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ORE DRESSING

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My invention relates in general to ore dressing.

It relates more in particular to an improved method for producing selective interface modification between the minerals or other constituents of an ore and the liquid medium in which they are suspended and their separation.

In a previous application I disclosed the use of certain new types of reagents for flotation purposes. Flotation involves the selective interface modification of one or more types of substances or minerals in an ore. The substances having selectively modified interfacial relations may be separated in various ways, the most widely used method in recent years being the so-called froth flotation method.

While my prior application was not limited to any particular method of securing actual separation, it was directed more particularly to the use of the froth flotation method of separation. For certain purposes, other means of separation of one constituent of an ore from another is preferred. One method which has had some use is the so-called agglomeration or granulation method of which the Cattermole & Murex processes are illustrative.

In froth flotation as ordinarily carried out one constituent of an ore is selectively modified by the reagents added. These reagents may modify the mineral surface by chemical action or adsorption or both or may modify the interfacial relations with the liquid. In most cases it is the function of flotation reagents to so modify interfacial relationships that the mineral particles to be floated are water repellant. Another function of flotation reagents is to produce a froth wherein the selectively modified mineral will be included.

In the method of agglomeration or granulation I have mentioned the selectively modified mineral-liquid interface is wetted with an oleaginous substance to produce or increase water repellancy and the water repellant oiled particles separated by mechanical means such as the conventional ore dressing table. The frothing element necessary in froth flotation need no longer be present. I have found however, that it is sometimes advantageous to separate the selectively oiled particles by froth flotation and this may be readily done in most cases by the addition of a frother if the particles are not too large. It will be seen from this illustration that the first steps in the agglomeration and flotation processes are identical, namely the production of a selectively modified interfacial relationship between the minerals and the liquid surrounding them.

My present invetion relates to reagents for producing interface modification and particularly to selective oiling of mineral particles and then separation by granulation and tabling or froth flotation.

The principal object of my present invention is the provision of improved means of selectively modifying interfacial relations of minerals in an ore pulp by the use of certain improved types of reagents of my invention and the separation of these minerals by virtue of this interface modification.

Another object is the provision of an improved method for separating minerals by means of agglomeration.

Other objects and features of the invention will be apparent as the detailed description progresses.

The reagents I employ are of a type in which at least one lipophile group of relatively high molecular weight—from six carbon atoms up and a hydrophile group, in the form of an oxygenated acid sulphur containing radical neutralized with a suitable base are present in the same molecule. Preferably a polyhydroxy substance is employed to link the two groups. The type of substance which I use has the lipophile and hydrophile groups in such a state of "balance" that very many of my substances will function as anti-spattering agents which will substantially reduce spattering of margarine during frying when employed in margarine made in the conventional manner from milk and oils and fats in small proportions. The character of these reagents will be more fully understood by more specific references thereto.

Some of the most efficient of my reagents are glycol derivatives in which a high molecular weight fatty acid is esterified with one hydroxy group of the glycol, and the other hydroxy group of the glycol is esterified with sulphuric acid or some equivalent thereof, the sulphate group being neutralized with a suitable alkaline material such as alkali metal hydroxide including sodium and other metals, ammonia, amines and the like. Of this class I have obtained very good results with lauryl diethylene glycol sulphate (neutralized) and cocoanut fatty acid di-ethylene glycol sulphate (neutralized). Other fatty acids may be employed as a source of lipophile groups in the same type of substance, such as oleic acid, palmitic acid, stearic acid, and other acids derived from fats and oils, either substantially pure or mixtures thereof. For many purposes improved results seem to be obtained if a mixture of fatty acids is employed as a source of lipophile groups, and these acids esterified with at least one hydroxy group of a polyhydroxy substance, leaving at least one free hydroxy group which is afterward esterified with a sulphuric acid radical. In this latter step I may employ any of the usual methods of esterification, employing sulphuric acid directly, chlorosulphonic acid under proper conditions, sulphur trioxide, mixtures thereof, or any other reagent or method

by means of which a sulphuric acid radical can be introduced at the hydroxy group.

In place of carboxylic acid esters of glycol, I may employ the alkyl ethers thereof, and then sulphate the same to produce products typified generally by the substance dodecyl diethylene glycol ether sulphate (ethanol amine salt), or the sulphated mixed esters of diethylene glycol with the mixture of alcohols obtained by the reduction of mixed cocoanut fatty acids, or other fatty acids derived from ordinary oils and fats known to commerce.

In place of a glycol I may employ glycerol or polymerized products thereof. The methods of producing the reagent are substantially the same as when a glycol is used. Similarly I may use any suitable fatty acids having at least six carbon atoms in their molecular structure. Examples of glycerol derivatives which I may employ with good results are cocoanut fatty acid esters (sulphated and neutralized), oleic acid esters of glycerine in which at least one hydroxy group of the glycerine is esterified with sulphuric acid, and the like.

In place of employing fatty acids for esterifying with glycerine or glycols, or the like, I may re-esterify a suitable fat or oil with a polyhydroxy substance such as glycerine or glycol or polyglycerol by the use of an alkaline or potentially alkaline catalyst, the re-esterification being carried on at a temperature between approximately 200 and 275° centigrade. It will be understood that this is illustrative, as any suitable means of re-esteriying a fat or oil can be used. This reaction mixture consists essentially of a mixture of fatty acid esters of polyhydroxy substances having free hydroxy groups and at least one free hydroxy group is then esterified with a sulphuric acid radical to produce a final product which when neutralized is suitable for use according to my invention.

The polyglycerols which I may employ are produced by polymerizing glycerine employing a relatively small amount, from about one-tenth per cent to one percent of an alkaline catalyst, such as sodium hydroxide, and heating the mixture preferably in a non-oxidizing atmosphere until a molecular weight determination indicates that the desired amount of polymerization has taken place. A product having the average molecular weight of a diglycerol or triglycerol is in general suitable for the purpose of my invention. This polyglycerol product is then treated to produce fatty acid esters thereof with at least one free hydroxy group, and the resulting product is thereafter treated to produce the sulphate according to any suitable or conventional method.

I may also employ other types of polyhydroxy substances such as sugars, sugar alcohols, mannitol, sorbitol and the like, or, in fact, any polyhydroxy substance capable of being esterified with fatty acids to produce esters with free hydroxy groups which may afterwards be sulphated to produce the final product. I may also employ alkyl sulphates or sulphonates of relatively high molecular weight in my present invention, although for some purposes they do not give as suitable and satisfactory results as the substances previously described, wherein a polyhydroxy substance is employed to link the lipophile group and the hydrophile sulphate group.

In the sulphating step, as previously noted, any conventional or suitable procedure may be used. Generally it is not admissible to subject the product to too rigorous a treatment, and in some cases unesterified hydroxy groups will usually be present. In fact, some portion of substances may be entirely free of sulphate groups. The product may be used, nevertheless, as the presence of a proportion of unsulphated product may be used; in fact, at times, somewhat better results are obtained.

These reagents selectively modify the interface relationships of certain minerals so they may be oiled and separated by either froth flotation or agglomeration and tabling. In some cases the oiling is not necessary—the reagents themselves being sufficient,—some examples of this type are discussed later. The oiling when done may be done simultaneously with the selective interfacial modification produced by my reagents or may be carried on subsequently in a separate step.

In the case of froth flotation, the oil and reagent may be advantageously added as emulsion with water. I have found that in this way highly selective separations may be made by varying the interface modifying reagent and the oil. As an example of such a separation a complex lead zinc iron sulphide ore from Utah may be considered. This ore had the composition—lead 8.8%; zinc 9.7%; iron 28.2%, the remainder was silica and silicates. The ore was ground to pass a 60 mesh screen and made into a pulp containing 20% solids. This pulp was conditioned with 2 lbs. per ton sodium carbonate for 5 minutes and then subjected to froth flotation using as a reagent a water emulsion containing 1% lauryl diethylene glycol sulphate (ammonium salt) and 2% corn oil. An amount of this reagent was initially added to give .2 lb. per ton of ore of the lauryl diethylene glycol sulphate (ammonium salt). The mineralized froth which formed immediately was removed as concentrate No. 1. Additional emulsion to double the original amount was then added and after several minutes further mineralized froth formed; this was removed as concentrate No. 2. When no more mineral appeared in the froth .2 lb. per ton of ore of copper sulphate was added and another concentrate removed. This was concentrate No. 3. The mineral remaining in the machine was removed as tailings. The analyses of these products is shown in the following table.

FROTH FLOTATION OF UTAH COMPLEX ORE

Head analysis Lead 8.8% Zinc 9.7% Iron 28.2%

	Analysis, percent			Recovery, percent		
	Pb	Zn	Fe	Pb	Zn	Fe
1st concentrate	76.2	1.9	0.5	93		
2nd concentrate	1.8	60.5	1.8		89	
3rd concentrate	.2	.8	50.2			86
Tailing	.03	.08	1.9			

It will be seen that the lead zinc iron and insoluble have been very thoroughly separated. I have found that the lauryl diethylene glycol sulfate (ammonium salt) used in this example may be replaced with other compounds of the type disclosed and in particular by sodium dodecyl sulfate, butyl carbitol sulfate (sodium salt), oleyl diethylene glycol sulfate (ammonium salt), stearyl diethylene glycol (ammonium salt), sodium salt of mono-n caprylil diethylene glycol sulfate, monoethanol amine salt of butyl carbitol sulfate, lauryl sulfonic acid (sodium salt) normal octyl sodium sulfate, heptyl sodium sulfate, olein disulfate, sulfated oleic acid ester of di-

glycerol, sulfated monofatty acid ester of glycerol and the sulfated stearic acid ester of glycerol. Not all of these compounds yield as good results as the lauryl diethylene glycol sulfate (ammonium salt) and none of them were useful in as small amounts. I have also found that the corn oil may be replaced with substantially the same results by cottonseed oil, olive oil or palm oil. The use of petroleum oil of various grades gives a somewhat lower selectivity but may be preferred on account of its low cost. Sardine oil, menhaden oil and lard oil may be used with results intermediate between the vegetable oils and mineral oil.

As another example I may cite the separation of ilmenite from a gangue material composed of phosphates, quartz and garnet. This ore analyzed 1.8% TiO_2 as ilmenite. The ore was ground to pass a 60 mesh screen and conditioned with .2 lb. per ton H_2SO_4 and .1 lb. per ton ferric ammonium sulfate. The pulp containing 20% solids was then subjected to froth flotation using an emulsion of 2% crude oil in water and 1% of the sulfated glycerol derivative of mixed cocoanut oil fatty acids neutralized with triethanol amine. An amount of the emulsion equivalent to .5 lb. of oil per ton of ore was used. The concentrate contained 37% TiO_2 and represented a recovery of 94.5%.

In another example malachite was floated from a New Mexico copper ore using an emulsion of 1% sardine oil and 1% normal decyl sodium sulfate in water. The ore contained 1.0% copper and gave an uncleaned concentrate analyzing 38.2% copper.

This technique which I designate as the emulsion technique has been used successfully in slightly acid circuit, on chromite ore, on rutile ore, on hematite ore, and on magnetite ore, in alkaline circuit with the addition of copper sulfate it may be used to float silica, limestone barite, fluorspar, and magnesite. In some cases, particularly when the minerals may be freed at relatively coarse sizes, the froth flotation step may be replaced by agglomeration or granulation and tabling. The first step in this instance, namely selective oiling, may be carried out exactly as in the emulsion technique for flotation.

As an example we may consider an ore of rutile and apatite. This ore contained 3.6% TiO_2 as rutile. It was ground thru 20 mesh and conditioned in a thick pulp with an emulsion of water, corn oil and the sulfated diethylene glycol derivative of the mixed cocoanut oil fatty acids. Using in all .4 lb. per ton of the sulfated reagent and 3 lbs. per ton corn oil, the ore was conditioned by thorough mixing. Water was then added to produce a pulp suitable for tabling. The result of tabling is shown in the following table:

Product	Weight, percent	TiO_2, percent
Table conc.	4.1	88.0
Table tails	95.9	4.9

In general, however, it is preferable to add the surface modifying agent first in a very thick pulp followed by oil with subsequent dilution of the pulp to the proper density for separation on the table. As a typical case we may consider the concentration of an iron ore. An ore from the Lake Superior district contained 30.2% Fe, the gangue being silica. The ore was ground to pass 14 mesh and mixed with a little water, 2 lb. per ton H_2SO_4 and 1 lb. per ton sulfated diethylene glycol ester of mixed cocoanut oil fatty acids. Crude mineral oil in amount of 6 lbs. per ton was then added and the whole mixed. After dilution and tabling the results are shown in the following table

Product	Weight, percent	Fe, percent
Table conc.	51.2	63.2
Table tails	49.8	8.2

This process may be used on chromite, magnetite, apatite, limestone, dolomite, magnesite and bauxite, without especial care in the selection of reagent or oil. In other cases however the selection of interface modifying agent is very critical. Such a case is the separation of sylvite and halite as they occur at Carlsbad, N. M. Since these minerals are soluble, the surface modifying agent must be stable to saturated brine. That is the reagent must be soluble enough to promote oiling but must selectively effect the interfacial relations between either sodium or potassium chloride and brine. Since potassium salts are in general more insoluble than sodium salts, I have hypothecated that the reagent acts in this case by precipitation of a film of potassium salt, but that enough must remain in solution to serve as an oil carrier.

The reagent which has produced unusually good results for the separation of these two minerals is mixed cocoanut fatty acid diethylene glycol sulphate neutralized with ammonia, sodium hydroxide, ethanol amine, or tri-ethanolamine. Still other neutralizing substances may be used but in general very satisfactory results have been obtained if the product is neutralized by the substances described. My process may be carried out according to several procedures to produce a mixture of brine, mineral oil and the fatty acid diethylene glycol, sulphate, neutralized with triethanolamine, or ammonia, wherein the oil is selectively adsorbed by the sylvite but does not coat the halite, with the result that the sylvite is formed into glomerules of such composition and size that ordinary tabling is sufficient to separate them. The concentrate consists of 85 to 95% potassium chloride, the tailings containing only about 5% of potassium chloride, or less. The concentrate may be air dried and treated to produce a product acceptable for agricultural purposes. The presence of small amounts of oil is not objectionable.

According to one procedure I form an emulsion of 25 pounds of oil, one pound of the reagent, and enough brine made from the ore to produce a total of 100 pounds of emulsion. This emulsion is then added to the ore, which is in the form of a relatively thin pulp of 12 to 16 mesh ore, the proportions being such that about one and one-half to four pounds of reagent and 10 to 15 pounds of oil are present in about a ton of ore. The ore with the emulsion added thereto is agitated slowly by means of a slow-moving stirring-arm, or in any other suitable manner, for approximately five minutes, until the sylvite is agglomerated into particles of a sufficient character and size to permit easy separation. The glomerules are easily observed by the operator for the purpose of determining when the product has advanced to a suitable condition for treatment on a separating table. Although tabling is very satisfactory for the purpose, any other

suitable method of separation commonly used in the ore dressing industries can be employed.

Another method is to add the oil to a very thick pulp and introduce the reagent dispersed in an additional amount of water. By this method the amount of reagent may be reduced to 1.6 lbs. per ton of ore. The results of a test made in this way are shown in the following table.

Product	Weight, percent	Percent KCl	Total KCl, percent
Table concentrates	45.2	85.1	95.2
Table tails	54.8	4.0	4.8
Composite	100	40.6	100

According to another modification, 2,000 lbs. of sylvinite reduced to a size of 12 to 16 mesh, are moistened with a brine (a saturated brine prepared from the ore is convenient). To this are added 4 lbs. of ethanol amine salt of mixed cocoanut fatty acids esters of diethylene glycol sulfate, with thorough stirring to produce a substantially uniform mixture. This mixture can be seen to have incorporated considerable air. Fifteen pounds of crude oil are now stirred in and dispersed uniformly. Approximately 2,000 lbs. of brine are incorporated, and the total of approximately two tons tabled. A high grade concentrate of sylvite, averaging about 90% KCl, is obtained, with only about 5% KCl in the tails. The tails may be in part recirculated to increase the proportionate yield of potassium. The concentrate may be dried suitably, in air, for example, and may be crushed if desired to give an acceptable agricultural potassium chloride product.

The amount of reagent and oil used are not extremely critical insofar as separation is concerned, but in the interest of economy no more reagent should be used than is sufficient to produce a good separation. No more than enough oil to wet the sylvite particles should be employed because it has a tendency to separate out on the tables or other equipment used for separation, and this requires periodic cleaning which can be avoided if the amount of oil is cut down.

While many oil constituents may be employed, the best results are obtained if a crude oil is used. I have found that Gulf Coast crude oils produce particularly good results. I have also found that if the crude oil is treated to remove some of the volatile constituents, the amount of oil can be decreased and in general somewhat better results are obtained.

Other reagents may be successfully used in the agglomeration of sylvite such as oleyl diethylene glycol sulphate (sodium salt), mixed cocoanut fatty acid glycerol sulfate (ammonium salt), sodium salt of sulfated cocoanut fatty acids, lauryl sulfonic acid, octyl sulfonic acid, decyl sulfonic acid. With any of these reagents the oiled sylvite may be separated by froth flotation instead of agglomeration and tabling by decreasing the amount of ore and adding suitable frother if necessary.

The sylvite may also be separated by froth flotation without oiling. For this purpose it is necessary according to my hypothesis to use a reagent which precipitates an insoluble potassium salt with a long lipophile group outward so as to make the particles water repelling. For this purpose I have found the sodium or ammonium salts of the fatty alcohol sulfates having 6–14 carbon atoms effective, particularly octyl sodium sulfate. To produce the best results the ore is ground to pass a 48 mesh screen and conditioned by the addition of a small amount of aqueous solution of normal octyl sodium sulfate amounting to 0.8 lb. per ton ore. The ore is then made to a 20% pulp in saturated brine made from the mineral and subjected to froth flotation. The results are shown in the following table:

Product	Weight %	KCl %	Total KCl
Cleaner conc	42.8	95.6	94.2
Middlings	6.8	25.2	3.2
Rougher conc	50.8	85.8	98.8
Tailings	49.2	1.4	1.7
Composite	100	42.9	100

Separation can be obtained with sodium dodecyl sulphate or lauryl sulphonic acid (sodium salt) although not nearly so satisfactorily as with octyl sodium sulphate.

Since according to my hypothesis this flotation action depends on the formation of an insoluble potassium salt, the method would be applicable to the separation of any mixture containing a soluble potassium salt. I have found that cement dust containing 10% K_2O may be concentrated by flotation by adding 2 lb. per ton H_2SO_4 and 1.2 lb. per ton normal octyl sodium sulfate. The concentrate analysed 48.7 K_2O.

I have also found that the mineral langbeinite containing potassium sulfate may be concentrated by flotation from its associated halite using exactly the same methods as described for sylvite. I have also found that other salts as those of barium, lead, and zirconium and ferric iron may be separated from salts of potassium zinc calcium or magnesium by the use of sodium dodecyl sulfate or normal octyl sodium sulfate as flotation reagents.

In still other cases I artificially produce coatings of ferric iron on minerals to be separated and treat these coated minerals for separation by froth flotation using reagents like sodium octyl sulfate or sodium dodecyl sulfate.

It will be obvious that examples of the application of my invention to the separation of soluble salts might be multiplied indefinitely but the foregoing will make my invention clear and I wish to be limited only by the appended claims.

Wherever the term "higher" is employed herein and in the claims, it will be understood to mean from six to fourteen carbon atoms unless otherwise specifically stated.

I claim:

1. A process for concentrating ores containing potassium chloride and sodium chloride, which comprises subjecting the ore pulp, in a substantially saturated brine, to a froth flotation treatment in the presence of octyl sulphate or soluble salts thereof.

2. A process for separating sylvite from halite which comprises forming a substantially saturated brine from an ore containing the same and subjecting the resulting mass to froth flotation in the presence of a small amount of octyl sodium sulphate.

3. The separation of soluble salts of the group consisting of potassium, barium, lead, ferric iron, and zirconium from soluble salts of the group consisting of sodium, calcium, magnesium, and zinc, by adding thereto octyl sulphate or soluble salts thereof and subjecting the mixture to froth flotation in a substantially saturated solution of the salts in the mixture.

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