent (1 mol) of tall oil used in preparing the first intermediate reaction product above, and not more than about 2 equivalents (1 mol) per equivalent (mol) of tall oil.

The range of proportions of dichloroethylether which may be used to prepare reagents of acceptable effectiveness in my process cannot be stated with decimal exactness. There is no abrupt change in effectiveness of the products as the proportion of dichloroethylether used in their preparation is varied. As a practical matter, I can state that unless I employ about 0.5 equivalent of dichloroethylether for each equivalent of tall oil, and unless I so conduct the reaction that at least about 35% of the total chlorine present is converted to chloride ion, the resulting product is of inferior quality when used in my process.

After conducting the foregoing two reactions, separately and in the sequence stated, the final reaction mass is mixed with a substantial proportion of a petroleum distillate, preferably a high-boiling aromatic petroleum solvent, either before or after being partially neutralized (if partial neutralization is employed).

This petroleum constituent of my finished reagents is not optionally added to the other ingredients, when it is desired to reduce their viscosity or lower the products' cost. On the contrary, its presence is essential. Its presence is in part responsible for the high effectiveness of my reagents.

I believe there is an explanation of this important discovery. When my reagents are dispersed in water, either in a solution tank prior to introduction into the flotation cell or else in the cell, the reagent particle that so disperses includes an appreciable proportion of petroleum distillate; and the behavior of the particle is different, and more favorable to the flotation of sylvite, than it would have been in absence of the petroleum distillate constituent.

At any rate, I require that my finished flotation reagent include from about 25% to about 75% of petroleum distillate. There is no option in this matter; the finished reagent must include such constituent. No figure can be given for the optimum proportion of such constituent to be used. However, if one uses less than about 25% petroleum distillate and more than about 75% of final reaction product, prepared as above described, the favorable effect of the combination becomes so small as to be negligible. If one uses more than about 75% petroleum distillate and less than about 25% of reaction product, dispersibility in water becomes poor; and the effectiveness of the reagent is further reduced because in part the petroleum distillate is acting simply as a diluent.

I prefer that my finished flotation reagents include about 50% reaction product and about 50% petroleum distillate. Such proportions of reaction product and petroleum distillate should preferably lie at least between 40% and 60%.

I greatly prefer that the petroleum distillate constituent of my finished reagents be a so-called high-boiling aromatic petroleum solvent. Such liquids are available from refineries, as well-known articles of commerce. They have boiling ranges of the order of 400° F. initial to over 600° F. endpoint. They are usually sold on specification reciting their content of sulfonatable constituents, a value determined by reacting the distillate with 98% sulfuric acid and noting the percentage of the sample that dissolves in such sulfonating agent. Both the aromatic and the unsaturated constituents of the petroleum distillate dissolve under such conditions. I do not distinguish between these two classes of constituents in my preferred petroleum distillate, because I do not know their respective proportions in the liquids I have used. I do prefer that the petroleum distillate employed as a constituent of my finished flotation reagent contain a major proportion of sulfonatables, i. e., of aromatics and unsaturates, and preferably at least about 75% thereof.

Specifications of two representative high-boiling aro-

matic petroleum solvents which I have used in preparing my present reagents are as follows:

	Solvent A	Solvent B
Gravity, API Degrees	16.0	14.6
Flash Point, Degrees Fahrenheit	150 min.	245
Mixed Aniline Point	80–95	92.7
Sulfur, Percent by weight	2.25 max.	0.78
Aromatics and Unsaturates, Percent by volume	75–85	75
Distillation, ASTM, Degrees Fahr.:		
Initial	400 min.	442
10% Recovered	470	518
50% Recovered	502	572
90% Recovered	556	642
Endpoint	650 max.	679

So far as I am aware, such high-boiling aromatic petroleum solvents have not been used in the potash industry, and particularly not in connection with the separation of sylvite from its ores. So far as I know, such liquids have never been proposed for use as diluents with the conventional aliphatic amine acetate reagents. (For that matter, I do not believe even kerosine has been suggested to date as a solvent for such conventional reagents; because they are not soluble in kerosine at atmospheric temperatures. Where it has been proposed to prepare solutions of such conventional reagents, alcohols have been suggested.)

It should be clearly understood that my mixture of reaction product and high-boiling aromatic petroleum solvent is a homogeneous, single-phase system, not a dispersion or emulsion or suspension of one constituent in the other.

The homogeneous mixture of reaction product and petroleum distillate, prepared as just described, may be partially neutralized with a suitable acidic neutralizing agent. I have employed acetic acid, although it is equally practicable to use hydroxyacetic acid or other organic acid of low molecular weight. It is equally practicable to use mineral acids like sulfuric and hydrochloric acids. Acetic acid appears to produce reagents having very desirable physical properties; it is my preferred neutralizing agent. I prefer to use it in 94% concentration, although I have used other concentrations. In one instance, I have added common vinegar (5% acetic acid) to the factory-finished reagent, when it became desirable to examine the effect of slight additional neutralization and vinegar was the only form of acetic acid there available.

Only sufficient neutralizing agent is used to produce a reagent capable of making a smooth, creamy, stable dilute aqueous dispersion, but not so much as to neutralize the basic constituents of the reagents completely or even nearly completely. If no neutralizing agent is used the aqueous dispersions of the product may in some cases contain particles sufficiently coarse or large so that the collector does not do as good a job, even though the dispersion may appear stable to the eye. If too much neutralizing agent is used, the tendency of the reagent particles to concentrate at the solid-air-liquid interface may be reduced.

Since the present application of my reagents involves systems usually saturated with KCl and NaCl or similar salts, considerable salting-out of my reagent may be expected. Consequently, it is usually desirable to employ it in more completely neutralized form than it would be used in some other applications.

The foregoing statement does not imply that the proportion of neutralizing agent usable is so critical that manufacture and use of the reagent are impracticable. A slight deficiency in degree of neutralization is not fatal. Minor proportions of neutralizing agent may be added in the field to the product as manufactured and shipped from the factory. Similarly, slightly excessive neutralization of my reagents is not critical. Use of a minor proportion of an alkali like caustic soda will correct such over-neutralization in the system. In fact, it may in some cases be desirable to supply the reagents in slightly over- or under-neutralized form, and then control the final degree of neutralization (and their dispersibility) by concomitantly feeding acid or alkali to the system.

While I prefer to neutralize my reagents after admixing the reaction product with the petroleum distillate, it is entirely feasible to effect any neutralization of the reaction product and then mix the neutralized reaction product with the petroleum distillate. Neutralizing the mixture of reaction product and petroleum distillate is usually more practicable, because such mixture has a viscosity lower than that of the reaction product alone; and distribution of the neutralizing agent is more readily effected in such procedure.

Although I have emphasized the use of aromatic petroleum solvents in preparing our reagents, I have also referred to this general class of constituent as "petroleum distillates." I do not intend, by emphasizing the one example of the class, to imply that it is the only petroleum distillate that may be used. For example, I have used kerosine in preparing my reagents; and a partially neutralized mixture of reaction product and kerosine, within the proportion limits previously set out, is a reagent of high effectiveness in the present application.

I have above described in detail my preferred reactants and the proportions thereof employed to produce my finished flotation reagents. The following examples describe the preparation of a number of my reagents from such reactants and by such procedures. It is not intended that they should limit the preceding description.

Example 1

I first react 2070 pounds of commercial crude tall oil with 450 pounds of a mixed polyamine, 80% by weight diethylenetriamine and 20% triethylenetetramine, in a steel processing vessel equipped with stirrer, and gas-fired. The mass is brought to a temperature of 285–290° C., in the course of about 9.5 hours, care being taken to avoid foam-overs; and reaction is continued at this temperature for 2.25 hours.

This first intermediate reaction product is allowed to cool to 100° C. in the vessel, at which temperature 300 pounds of commercial dichloroethylether are added, with stirring. The ensuing exothermic reaction raises the temperature to about 123° C. within 1.25 hours, after which the reaction mass is maintained at that temperature for an additional 0.75 hour. An increase in viscosity accompanies this second reaction; and about 40% of the chlorine atoms present are converted to chloride ions.

The reaction mass is then transferred to another vessel containing 250 gallons of high-boiling aromatic petroleum solvent (solvent A, above); and the mixture is stirred for 30 minutes. The resulting homogeneous liquid is allowed to cool to atmospheric temperature; after which 98 pounds of 94% commercial acetic acid are added. The whole is stirred for another 30 minutes until the acid is well distributed and neutralization has been accomplished.

The finished reagent, so prepared, is an effective flotation reagent for separating sylvite from its ores.

The performance of my collector reagent, of which the product of Example 1 is representative, may frequently be improved by using it in conjunction with a minor proportion of a somewhat related composition which I believe to be a depressor for the other minerals in sylvinite. At any rate, the effect of incorporating such depressor in my finished flotation reagent appears to be to make the reagent more selective for sylvite. The ability of the collector component to float sylvite is seemingly not adversely affected by the presence of minor proportions of such depressor.

The depressor component's composition is closely allied to the composition of the collector component of those of my reagents which include both components. Both

collector and depressor components are made from tall oil. Both are made from any of the polyamines recited above. Both are made using dichloroethylether in the second intermediate reaction procedure. Both are eventually mixed with a petroleum distillate; and both may be used in unneutralized or partially neutralized state.

The essential difference between the depressor component class and the collector component class is that the former is made from an oxyalkylated derivative of one or more of the foregoing polyamines, rather than from the polyamine itself.

I prefer to employ ethylene oxide alone, of the alkylene oxides, for this purpose, although propylene oxide sometimes is valuable. At times, a mixture of propylene oxide and ethylene oxide will give the best depressor action; but where both are used I prefer that the propylene oxide be reacted first, followed by the ethylene oxide. Butylene oxide is not useful alone; but is useful in conjunction with ethylene oxide.

I prefer that approximately 1 mol of alkylene oxide be used per mol of polyamine. If more than about 2 mols of alkylene oxide are used, per mol of polyamine, the desirable characteristics of this depressor component are greatly reduced. Where more than one alkylene oxide is used, the molal ratio is for total alkylene oxide-to-polyamine; and prefer to use a ratio less than about 2:1 in any case. Most desirably, I use not more than about 1 mol total alkylene oxide to 1 mol of polyamine.

The following is an example of the preparation of such depressor component.

Example 2

I first react 750 pounds of the mixed polyamine of Example 1 with 295 pounds of ethylene oxide in the conventional manner, employing a reaction temperature of 130°–135° C. No catalyst is required, in light of the natural basicity of the starting material. The oxyethylation reaction is complete in 2.5 hours. By this reaction 1 mol of ethylene oxide is introduced into each mol of polyamine.

Thereafter, the procedure is essentially that of Example 1 above. I react 2070 pounds of tall oil with 627 pounds of the oxyethylated polyamine just prepared, raising the temperature to 285°–290° C. in about 10 hours; and maintaining it at that level for 2.5 hours.

Such first intermediate reaction product is cooled in the reaction vessel to 100° C., as before; then 300 pounds of dichloroethylether are reacted as before. The reaction rises spontaneously to about 125° C., where it is maintained for 1 hour. Conversion of chlorine atoms to chloride ions is about 45%.

The reaction mass is thereafter mixed with 300 gallons of high-boiling aromatic petroleum solvent (solvent B, above), and stirred until the mixture is homogeneous. Thereafter, 100 pounds of acetic acid (94%) are added; and the mass is stirred an additional 30 minutes.

The finished reagent so prepared, when mixed in minor proportions with a collector component like that of Example 1, improves the selectivity of that reagent in removing sylvite from its ores.

I have found it advantageous to prepare a mixture of such collector and depressor components, i. e., my preferred flotation reagent, simultaneously in a single manufacturing procedure. The following example illustrates such procedure.

Example 3

I prepare a flotation reagent having both collector and depressor constituents, as follows: I first oxyethylate 35 pounds of a mixed polyamine, having 80% by weight diethylenetriamine and 20% triethylenetetramine, with 13 pounds of ethylene oxide. I then react together 2229 pounds of crude commercial tall oil, 447 pounds of the above polyamine, and 48 pounds of the above oxyethylated polyamine, using a maximum reaction temperature of 285°–290° C. for 2.25 hours, after taking some 10 hours to raise the reaction mass to this temperature from atmospheric. I cool the reaction mass to 100° C., and add 323 pounds of commercial dichloroethylether. The exothermic reaction which ensues raises the temperature of the mass to about 123° C. Conversion of chlorine atoms to chloride ions is about 40%. Thereafter, I mix such final reaction product with 268 gallons of high-boiling aromatic petroleum solvent (solvent A, above), producing a homogeneous liquid. Finally, I add, with stirring and at room temperature, 105 pounds of 94% commercial acetic acid, and stir the mass until the acid has been distributed through it.

The finished product is an effective flotation reagent for separating sylvite from its ores; and has good selectivity.

Other examples of my reagent, including collector, depressor, and collector-depressor types, are as follows:

Example 4

I repeat Example 1 above, but substituting for some of the reactants and proportions, as follows: I react 1850 pounds of tall oil with 587 pounds of triethylenetetramine, proceeding as before. I thereafter react with such first intermediate reaction product 100 pounds of dichloroethylether, as before. I then mix this second intermediate reaction product with 2600 pounds of high-boiling aromatic petroleum solvent (solvent A, above), as before. Finally, I partially neutralize the mass with 110 pounds of 94% acetic acid, as before. The finished product is an effective flotation reagent for the present purpose.

Example 5

I first react 2070 pounds of tall oil with 965 pounds of commercial tetraethylenepentamine, using the procedure and conditions of Example 1, above. Thereafter, I cool the reaction mass to 105° C. and introduce, with stirring, 230 pounds of dichloroethylether. The temperature rises to about 130° C., where it is maintained 1 hour. The final reaction mass is dropped into 2000 pounds of high-boiling aromatic petroleum solvent (solvent A, above); and after cooling to room temperature is mixed with 98 pounds of 94% commercial acetic acid. The finished product is an effective flotation reagent for separating sylvite from its ores.

Example 6

I prepare a depressor component of the kind described in Example 2 above; but with the following reactants and proportions: I use 2070 pounds of tall oil, as before. I use 965 pounds of an oxyethylated triethylenetetramine (prepared as in Example 2, but from 978 pounds of triethylenetetramine and 295 pounds of ethylene oxide). These two reactants are reacted as in Example 2, to produce a first intermediate reaction product. This is next reacted with 230 pounds of dichloroethylether, as before, maximum temperature produced by the exothermic reaction being about 120° C. Thereafter, I mix the final reaction product with 3000 pounds of kerosine; and neutralize the mass partially with 110 pounds of 94% acetic acid.

Example 7

I prepare another example of my depressor component as follows: I react 447 pounds of tetraethylenepentamine and 105 pounds of ethylene oxide, following the procedure set out in Example 2, above. I then react 552 pounds of this oxyalkylated polyamine with 1290 pounds of tall oil; and thereafter react this last reaction product with 290 pounds of dichloroethylether, using the procedures and conditions of Example 2, above. (In the reaction with dichloroethylether, about 70% of the chlorine is converted to chloride ion.) The final reaction product is mixed with 2800 pounds of high-boiling aromatic petroleum solvent; after which the homogeneous

liquid is partially neutralized, using 63 pounds of 94% acetic acid.

Example 8

I prepare a flotation reagent having both collector and depressor constituents, by adding, to 900 pounds of the product of Example 1, 100 pounds of the product of Example 2, above, and stirring until thoroughly mixed. The mixture is homogeneous and is an effective collector for separating sylvite from its ores. It has good selectivity in such application.

Example 9

I prepare a flotation reagent having both collector and depressor components, by adding, to 870 pounds of the product of Example 4, above, 130 pounds of the product of Example 6 above, and stirring thoroughly. The homogeneous mixture is an effective collector for separating sylvite from its ores. It has good selectivity in such application.

Example 10

I prepare a flotation reagent having both collector and depressor components as follows: I react 8321 pounds of commercial crude tall oil with 2536 pounds of commercial triethylenetetramine for 2.25 hours at a temperature of 285°–290° C., after taking about 10 hours to raise the temperature to this level. The product is cooled to 105° C.; and 1216 pounds of dichloroethylether are added, with stirring. The reaction mass temperature rises to about 130° C. (About 60% of the chlorine present is converted to chloride ions.) Then, 7425 pounds of this second intermediate reaction product are dumped into 8112 pounds of a high-boiling aromatic petroleum solvent (solvent A, above); and the mixture is stirred for 45 minutes. Thereafter, 160 pounds of 94% commercial acetic acid are added at atmospheric temperature; and the mass is stirred for another hour. Then, 15,697 pounds of this finished product are mixed with 1429 pounds of the product of Example 7, above. The homogeneous liquid so prepared is a very effective collector for separating sylvite from its ores. It has good selectivity in such application.

Example 11

Example 1 is repeated exactly, except that, instead of neutralizing with 98 pounds of 94% commercial acetic acid, I neutralize with 180 pounds of commercial muriatic acid. The product is an effective collector for separating sylvite from its ores.

Example 12

I prepare a depressor component of the kind described in Example 2. Example 2 is repeated; but instead of introducing 1 mol of ethylene oxide into the polyamine as a first step, I react 750 pounds of the polyamine first with 195 pounds of propylene oxide and then with 148 pounds of ethylene oxide, conditions being substantially the same as in Example 2. Thereafter, I follow the procedure of Example 2 to the end thereof, but using 656 pounds of the present oxyalkylated polyamine instead of 627 pounds of the derivative of Example 2.

Example 13

Example 1 is repeated exactly except that, instead of neutralizing with 98 pounds of 94% commercial acetic acid, I neutralize with 165 pounds of 70% commercial hydroxyacetic acid. The product is a highly effective collector for separating sylvite from its ores.

Example 14

I prepare another example of a depressor component as follows: Example 2 is repeated except that, instead of first reacting 750 pounds of the 80/20 mixture of diethylenetriamine/triethylenetetramine with 295 pounds of ethylene oxide, I use 590 pounds of this alkylene oxide. The oxyalkylation reaction time is approximately 5 hours. The oxyalkylated polyamine is thereafter used in the procedure of Example 2, employing 804 pounds of the present oxyalkylated derivative instead of 627 pounds of the derivative used in Example 2.

Example 15

I repeat Example 1 exactly; but instead of using 2000 pounds of high-boiling aromatic petroleum solvent I use only 840 pounds of such solvent. The product is an effective collector for separating sylvite from its ores.

Example 16

I repeat Example 1 exactly; but instead of using 2000 pounds of high-boiling aromatic petroleum solvent I use 7500 pounds of such solvent. The product is an effective collector for separating sylvite from its ores.

Example 17

I repeat Example 1 above, except that I use, instead of 450 pounds of an 80/20 mixture of diethylene triamine/triethylenetetramine, 930 pounds of a still residue from the manufacture of polyethylenepolyamines. This is available from at least one manufacturer, under the designation "Residue H." The first reaction described under Example 1 is then conducted as there described, except that heat-up time is extended to some 12 hours. The other conditions and reactant proportions are substantially as stated in Example 1. The product is an effective flotation reagent for separating sylvite from its ores.

Example 18

I react 2455 pounds of crude tall oil, 492 pounds of mixed polyamine (80% by weight diethylenetriamine, 20% triethylenetetramine), and 53 pounds of the monooxyethylated polyamine of Example 2, using the procedure of Example 3, above. The first intermediate reaction product, 2705 pounds, is next reacted with 367 pounds of commercial dichloroethylether, using a starting reaction temperature of 100° C. and prudently raising the temperature to 150° C. The latter temperature is maintained for 1 hour. Thereafter, 3072 pounds of such second reaction product are mixed with 2365 pounds of aromatic petroleum solvent (solvent B, above); and the mixture is partially neutralized with 88 pounds of 94% acetic acid. Temperature of the mass at time of neutralization is about 80° C. Such finished reagent is an effective flotation reagent for separating sylvite from its ores. It has good selectivity when so used.

Example 19

I react 2291 pounds of crude tall oil, 459 pounds of the mixed polyamine of Example 18, and 50 pounds of the oxyalkylated polyamine of Example 2. Reaction conditions are as recited in Example 3, above. To 2524 pounds of this first intermediate reaction product, I add 253 pounds of dichloroethylether at 150° C., adding the latter reactant slowly. Thereafter, I raise the reaction mass to 200° C., and maintain that temperature for 0.5 hour. After cooling, the second reaction product is mixed with 2153 pounds of aromatic petroleum solvent (solvent A, above); and 101 pounds of 94% acetic acid are then added, with stirring. The finished reagent, so prepared, is an effective flotation reagent for separating sylvite from its ores. It exhibits good selectivity when so used.

Example 20

I repeat each of the foregoing examples, Examples 1–19 inclusive; but I omit the neutralization step and employ the reagent in unneutralized form. The finished reagents, so prepared, are effective flotation reagents for separating sylvite from its ores. They exhibit good selectivity when so used, especially in those cases where a depressor component is included in the reagent.

Of all the foregoing examples, I consider the product

of Example 3 to represent my preferred reagent. As a second choice, I prefer the product of Example 10. As a third preferred example of my reagents, I name the reagent of Example 3, but in unneutralized form.

Because my reagents are most advantageously used in conventional flotation plants in the potash industry, it is not necessary here to describe in detail how they are used. When they are employed, the operation of the plant is continued in normal fashion, the only change being the substitution of my reagents for the conventional flotation reagents otherwise used. As explained above, my reagents may influence the nature and amount of auxiliary reagents required to be used, or may in some instances even make such auxiliary reagents unnecessary; but my invention relates essentially to the collector element of the mineral beneficiation procedure.

For sake of completeness, the following brief example of their use is presented, without limiting the invention in any degree:

A sylvite ore is dry-crushed to —6 mesh size, with as little production of fines as possible. The crushed ore is scrubbed with saturated salt brine, to scour the surface film of clay slime from the salt crystals. The scrubber discharges a slurry which is then hydraulically classified, the overflow being set at about 28 mesh. The salt bed in the classifier is brine-washed to remove as much of the primary slimes as possible. The classifier overflow is further deslimed to reject the truly colloidal slimes and recover a fine crystalline salt for flotation feed.

This product is then ground till all is —14 mesh. Desliming is again accomplished, as before. The deslimed and classified salts, as a 60%-solids pulp, are conditioned, using a conventional reagent like starch or Guar gum to depress any remaining slimes. In a second conditioner, the feed is contacted with the reagent of Example 3 above, using 0.2–0.4 pound of reagent per ton of ore fed, which operation renders the ore floatable, but does not equally activate the halite and other constituents. It is preferable to include about 0.1–0.3 pound per ton of pine oil, as a frother.

The conditioned ore is then fed to a conventional flotation cell, using a pulp density of about 25–30% solids. Flotation is ordinarily effected quite rapidly, if the conditioning has been adequate. Concentrates from this rougher flotation operation are cleaned in a second or cleaner cell. Tailings from the latter are returned to the rougher cell. Final flotation tailings contain less than 1% K_2O and concentrates are plus-60% K_2O, with 95% recovery, when the operation is efficiently conducted.

In another example of my process, the reagent of Example 10 is substituted for the reagent of Example 3. Otherwise, the operating procedure is as just described. In a third example of my process, the reagent of Example 10, in unneutralized form, is substituted for the reagent of Example 3; the process is otherwise conducted as just described.

I consider the reagent of Example 3 to be my preferred reagent. As a second choice, I prefer the product of Example 10; and as a third preferred example I elect the reagent of Example 3, but in unneutralized form. My preferred procedure for employing my reagents is as recited just above.

As another example of an acceptable operating procedure, the following is recited: The sylvinite ore is crushed to —20 mesh and deslimed. The deslimed ore is pulped in a flotation cell with a saturated brine solution. The pulp produced is conditioned for 60 seconds with 1 pound per ton (solids basis) of a starch derivative; and then for 30 seconds with 0.5 pound per ton of the reagent of Example 10 and 0.1 pound per ton of pine oil. The conditioned pulp is then subjected to flotation, in the conventional manner. Flotation is rapid; and the recovered froth product is satisfactorily rich in KCl.

As stated, I may use auxiliary reagents along with my flotation reagents. For example, the above description has noted that pine oil may be included, as a frother, and that starch or starch derivatives may be included, especially as slime-controlling agents. Fuel oil is sometimes desirably employed, and in rather large proportions.

My invention resides essentially in the use of a novel class of flotation reagents in procedures which are conventional in the industry.

While the foregoing portion of this specification has emphasized the application of my reagents in froth flotation procedures, I wish to state clearly that my reagents are likewise adapted to use in any of the other conventional concentration processes in the industry, such as film flotation and tabling, wherein the conventional aliphatic amine reagents find utility. In the appended claims, I have therefore claimed the use of my reagents in such related processes. An important application of my reagents is believed to lie in the froth flotation procedure for separating sylvite from its ores, as conventionally practised in the potash fields of New Mexico.

The proportion of my reagents required to be used will in each case depend upon the composition of the potash ore with which they are used. However, I believe my reagents will be used in proportions not greater than those in which the conventional aliphatic amine reagents are used in this industry. Because my reagents are generally more effective, pound for pound, such superiority may be expressed in either of two ways: a smaller feed rate will produce a cooncentrate of equal quality; or an equal feed rate will produce a concentrate of higher quality.

In some of the foregoing examples, I have shown the use of an acid and the partial neutralization of the reagent. It should also be pointed out that where it is desired to use my reagents in partially neutralized form, they might equally well be manufactured in the factory without using any neutralizing agent whatever; and any neutralizing acid be added to the reagent later, e. g., as the latter is introduced into the solution tank at the flotation plant or to the cells. It is essential only, in such cases, that the reagent, as it reaches the flotation cell, be partially neutralized, as described.

I have specified that my depressor component, if present at all, be present in only minor amounts. To be more specific, I believe it should comprise not more than about 20% of the total finished reagent. The exact maximum tolerable proportion will of course depend on the individual characteristics of the collector and depressor components of that particular composition.

In the foregoing specification and in the appended claims I refer to "mols of tall oil." It is obvious that, since tall oil is a mixture of fatty and rosin acids, it cannot strictly be said to have a molecular weight. However, since the acids of tall oil are monocarboxylic, 1 equivalent of tall oil will be the same as 1 mol, total, of the various acidic constituents of tall oil. Stated another way, if tall oil has an acid number of 173.2, it has an equivalent weight of 324. One equivalent weight of tall oil is composed of fractional mols of its respective constituent acids, such fractional mols totaling 1.

I have noted above that my reagents may be used in unneutralized or partially neutralized state. It is not possible to state exactly any maximum permissible level of neutralization. Ordinarily, when my finished reagents have been neutralized to a point where their 5% aqueous dispersions have a pH of about 4.0–4.5, additional neutralization is undesirable, both from a performance standpoint and from a corrosion standpoint. Stated another way, after one has neutralized the finished reagent to a degree where it produces a smooth creamy dilute aqueous dispersion, additional neutralization accomplishes no desirable purpose. Also, as stated above,

at more extensive levels of neutralization the performance of the reagents usually deteriorates somewhat. Stated in practical terms, if one uses from about 2 to 4% of 100% acetic acid, based on the amount of undiluted final reaction product present in the finished reagent, additional neutralization is unnecessary. Equivalent proportions of other neutralizing acids would be used, in such cases.

I claim:

1. A concentration process using differential wettability principles for separating sylvite from its ores, characterized by subjecting the ore to the action of a material selected from the class consisting of (I) *a* liquid reagent which includes: (A) a reaction product obtained by (1) first reacting tall oil and a polyethylenepolyamine to provide an intermediate, said reaction including a reaction temperature between 270° and 300° C., the molal proportion of polyamine to tall oil being between about 0.6:1 and 0.8:1, then (2) reacting such intermediate with dichloroethylether, the molal proportion of dichloroethylether to tall oil being between about 0.25:1 and 1:1; (B) a high-boiling petroleum distillate, the proportion of such petroleum distillate in the finished reagent being between about 25% and 75%; and a minor proportion of a depressor (C), which depressor is a reaction product obtained by (1) first reacting tall oil and an oxyalkylated polyethylenepolyamine, said reaction including a reaction temperature between 270° and 300° C., the molal proportion of oxyalkylated polyamine to tall oil being between about 0.6:1 and 0.8:1, the oxyalkylated polyamine being derived by reacting the polyamine with a material selected from the class consisting of ethylene oxide and propylene and ethylene oxide, using not more than about 2 mols of total alkylene oxide for each mol of polyamine; and then reacting such tall oil-oxyalkylated polyethylenepolyamine reaction product with dichloroethylether, the molal proportion of dichloroethylether to tall oil being between about 0.25:1 and 1:1; and (II) partial neutralization products thereof.

2. The process of claim 13, in which the concentration process for separating sylvite from its ores is a froth flotation process in which such sylvite is floated from such ore.

3. The process of claim 2, in which the petroleum distillate is a high-boiling aromatic petroleum solvent, and of which the finished reagent includes about 40% to 60%.

4. The process of claim 3, in which the high-boiling aromatic petroleum solvent contains, as a minimum, about 75% of sulfonatable constituents.

5. The process of claim 4 in which the reaction with dichloroethylether produces a conversion of chlorine atoms to chloride ions of at least about 35%.

6. The process of claim 5 in which the reaction with dichloroethylether produces a conversion of chlorine atoms to chloride ions between about 40% and 70%.

7. The process of claim 1 in which the depressor component, (C), included in the finished flotation reagent is not more than about 20% of the finished reagent.

8. The process of claim 7, in which the oxyalkylated polyamine used to produce the depressor component is an oxyethylated polyamine in which the molal ratio of ethylene oxide residues to polyamine is not greater than about 1:1.

9. The process of claim 8, in which the collector and depressor components of the reagent are prepared simultaneously by using a mixture of polyamines and monooxyethylated polyamines in the reaction.

10. The process of claim 6, in which the polyamine reactant employed to produce the reagent includes a major proportion of diethylenetriamine.

11. The process of claim 10, in which the reagent is at least partially neutralized as manufactured, and before being used.

12. The process of claim 11, in which the neutralizing agent employed is acetic acid.

13. A concentration process using differential surface wettability principles for separating sylvite from its ores, characterized by subjecting the ore to the action of a material selected from the class consisting of (I) a liquid reagent which includes: (A) a reaction product obtained by (1) first reacting tall oil and a polyethylenepolyamine to provide an intermediate; said reaction including a reaction temperature between 270° and 300° C., the molal proportion of polyamine to tall oil being between about 0.6:1 and 0.8:1, then (2) reacting such intermediate with dichloroethylether, the molal proportion of dichloroethylether to tall oil being between about 0.25:1 and 1:1; (B) a high-boiling petroleum distillate, the proportion of such petroleum distillate in the finished reagent being between about 25% and 75%; and (II) partial neutralization products thereof.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,839,192 June 17, 1958

Louis T. Monson

It is hereby certified that error appears in the printed specificatic of the above numbered patent requiring correction and that the said Lette Patent should read as corrected below.

Column 10, line 25, for "100 pounds" read --800 pounds--; column 14, lines 9 and 10, for "convention" read --conventional--; column 15, line 3, for "oxide", second occurrence, read --oxides--.

Signed and sealed this 14th day of October 1958.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSOI
Commissioner of Pater