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DEMULSIFYING COMPOSITIONS

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9 Claims. (Cl. 252—336)

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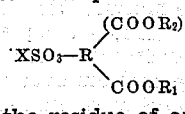
This invention relates to demulsifying compositions of a type suitable for use in breaking either oil-in-water emulsions or water-in-oil emulsions of mineral, vegetable or synthetic oils, waxes, resins and the like, including those prepared by the use of soap or synthetic emulsifying agents. The invention includes the novel demulsifying compositions hereinafter described and processes of breaking emulsions of the water-in-oil type or the oil-in-water type by subjecting the emulsion to the action of a demulsifying agent containing these compositions.

In its broader aspects, the invention includes demulsifying compositions containing a surface-active ester of an aliphatic sulfopolycarboxylic acid together with an aspartate amide of an aliphatic sulfopolycarboxylic acid, as hereinafter defined. I have found that these two classes of demulsifying agents cooperate to produce results which are not obtainable with either ingredient when used alone, and that a much more effective demulsifier is obtained when the two types of compounds are used together.

The surface-active esters of aliphatic sulfopolycarboxylic acids are well-known demulsifying agents. Thus, for example, in U. S. Patent No. 2,072,085 the effectiveness of the salts and esters of sulfosuccinic acid is demonstrated in the treatment of oil-field petroleum emulsions of the water-in-oil type. Similarly, the effectiveness of the esters and salts of sulfotricarboxylic acids as demulsifying agents is stated specifically in U. S. Patent No. 2,315,375. Any of the aliphatic sulfopolycarboxylic acid esters described in either of these patents may be used in the compositions of the present invention, and therefore the preparation of specific compounds of this class need not be described in detail. I prefer to employ the diesters of aliphatic sulfodicarboxylic acids such as diamyl, dihexyl, dioctyl or didecyl sulfosuccinates, since these have produced excellent results in practice. However it should be understood that the esters of aliphatic sulfotricarboxylic acids, and particularly the triesters such as tributyl, triamyl or trihexyl sulfotricarballylate may also be employed if desired. It will be understood that the term "surface-active esters of aliphatic sulfopolycarboxylic acids" is intended to mean compounds of the formula



in which R is the residue of an aliphatic polycarboxylic acid, R_1 is an alkyl radical of 4–18 carbon atoms, R_2 is a member of the group consisting of alkyl radicals and cationic salt-forming radicals, n is 1 or 2 and X is a cationic salt-forming radical, these compounds being described in U. S. Patents Nos. 2,028,091 and 2,315,375.

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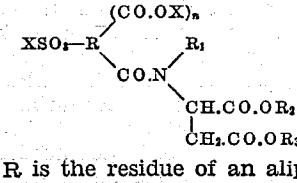
The aspartate amides of aliphatic sulfopolycarboxylic acids used in the compositions of the present invention are compounds having the formula



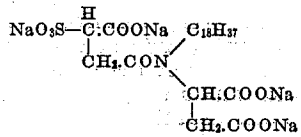
in which R is the residue of an aliphatic polycarboxylic acid, R_1 is an alkyl or alkoxyalkyl radical of 8–18 carbon atoms, R_2 and R_3 are members of the group consisting of hydrogen, cationic salt-forming radicals and alkyl radicals, each X is a member of the group consisting of hydrogen and salt-forming radicals and n is 1 or 2. These compounds are preferably prepared by reacting an N-alkyl or alkoxyalkyl substituted aspartate with maleic anhydride or with maleic or fumaric acid, or with an alky maleate or fumarate or with aconitic acid or anhydride or a salt or ester thereof followed by sulfonating the resulting mono-amide. Suitable methods of preparation are described in the following specific examples. Although the compounds prepared from the esters of maleic or fumaric acid such as the dimethyl, diethyl or dibutyl esters, may be employed if desired, I prefer those compounds in which the carboxylic acid groups of the aspartate radical are neutralized with a cationic salt-forming radical, and are therefore in the form of carboxylic acid salts. The sodium, potassium and ammonium salts are preferred. This is also true of the free carboxylic acid radical or radicals of the aliphatic sulfopolycarboxylic acid, corresponding to —CO.OX in the above formula.

As is indicated above, the two essential ingredients of the compositions of my invention may be used in any desired ratio; i. e., the quantity of aliphatic sulfopolycarboxylic acid esters may be greatly in excess of the quantity of aliphatic sulfopolycarboxylic acid aspartate or vice versa. However those compositions in which a surface-active ester of an aliphatic sulfopolycarboxylic acid is present in amounts at least equal to or preferably greater than the amount of aspartate amide are preferred, since the aliphatic sulfopolycarboxylic acid esters are usually cheaper than the aspartate amides. In general, I prefer those compositions containing about 5–9 parts by weight of the aliphatic sulfopolycarboxylic acid

ester for each 1–6 parts of an aspartate amide of an aliphatic sulfodicarboxylic acid of the type defined by the above formula.

In the demulsifying compositions of my invention the active demulsifying agents may be dissolved in water or in an organic solvent such as methyl, ethyl or propyl alcohol or in a non-polar solvent such as benzene, toluene and the like. Concentrated solutions are preferably prepared in water-soluble solvents such as ethanol or propanol and may be added to the emulsion as such or after dilution with water or other solvent to the desired concentration.

One of the principal advantages of the compositions of the present invention resides in the range of concentrations in which they may be used. Experience has shown that the aliphatic sulfopolycarboxylic acid esters, when used alone, are quite specific in their action; i. e., they are good demulsifying agents at one particular ratio of ester to emulsion but show a sharp reduction in their demulsifying power when used in smaller or even sometimes in greater quantities. Thus, for example, a wide variety of oil-field petroleum emulsions of the water-in-oil type can be broken with sodium dioctyl sulfosuccinate when used at a concentration of 0.05%, based on the weight of the emulsion, but the resolution is incomplete when smaller quantities are used. In tests conducted with the same emulsion, which was an emulsion of salt water in California crude oil, successful results were obtained throughout a range of 0.025–0.25% of a demulsifier containing equal quantities of sodium dioctyl sulfosuccinate and the compound



The compositions of the present invention give a much faster and more complete resolution of emulsions than do the corresponding esters of aliphatic sulfopolycarboxylic acids when used alone, and this action persists throughout a much wider range of concentrations of demulsifying agent in the emulsion.

Although excellent results are obtained with compositions in which the two types of ingredients specified above constitute the only demulsifying agents present, it will be understood that the invention includes compositions in which other known or approved demulsifying agents are also present. Thus, for example, salts of aromatic sulfonic acids or their condensation products with formaldehyde or other aldehydes, alkylated aryl sulfonates such as sodium isopropyl naphthalene sulfonate, sodium keryl benzene sulfonate, ethylene oxide condensation products of alkylol amides of higher fatty acids such as ethanol stearamide and the like may be present in the compositions of the present invention if desired. These and other known demulsifying agents can frequently be used to advantage by those skilled in the art as ingredients of the compositions of the present invention.

In practicing the process of the present invention, in which emulsions of the oil-in-water type or of the water-in-oil type are broken or resolved by contact with the compositions defined above, any of the known methods of treatment may be used. The demulsifying composition may be added continuously or intermittently to pipe lines through which the emulsion is being pumped, or it may be added to storage tanks containing the emulsion, or it may be brought into contact with or caused to act upon the emulsion in any of the various types of apparatus now generally employed to resolve or break emulsions, and at ordinary or at elevated temperatures. In the treatment of oil-field emulsions the compositions may be used with success at ratios of active demulsifying agent to emulsion of 1:10,000 or higher, although for best results the range of 0.025–0.25% given above is usually preferred. In breaking emulsions of the oil-in-water type it is frequently desirable to use larger quantities of the demulsifying agent.

Although the following examples may describe certain preferred embodiments of the invention, they are given primarily for purposes of illustration. These examples describe particularly the method of preparation of the aspartate amides of aliphatic sulfopolycarboxylic acids, since these methods are not readily available. As is noted above, the methods of preparing the aliphatic sulfopolycarboxylic acid esters are quite well-known, and are described in the patents referred to at the beginning of the present specification.

Example 1

A solution of 142 grams of N-dodecylamine in 250 cc. of t-butanol was prepared and 105 grams of dimethyl maleate was added with stirring. The mixture was allowed to stand at room temperature for 69 hours, after which it was heated to 60° C., 79 grams of maleic anhydride was added with stirring, and the reaction mixture was heated at 85°–90° C. for one hour. The resulting product was poured into a hot solution of 100 grams of sodium sulfite in 375 cc. of water and heated for 10 minutes. After evaporating the solvent the N-dodecyl N-(disodium sulfosuccinyl) dimethyl aspartate was obtained as a cream-colored solid.

This product may be used as such for admixture with esters of aliphatic sulfopolycarboxylic acids or it may be converted into the N-dodecyl N-(disodium sulfosuccinyl) disodium aspartate by saponification with excess sodium hydroxide solution.

A mixture of 40 grams of triamyl sulfotricarballylate and 20 grams of the N-dodecyl N-(disodium sulfosuccinyl) dimethyl aspartate was dissolved in 50 cc. of isopropanol. This solution was added to an emulsion of the water-in-oil type prepared by agitating 25 parts by weight of sea water with 75 parts of a California crude petroleum from the Ventura Avenue field. The emulsion was broken at a concentration of 0.03% of the demulsifying composition (100% solids) based on the weight of the emulsion.

Example 2

144 grams of dimethyl maleate was added slowly with stirring to a solution of 265 grams of octadecylamine in 500 cc. of tertiary butanol at 50° C. and the mixture was allowed to stand at 28° C. for 65 hours. 100 grams of maleic anhydride was then added slowly with agitation at 50°–60° C. and the mixture was heated at 85°–90° C. for one hour to insure completion of the reaction. The product was then sulfonated by slowly adding the maleamic acid solution to a solution of 130 grams of sodium sulfite in 300 cc. of hot water with good agitation. The sulfonation product, N-octadecyl N-(disodium sulfosuccinyl) dimethyl aspartate, was obtained as a clear

yellow solution which dried to a cream-colored powder.

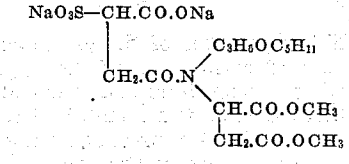
Equal parts by weight of this powder and of sodium dioctyl sulfosuccinate were dissolved in isopropanol and used for the resolution of a petroleum emulsion of the water-in-oil type, prepared as described in Example 1. The emulsion was broken at concentrations of 0.05% of the mixture, based on the weight of the emulsion.

A sodium salt was prepared by adding a concentrated aqueous solution containing 8 grams of NaOH to 40 grams of the N-octadecyl N-(disodium sulfosuccinyl) dimethyl aspartate and allowing the mixture to stand for 2 hours. The solution was then adjusted to a pH of 7 by adding dilute hydrochloric acid and the product, N-octadecyl N-(disodium sulfosuccinyl) disodium aspartate, was recovered by evaporating the solution. The product was mixed with sodium dioctyl sulfosuccinate to form a solution containing 40 parts by weight of each of the two surface-active agents (100% basis) and 20% isopropanol. This mixture broke the same emulsion at a concentration of 0.025%.

Example 3

N-amoxypropyl dimethyl aspartate was prepared by dissolving 145 grams of amoxypropylamine in 400 cc. of tertiary butanol, adding 144 grams of dimethyl maleate slowly and allowing the mixture to stand for 75 hours, followed by evaporation of the solvent at reduced pressure.

58 grams of this product was added slowly with stirring to 20 grams of molten maleic anhydride while keeping the temperature between 55° and 70° C. The resulting maleamic acid was poured into a hot solution of 26 grams of sodium sulfite in 150 cc. of water and the mixture was heated at 80°–90° C. for one hour. The resulting solution was evaporated to dryness yielding N-amoxypropyl N-(disodium sulfosuccinyl) dimethyl aspartate of the formula

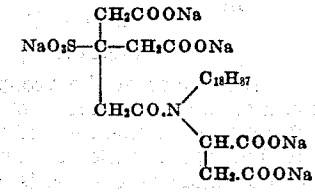


A mixture of 9 parts by weight of sodium diamyl sulfosuccinate with one part of this product was dissolved in 10 parts of isopropanol. When tested on the emulsion described in Example 1 it was found to be an effective demulsifier at a concentration of 0.04%.

Example 4

Dimethyl N-octadecyl aspartate was prepared from 11.2 grams of dimethyl maleate and 21.6 grams of octadecylamine by heating these in 64 ml. of t-butanol at 85° C. for 10 hours. To the solution was added slowly 12 grams of aconitic anhydride, and heating was continued for one hour. The mixture was then poured into 300 cc. of a solution containing 3.2 grams of sodium hydroxide and 10.5 grams of sodium sulfite. After stirring for 40 minutes on the steam bath the solution was cooled, washed with ether, and evaporated to dryness. The product was trisodium N-octadecyl N - (1,2 - dicarbomethoxyethyl) sulfotricarballylamate, a soft orange-colored water-soluble solid.

This product was tested as a demulsifier in admixture with 20–60% of its weight of sodium dioctyl sulfosuccinate and of trihexyl sulfotricarballylate, and the mixtures were effective when tested against the emulsion described in Example 1 at concentrations of 0.02–0.04%. Even better results were obtained from a portion which was saponified with an excess of strong sodium hydroxide solution to produce the pentasodium salt of the formula



A solution of 6 grams of this product and 4 grams of sodium dioctyl sulfosuccinate in 10 cc. of ethanol was tested on the same water-in-oil petroleum emulsion and was found to be an excellent demulsifying agent at 0.025% concentration.

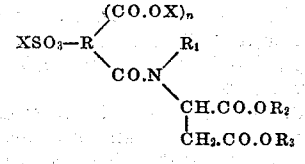
Example 5

The demulsifying compositions described in the preceding examples are of great value in separating industrial emulsions, many of which are very troublesome. Thus, for example, in the extraction of vanillin from neutralized sulfite liquor with benzene an emulsion of the oil-in-water type containing about equal volumes of benzene and sulfite liquor is formed which is stabilized by the colloids of the sulfite liquor and is very difficult to break. I have found, however, that this emulsion can be separated by treatment with compositions of the present invention.

A sample of the emulsion treated with amounts up to 0.25% its weight of sodium dioctyl sulfosuccinate was broken only very slowly and with difficulty. Addition of a water solution of N-octadecyl N-(disodium sulfosuccinyl) disodium asparate, prepared as described in Example 2, gave similar results. However, upon adding a water solution containing 12.5% of sodium dioctyl sulfosuccinate and 12.5% of N-octalecyl N-(disodium sulfosuccinyl) disodium aspartate in amounts of 0.4% on the weight of the emulsion (corresponding to 0.1% of the active materials) the emulsion broke in 2 minutes.

What I claim is:

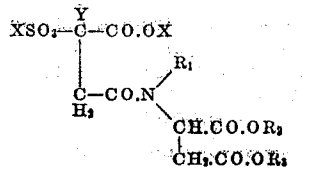
1. A demulsifying composition comprising a mixture of about 17% to 90% by weight of a surface-active ester of an aliphatic sulfopolycarboxylic acid and about 83% to 10% by weight of an aspartate amide of an aliphatic sulfopolycarboxylic acid having the formula



in which R is the residue of an aliphatic polycarboxylic acid, R_1 is a member of the group consisting of alkyl and alkoxyalkyl radicals of 8–18 carbon atoms, R_2 and R_3 are members of the group consisting of hydrogen, cationic salt-forming radicals and alkyl radicals, n is a whole number not greater than 2 and each X is a member of the group consisting of hydrogen and cationic salt-forming radicals.

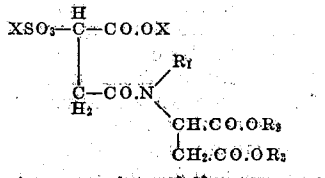
2. A demulsifying composition comprising a mixture of about 17% to 90% by weight of a surface-active ester of an aliphatic sulfopolycarboxylic acid and about 83% to 10% by weight

of an aspartate amide of an aliphatic sulfopolycarboxylic acid having the formula



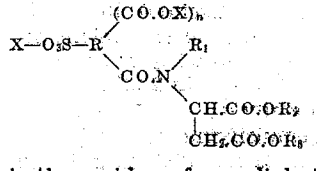
in which R_1 is a member of the group consisting of alkyl and alkoxyalkyl radicals of 8–18 carbon atoms, R_2 and R_3 are members of the group consisting of hydrogen, cationic salt-forming radicals and alkyl radicals, each X is a member of the group consisting of hydrogen and cationic salt-forming radicals and Y is a member of the group consisting of hydrogen and $-CH_2COOX$.

3. A demulsifying composition comprising a mixture of about 17% to 90% by weight of a surface-active ester of an aliphatic sulfopolycarboxylic acid and about 83% to 10% by weight of an aspartate sulfosuccinamate having the formula



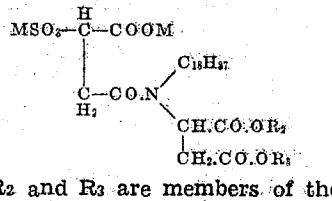
in which R_1 is a member of the group consisting of alkyl and alkoxyalkyl radicals of 8–18 carbon atoms, R_2 and R_3 are members of the group consisting of hydrogen, cationic salt-forming radicals and alkyl radicals and each X is a member of the group consisting of hydrogen and cationic salt-forming radicals.

4. A demulsifying composition comprising a mixture of 5–9 parts by weight of a surface-active ester of an aliphatic sulfopolycarboxylic acid and 1–6 parts of an aspartate amide of an aliphatic sulfopolycarboxylic acid of the formula



in which R is the residue of an aliphatic polycarboxylic acid, R_1 is a member of the group consisting of alkyl and alkoxyalkyl radicals of 8–18 carbon atoms, R_2 and R_3 are members of the group consisting of hydrogen, cationic salt-forming radicals and alkyl radicals, n is a whole number not greater than 2, and each X is a member of the group consisting of hydrogen and cationic salt-forming radicals.

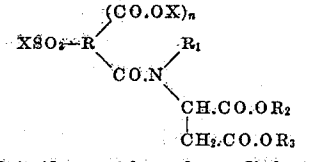
5. A demulsifying composition comprising a mixture of 5–9 parts by weight of a surface-active ester of an aliphatic sulfopolycarboxylic acid and 1–6 parts of an aspartate sulfosuccinamate of the formula



in which R_2 and R_3 are members of the group consisting of hydrogen, cationic salt-forming radicals and alkyl radicals and each M is an alkali metal.

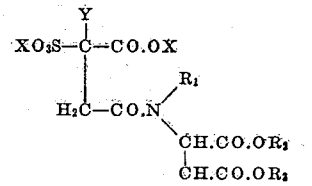
6. A demulsifying composition comprising a mixture of 5–9 parts by weight of sodium dioctyl sulfosuccinate and 1–6 parts by weight of N-octadecyl N-(disodium sulfosuccinyl) disodium aspartate.

7. A process for breaking aqueous emulsions which comprises subjecting the emulsion to the action of a demulsifying agent comprising as the principal active demulsifying ingredients a mixture of an ester of an aliphatic sulfopolycarboxylic acid and a compound of the formula



in which R is the residue of an aliphatic polycarboxylic acid, R_1 is a member of the group consisting of alkyl and alkoxyalkyl radicals of 8–18 carbon atoms, R_2 and R_3 are members of the group consisting of hydrogen, cationic salt-forming radicals and alkyl radicals, n is a whole number not greater than 2 and each X is a member of the group consisting of hydrogen and cationic salt-forming radicals, the two ingredients being present in a weight ratio of about 17% to 90% of the first to about 83% to 10% of the second.

8. A process for breaking aqueous emulsions which comprises subjecting the emulsion to the action of a demulsifying agent comprising as the principal active demulsifying ingredients a mixture of an ester of an aliphatic sulfopolycarboxylic acid and a compound of the formula



in which X is a member of the group consisting of hydrogen and cationic salt-forming radicals, Y is a member of the group consisting of hydrogen and CH_2COOX, R_1 is a member of the group consisting of alkyl and alkoxyalkyl radicals and R_2 and R_3 are members of the group consisting of hydrogen, cationic salt-forming radicals and alkyl radicals, the two ingredients being present in a weight ratio of about 17% to 90% of the first to about 83% to 10% of the second.

9. A process for breaking aqueous emulsions which comprises subjecting the emulsion to the action of a demulsifying agent comprising as the principal active demulsifying ingredients a mixture of 5–9 parts by weight of sodium dioctyl sulfosuccinate with 1–6 parts of N-octadecyl N-(disodium sulfosuccinyl) disodium aspartate.

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The following references are of record in the file of this patent:

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