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3,294,703

DISPERSING AGENTS

Keith Liddell Johnson, Park Forest, Ill., assignor to Swift & Company, Chicago, Ill., a corporation of Illinois

No Drawing. Filed Oct. 27, 1961, Ser. No. 148,033

5 Claims. (Cl. 252—353)

This invention relates to emulsifiable compositions and to the process of preparing emulsifiable compositions which are dispersible in water to form oil-in-water emulsions. More particularly, the invention pertains to non-ionic-anionic mixtures and to the process of preparing nonionic-anionic mixtures of surface-active agents which may be dissolved in oily materials for the purpose of making such emulsifiable compositions.

Mixtures containing various concentrations of two or more types of surface-active agents have been disclosed for particular purposes in the various arts. Combination emulsifiers in which one of the components is the salt of a sulfonated organic material and the other is a non-ionic surface-active agent have, in particular, been found useful in the preparation of readily emulsifiable oil concentrates. Such concentrates are useful as carriers for herbicides and insecticides for agricultural purposes.

In order to facilitate the rapid and thorough distribution of agricultural pesticides, fertilizers, disinfectants, herbicides, fungicides, rodenticides, germicides, weed control agents and their solutions, a system in which the active agent and its carrier solvent, if any, are dispersed or dissolved in water immediately prior to application to the proposed treatment area is commonly utilized. The most important components determining the feasibility of such a system are the combination of surface-active agents that, when present, facilitate the production of a uniform solution or dispersion of the concentrate in the aqueous carrier which is generally the continuous medium or external phase.

Heretofore the aforementioned surface-active agents have consisted of a mixture of a solution of an alkaline earth sulfonate and a polyalkylene glycol alkyl or alkyl aryl ether or ester. Anionic-nonionic mixtures comprising calcium dodecyl benzene sulfonate and nonionic emulsifiers which are derivatives of polyethylene or propylene glycol have found wide acceptance as emulsifiers for oil solutions of agricultural toxicants.

The ratio between the ionic and nonionic components is varied from system to system to enable one particular set of surface-active agents to achieve optimum performance regardless of the variant hydrophobic or hydrophilic nature of the active agent and/or its carrier solvent. These systems have the disadvantage that three separate manufacturing processes are necessary in their preparation. These processes are (1) manufacture of the non-ionic detergent; (2) manufacture and drying of the anionic detergent; and (3) blending of the nonionic and anionic detergent to form an acceptable emulsifier system. The sensitivity of these systems to variations in water hardness, temperature, and variations in dilution also leave much to be desired.

The proposed system alleviates the above difficulties by (1) cutting the number of steps necessary for the manufacture of the emulsifier system, and (2) providing a system that is relatively insensitive to variations in water hardness, temperature, and use concentrations. I have discovered that the reaction between a metal oxide, carbonate or hydroxide and the alkyl or alkyl aryl sulfonic acid which is used in the production of the anionic detergent for the emulsifier can proceed at a rapid and useful rate in the presence of the addition products prepared by condensing an alkylene oxide with a compound having an active hydrogen in its structure. Such alk-

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oxylated materials are quite commonly used in the non-ionic portion of said emulsifiers.

According to the present invention, an alkaline earth oxide carbonate or hydroxide is dispersed in a mixture of the alkoxylated nonionic detergent and the solvent diluent prior to the addition of the sulfonic acid. This procedure cuts the number of manufacturing steps to two by combining the production of the sulfonate salt and the mixing operations previously necessary.

In the prior art process of preparing emulsifiable compositions a calcium hydroxide slurry is added to a solvent solution of a sulfonic acid containing a nonionic emulsifier. The nonionic emulsifier is present to maintain a homogeneous reaction mixture. After the neutralization step in this process, the reaction mixture is vacuum-stripped to remove the excess water which is present.

In my method I do not use a slurry to accomplish the neutralization nor is the nonionic surfactant present to maintain a homogeneous reaction mixture. My process dictates that the nonionic detergent be present to catalyze the reaction in the absence of significant amounts of water, this fact being demonstrated by the observation that the neutralization will not take place in the reaction mixture in the absence of the nonionic detergent, but will take place in its presence, presumably due to an activation of the oxide, hydroxide, or carbonate by the polyether hydrophile of the nonionic detergent.

Inasmuch as the instant system is almost anhydrous, the removal of a considerable amount of water is also eliminated from the manufacturing procedure. The instant process is a substantial improvement in that the necessity for vacuum-stripping after filtration is eliminated.

Another advantage is gained in the proposed system by the use of higher molecular weight alkylated detergents. I have found that the keryl benzene sulfonates provide performance levels that are higher in a wider range of applications than are the corresponding dodecyl derivatives presently in common use. A similar advantage has been found in the utilization of dialkylated polyalkylene glycol monoethers such as ethoxylated dioctyl, dinonyl or didodecyl phenol. These advantages combine to offer an emulsifier system that has a wider spectrum of application than those heretofore described by the art while lowering manufacturing costs considerably.

An object of this invention is to provide a novel process for preparing mixed anionic-nonionic emulsifiers.

Another object is to provide a process for neutralizing sulfonated organic compounds while lowering manufacturing costs.

Additional objects, if not specifically set forth herein, will be readily apparent to those skilled in the art from the detailed description of the invention which follows.

Among the preferred organic sulfonic acids useful in the practice of this invention are the alkyl or polyalkyl aryl sulfonic acids containing from about 8 to about 22 carbon atoms or more in the alkyl radical.

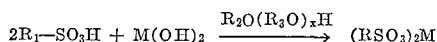
Of course, lower substituted aromatic sulfonic acids such as toluene, xylene, benzene, styrene, propylbenzene sulfonic acids, etc., are operable. Examples of higher alkyl substituted aromatic sulfonic acids include nonylbenzene, dodecylbenzene, tetradecylbenzene, octadecylbenzene, dinonylnaphthalene, polydodecylbenzene sulfonic acids as well as commercial mixtures of the above acids.

Among the metal reactants which are useful in this process are metal oxides, hydroxides, and salts. The invention is particularly applicable to the alkali and alkaline earth oxides, hydroxides, and carbonates, such as calcium hydroxide, barium hydroxide, magnesium oxide, strontium oxide, beryllium oxide, zinc oxide, magnesium oxide, calcium carbonate, etc.

Compounds falling in the category of the nonionic

agents utilized in the instant process are prepared by condensing an alkylene oxide with a compound having an active hydrogen in its structure. Examples of such alkoxylated materials are polyalkylene glycol, alkyl or alkyl aryl ethers or esters. Specific examples of such compounds are polyethylene glycol, propoxylated lauryl alcohol, polyepichlorohydrin, ethoxylated dodecylmercaptan, ethoxylated stearyl alcohol, ethoxylated palmitamide, ethoxylated 1,1,3,3-tetramethylbutyl phenol as well as other alkoxylated alkyl and polyalkyl phenols. It is understood that any of the polyalkyloxylated compounds mentioned hereinbefore may be utilized with any of the organic sulfonic acids and metal reactants.

The production of these materials can be represented by the following general reaction:



where R_1 is an alkyl or alkyl aryl organic radical, M is a metal, and R_2 is an alkyl, alkyl aryl, dialkyl aryl or trialkyl aryl radical and R_3 is a 1,2-ether with from 2 to 4 carbon atoms or more. The best results so far obtained have been with R_1 as keryl benzene, R_2O as dinonyl phenoxy, R_3 as ethylene and M as calcium with x varying from 10 to 50.

As mentioned above, the ratio between the nonionic and ionic components is varied from system to system, the ratio of nonionic to anionic being usually in the range of 1-10 to 6-1.

Usually an excess of the base is used such as a two-fold or threefold excess with respect to the sulfonic acid.

The neutralization reaction being exothermic, no heat need be applied. The reaction temperature starts at room temperature and usually goes up to around 170° F. However, at temperature range of 150°-190° F. or more is permissible. Of course, one may preheat any of the materials or solvents if the working area is such that the solvent employed is a solid at room temperature.

The following examples illustrate the invention, but such examples are not to be construed as limiting the scope of the invention.

Example I

A high performance emulsifier can be manufactured by the following process:

(1) Disperse 4-5 parts by weight calcium hydroxide in a mixture of 25-30 parts of "Igepal DM-710" which is ethoxylated dinonyl phenol containing 70-74% ethylene oxide by weight or "Igepal DM-730" which contains 73% ethylene oxide and 30-50 parts of an aromatic solvent such as Bronoco "Hi Sol 4-2" which contains aromatic naphtha.

(2) This mixture is reacted with 20-35 parts of an alkyl benzene sulfonic acid such as "Nacconol SZA," (a keryl benzene sulfonic acid) until an aqueous dispersion of the reaction product demonstrates a pH of 3-6.5. No heat is needed and the reaction goes to completion within a few minutes.

An example of wherein specific amounts are used follows.

Disperse 5.50 parts by weight of $Ca(OH)_2$ in 42.00 parts by weight of an aromatic naphtha and 26.25 parts by weight of ethoxylated dinonyl phenol. This mixture is reacted with 24.25 parts by weight of kerylbenzene sulfonic acid. Two parts by weight of a filter aid (diatomaceous earth) is added.

The above suffices to fully illustrate the invention and multiplication of the number of examples illustrating in detail the preparation of an emulsifying composition of the anionic-nonionic type will be avoided. Other specific combinations which may be prepared are presented below.

Example II

	Parts
Pluronic L-64 (a butylene oxide, ethylene oxide copolymer) -----	5-50
Zinc oxide -----	3-10
Solvent -----	20-70
Sulfonated vegetable oil -----	10-50

Example III

Calcium carbonate -----	5-20
Orthodichlorobenzene -----	0-70
Ethoxylated dodecylmercaptan -----	5-60
Turkey red oil -----	10-50

As mentioned above, an improvement resides in the step of conducting the reaction under substantially anhydrous conditions. A factor on the extent to which our reaction conditions are anhydrous is the amount of water present in the raw materials. This will generally run from 1.0 to 1.5 weight percent of the total formula weight, but may be as low as essentially nothing. In addition to this moisture, using calcium hydroxide for example, 1.6% moisture is theoretically produced. The other bases and salts under discussion would all produce lesser amounts of water.

Substantially anhydrous conditions are taken to be about 5%. The preferred range is from zero to about 2% while less than ½ % is most desirable. Above around 2% a separation into layers takes place.

In regard to the solvent employed, the generic type which are utilized is known as aromatic naphtha. Examples of this are Drake solvent D-74, Chempro 525 which contain benzene and mixtures of alkylated aromatics, and others. In certain instances solvents such as trimethyl benzene, benzene, toluene, etc., are acceptable, as are aliphatic solvents. Aliphatic solvents, although useful, are less preferred because they tend to produce materials of higher viscosities which are, therefore, more difficult to handle. Generally speaking, polar solvents should not be used as they would not dissolve the calcium sulfonate produced in the reaction.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The process of preparing an anionic-nonionic emulsifier composition which comprises: reacting a sulfonic acid having the formula R_1SO_3H wherein R_1 is an organic radical selected from the group consisting of alkyl and alkyl aryl radicals with a dispersion mixture comprising a member selected from the group consisting of Group II metal oxides, Group II hydroxides, and Group II metal salts in a solution of a polyethoxylated compound containing about 10 to 50 moles of ethylene oxide, said reaction being carried out in the presence of less than about 2% of water.

2. The process of claim 1 wherein the Group II hydroxide is calcium hydroxide.

3. The process of claim 1 wherein the polyethoxylated compound is a member selected from the group consisting of ethoxylated dioctyl phenol, ethoxylated dinonyl phenol, and ethoxylated didodecyl phenol.

4. The process of claim 1 wherein the sulfonic acid is a member selected from the group consisting of keryl benzene sulfonic acid and dodecyl benzene sulfonic acid.

5. The process of claim 1 wherein the Group II hydroxide is calcium hydroxide, the sulfonic acid is a member selected from the group consisting of keryl benzene sulfonic acid and dodecyl benzene sulfonic acid, and the

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polyethoxylated compound is a member selected from the group consisting of ethoxylated dioctyl phenol, ethoxylated dinonyl phenol, and ethoxylated didodecyl phenol.

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SAMUEL H. BLECH, *Primary Examiner.*

JULIUS GREENWALD, ALBERT T. MEYERS,
Examiners.

J. T. YOUNG, T. T. FEDIGAN, *Assistant Examiners.*