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STABILIZED WAX EMULSION

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This invention relates to emulsions and emulsifier compositions and more particularly to fluid emulsions of waxes which are solid at ordinary temperatures and emulsifier compositions therefor.

Emulsions of waxes, and emulsifying agents for use in preparing such emulsions are commercially valuable compositions and have been the subject of much investigation. For example, U. S. Patents 2,374,931 and 2,380,166, both granted to W. C. Griffin disclose emulsifiers as well as emulsifiable wax compositions and emulsions utilizing the emulsifiers, which comprise mixtures of lipophilic partial esters and hydrophilic hydroxypolyoxyethylene ethers of such esters. Emulsions of solid waxes prepared in accordance with the teachings of these patents are resistant to hard water, stand dilution well without precipitating wax, and are stable on storage. They have one disadvantage, however, in that certain types of agitation, particularly a reciprocating agitation such as is imparted by a back-and-forth shaking of a vessel partially filled with the emulsion, cause the wax particles to agglomerate into lumps, much as butter is separated from cream in churning. Particularly where concentrated wax emulsions are to be packaged for dilution in home use, as in liquid home laundry wax compositions, is this type of instability objectionable, since it is almost instinctive with the user to shake a bottle containing a creamy emulsion before withdrawing a portion for dilution.

It is an object of this invention to provide an improved emulsifier composition suitable for preparation of fluid emulsions of solidified wax.

A further object is to prepare improved emulsifiable wax compositions.

A still further object is to prepare fluid emulsions of solid waxes which are stable to the separation of wax agglomerates when subjected to shaking.

The above and other objects of the invention will become more apparent in the course of the following description and in the appended claims.

Compositions which accomplish the above objects in accordance with the present invention comprise the emulsifiers in the above mentioned Griffin patents and contain in addition to the lipophile partial esters and the hydrophile hydroxypolyoxyethylene ethers, a hexitol borate the pH of which has been adjusted to a value between 4.5 and 9.0. Preferably, though not necessarily, the compositions also include a solid long chain fatty acid, which appears to coact with the hexitol borate in further enhancing the effect of the

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latter in stabilizing the emulsion against shaking. Within the purview of the invention are emulsifier compositions containing the herein-disclosed stabilizing agents, emulsifiable wax compositions containing the emulsifiers and stabilizers, and emulsions employing the above mentioned emulsifying agents and the herein-disclosed stabilizers.

The following description of the mixed emulsifying agents employed in the stabilized compositions of the present invention is paraphrased from that in the specification of U. S. 2,380,166, mentioned hereinbefore.

For convenience in description the emulsifiers will be described generally as mixtures of type A and type B emulsifiers.

Type A emulsifiers comprise lipophilic partial long chain fatty acid esters of polyhydroxylic organic compounds. Type B emulsifiers include, in general, the highly hydrophilic hydroxypolyoxyethylene ethers of type A compounds.

The adjective "lipophilic" is here used to describe compounds which have good oil solubility or dispersibility and little or no water solubility. The term "highly hydrophilic" is descriptive of compounds which are from readily dispersible in to completely miscible with water.

More particularly the type A esters are the esters of water-insoluble fatty acids having at least 12 carbon atoms, such as those obtainable by hydrolysis of natural fats, waxes, and oils, or from oxidation of paraffins, and suitable aliphatic polyhydroxylic compounds. Partial esters of water-insoluble cyclic acids, such as naphthenic acids, are likewise satisfactory type A components of the present emulsifiers. Suitable polyhydroxylic compounds comprise ethylene glycol; di- and tri-ethylene glycol; glycerol and polyglycerols; pentaerythritol; pentitols; hexitols and the cyclic inner ethers thereof; cyclitols such as inositol; oligosaccharides such as glucose, sucrose, and lactose; the glycol and lower polyglycol ethers of such polyhydroxylic compounds; and other polyhydric compounds of typical hydrophile character.

In these type A partial esters, monoesters tend to be the most effective.

Particularly suitable partial esters are those of the mixed cyclic inner ethers of the hexitols, such as sorbitans and sorbides from sorbitol, or mannitans and mannides from mannitol. For optimum performance, in the said partial esters of cyclic inner ethers the ratio of hydroxyl value to ester value lies between 3 and 1 and preferably between 3 and 1.5.

The type B material, the second emulsifying component of the novel compositions of this invention, comprise the highly hydrophilic and preferably the readily water-soluble hydroxypolyoxyethylene ethers of the type A partial esters. The ether-esters become more hydrophilic as the number of oxyethylene units per mol increases, and it has been found particularly advantageous to employ compounds containing from 10 to 30 oxyethylene groups per mol. The longer the fatty acid radical in the ester and the higher the degree of esterification, the more oxyethylene group required for optimum results.

Methods of preparing the type A esters and type B ether-esters above described are presented in detail in aforesaid Patent No. 2,380,166 and need not be repeated here.

Likewise, the proportioning of type A and type B components to form emulsifiers for waxes, and emulsions containing waxes is adequately treated in the specification of said patent, and in the modified compositions of the present invention the same range of proportion of type A to type B components is employed. The proportion may be defined in terms of the ratio of oxyethylene units in the B component to the total number of ester groups in A and B. For emulsifying waxes, the said ratio of oxyethylene groups in B to ester groups in A and B lies between the limits of 1.5 and 9.

The paraffin waxes in emulsion are particularly susceptible of agglomeration and separating when shaken and it is to emulsifiable paraffin wax compositions, paraffin wax emulsions, and emulsifiers for paraffin wax that this invention is particularly directed. The said paraffin waxes include crude scale wax as well as more highly refined white waxes such as those used for household purposes. Also included are the so-called microcrystalline paraffin waxes which are available in a number of grades. So far as is known, the invention is applicable to emulsions of any wax which exhibits the property of "churning out" wax agglomerates on shaking.

In addition to the prior art components of emulsifiers for waxes, the emulsifier composition, emulsifiable waxes and emulsions of the present invention contain from 3% to 25% by weight, based on the sum of the weights of type A and type B components, of a partially neutralized hexitol borate, preferably a partially neutralized sorbitol borate. Sorbitol borates and variously neutralized sorbitol borates are the subject of U. S. Patent No. 2,223,949 to Bremer. Borates useful in the present invention are sorbitol monoborate dicondensation products in which sufficient of the acidic hydrogen of the resulting condensation product is replaced by a monovalent cation to result in a borate of pH between 4.5 and 9. Thus, the products of Examples 2, 3, 5 and 6 of the aforementioned patent are suitable ingredients. Equally satisfactory are sorbitol monoborate compositions which have been condensed to a lesser degree than taught in the above mentioned Bremer patent and neutralized to the indicated extent. The preparation of a suitable borate compound for the purpose is detailed in the following:

Example I

A reaction vessel equipped with an agitator and means of supplying heat was charged with 3040 pounds of 70% sorbitol solution and 723 pounds of boric acid. The charge was heated and agitated until the temperature of the vigorously boiling charge was 110° C. The contents of the vessel were then cooled to 90° C. and the acidity partially neutralized at that temperature, by the gradual addition of 385 pounds of sodium hydroxide added in the form of 50% aqueous solution. The resulting product has a pH, in 50% solution, of 7.0. It was butted with water to a concentration of 80% solids to yield a viscous pale yellow liquid drying to a resinous, tack free, surface when spread out in a film.

By varying the amount of caustic, the pH of the sorbitol borate resulting from the first step of Example I could have been controlled to any desired value within the range of 4.5 to 9.0 to produce borates suitable for use in the present invention. Furthermore, instead of caustic soda, there might have been employed any other neutralizing agent supplying a monovalent cation such, for example, as potassium hydroxide, ammonia, triethanol amine or the like.

While it has been found that emulsions containing from 3% to 25% of a partially neutralized hexitol monoborate based on the weight of the hereinbefore disclosed combined emulsifiers, have remarkably increased resistance to the separation of wax agglomerates upon shaking, a still further improvement can be effected in this direction by the incorporation of a solid long chain fatty acid, such for example, as stearic acid or palmitic acid, and preferred compositions in accordance with the invention contain this ingredient in an amount not greater than 2.5 times the weight of the added borate compound providing that the sum of the weights of said borate and said solid fatty acid shall be not more than 60% of the weight of the sum of the type A and type B emulsifiers in the composition. Particularly useful are those compositions containing 2 parts of stearic acid per part of sodium sorbitol borate and from 6 to 18% of said borate based on the sum of type A and type B components in the emulsifier composition.

In addition to the ingredients named above, the emulsifier compositions of the invention may contain minor amounts of other components to render the ingredients compatible, to perfume the product, to color it, or the like. In particular, a small amount of water is useful to properly incorporate the borate compound with the other ingredients.

Specific compositions illustrating the invention are described in the following examples.

Example II

Melt together 27.4 grams of commercial sorbitan monopalmitate (type A component), 34.7 grams of 20-polyoxyethylene sorbitan monopalmitate (type B component) and 17.1 grams of stearic acid, bringing the mixture to a temperature of about 60° C. Separately prepare a solution containing 8.3 grams of sodium sorbitol monoborate—pH 7, in 7.3 grams of water at the same temperature. Add the water solutions to the mixed emulsifier and stearic acid, mix thoroughly and cool rapidly. The resulting waxy solid is an excellent emulsifier for the preparation of paraffin wax emulsions.

Example II(a)

Melt together 40 grams of household paraffin wax and 7.35 grams of the product of Example II, bringing the temperature of the mixture to about 60° C. Add 52.65 grams of water, also at about 60° C., to the molten mixture stirring continuously. Allow the emulsion so formed to cool

to room temperature while stirring gently. The resultant concentrated emulsion is very resistant to agglomeration and separation of wax particles on vibration or shaking, and may readily be diluted with either soft or hard water to form stable emulsions.

Example III

The following instructions are for the preparation of an emulsifiable wax concentrate in solid form. Melt together 80.5 grams of household paraffin wax, 4.5 grams of commercial sorbitan monopalmitate, 5.7 grams of 20-polyoxyethylene sorbitan monopalmitate, and 2.8 grams of stearic acid. Separately prepare a solution of 1.4 grams of sodium sorbitol monoborate pH 7 in 5.3 grams of water and add the solution, at a temperature of about 60° C. to the molten wax and emulsifiers at about the same temperature. Upon cooling a solid waxy composition is obtained which may be readily converted to a stable emulsion by melting and stirring in warm water to adjust the concentration as desired.

Example IV

Melt together 23.4 grams of paraffin wax, 1.2 grams of commercial sorbitan monopalmitate, 1.8 grams of 20-polyoxyethylene sorbitan monopalmitate and 0.8 gram of stearic acid. To the molten mixture at about 60° C., add with continuous stirring a solution of 0.4 gram of sodium sorbitol monoborate—pH 5, in 72.4 grams of water. A stable emulsion, very resistant to wax agglomeration results.

Example V

Melt together 23.4 grams of paraffin wax, 1.05 grams of commercial sorbitan monostearate, 1.95 grams of 20-polyoxyethylene sorbitan monostearate and 0.8 gram of stearic acid to the mixture, at a temperature of about 60° C., add with continuous stirring, a solution of 0.4 gram of sodium sorbitol monoborate—pH 7 in 72.4 grams of water, also at about 60° C. Continue to stir the resulting emulsion gently as it cools to room temperature. The resulting emulsion is very stable.

Example VI

Substitute ammonium sorbitol monoborate—pH 7 for the sodium sorbitol monoborate—pH 5 of Example IV. An equally stable emulsion results.

Example VII

Substitute triethanol amine mannitol monoborate—pH 8 for the borate of Example IV. An equally stable emulsion results.

Example VIII

Melt together 20 grams of paraffin wax, 1.3 grams of commercial sorbitan monopalmitate, 1.7 grams of 20-polyoxyethylene sorbitan monopalmitate and 0.4 gram of stearic acid. Add to the molten mixture at a temperature of about 60° C., with continuous stirring, a solution of 0.2 gram of sodium sorbitol monoborate—pH 7 in 76.4 grams of water, also at about 60° C. Cool the resulting emulsion to room temperature with gentle stirring.

Example IX

Melt together 20 grams of paraffin wax, 1.3 grams of commercial sorbitan monopalmitate and 1.7 grams of 20-polyoxyethylene sorbitan monopalmitate. To the molten mixture at a temperature of about 60° C. add with continuous stirring, a solution of 0.6 gram sodium sorbitol monoborate—pH 7 in 76.4 grams of water, also at about 60° C. Cool the resulting emulsion to room temperature with gentle stirring. The emulsion shows markedly improved stability to shaking when compared with emulsions made in the absence of a borate compound.

Example X

Melt togteher 40 grams of paraffin scale wax, 5 grams of sorbitan monostearate, 9 grams of 20-polyoxyethylene sorbitan monostearate, and 0.5 gram stearic acid. Separately prepare a solution of 0.25 gram of sodium sorbitol monoborate—pH 7 in 45.25 grams of water and bring the molten mixture and the aqueous solution to temperatures between 60 and 100° C. With continuous agitation add the aqueous solution to the molten wax mixture in a slow stream. Continue gentle agitation as the resulting emulsion cools to room temperature. The resulting concentrated emulsion is a creamy fluid, stable against separation of wax agglomerates on shaking and amenable to dilution to any desired extent with soft or hard water to form stable dilute emulsions.

Example XI

Melt together 20 grams of paraffin scale wax 0.9 gram of sorbitan monopalmitate, 1.1 grams of 20-polyoxyethylene sorbitan monopalmitate, and 0.2 gram of stearic acid. Separately prepare a solution of 0.1 gram of sodium sorbitol monoborate—pH 7, in 77.7 grams of water. Bring the melt and the solution to temperatures between 60° and 100° C., and add the solution in a slow stream to the molten wax mixture while stirring constantly. Continue gentle agitation while the formed emulsion cools to room temperature. The resulting emulsion is relatively stable to storage and dilution, and shows marked improvement over a companion emulsion made without the addition of borate and stearic acid in respect to agglomeration and separation of wax upon shaking.

The above examples suffice to illustrate the invention amply, and multiplication of the number of examples illustrating in detail the use of the stabilizing agents with other wax emulsifiers taught in the Griffin patent will be avoided. Other specific emulsifier combinations which may be employed with the newly disclosed borate stabilizers of the present invention are presented in tabular form below:

Example	A Type Emulsifier	Parts	B Type Emulsifier	Parts
XII	Sorbitan mononaphthenate	3.5	20-POE* mannitan monopalmitate	3.5
XIII	Sorbitan monolaurate	12	20-POE sorbitan monolaurate	19
XIV	Glycerol monopalmitate	3.5	20-POE mannitan monopalmitate	3.5
XV	Mannitan mono-oleate	3.75	12-POE mannitan monooleate	11.25

*POE—polyoxyethylene.

For purposes of convenience the polyoxyethylene compounds have been designated throughout the examples by a number prefixed to the word polyoxyethylene to indicate the number of oxy-

ethylene groups. Thus "20-polyoxyethylene sorbitan monopalmitate" is to be understood as referring to the polyoxyethylene ether of sorbitan monopalmitate containing an average of 20 oxyethylene groups per mol.

The above examples are illustrative only, and not definitive of the limits of the invention. Variations therefrom which come within the scope of the invention will be obvious to those skilled in the art.

Emulsifiable wax compositions containing the stabilized emulsifier hereinbefore described usefully contain from 10% to 30% of said emulsifier and from 70% to 90% paraffin wax, or the like.

Emulsions which come within the purview of the patent may vary in concentration over a wide range. As far as is known they may be diluted almost infinitely with water although there is little practical use for paraffin emulsions containing less than about 5% paraffin wax and the invention is primarily concerned with emulsions containing upwards from this amount. In most fields of application emulsions containing from about 10% to about 25% paraffin wax are most useful and it is in this range of concentrations that the preferred compositions lie. Of nearly equal importance, however, are concentrated, or stock, emulsions which contain still higher proportions of paraffin and which may be diluted with either hard or soft water to form emulsions more suited to ultimate application. The improved emulsifiers of the present invention are particularly well adapted to stabilizing such concentrated emulsions against the agglomeration and separation of wax particles and emulsions containing as much as 50% of combined paraffin and emulsifier are within the purview of the invention. In the emulsions the proportion of paraffin wax to emulsifier falls within the same range as in the emulsifiable wax compositions, namely between the limits of from 10% to 30% of the emulsifier and from 90% to 70% paraffin wax.

The emulsions of the present invention are useful in any of the known applications of paraffin emulsions. Among such uses may be mentioned the water-proofing of textiles or of porous woods, the wax coating of paper, chip board; and the like. Such emulsions comprise particularly useful means of introducing emulsified wax into fluid dispersions with other ingredients as for example in combined fluid starch-wax dispersions as laundry aids.

What is claimed is:

1. An emulsifier composition comprising (*a*) a mixture of lipophilic partial ester of a long chain fatty acid and a hydrophilic polyhydroxylic organic compound, a highly hydrophilic hydroxypolyoxyethylene ether of a lipophilic partial ester of a long chain fatty acid and a hydrophilic polyhydroxylic organic compound, said hydroxypolyoxythylene ether containing at least 10 oxyethylene groups; said partial ester and said hydroxypolyoxyethylene ether being present in the mixture in such proportions that the ratio of oxyethylene groups in said hydroxypolyoxyethylene ether to the total ester groups (both in the free ester and in the hydroxypolyoxyethylene ether) is in the range of from about 1.5 to 9.0 and (*b*) from about 3% to about 25% by weight, based on the weight of the said mixture, of a hexitol monoborate the pH of which has been adjusted to a value between 4.5 to 9.0 by replacement of acid hydrogen of the said monoborate with a monovalent cation other than hydrogen.

2. An emulsifier composition consisting essentially of the composition of claim 1 and a solid long chain fatty acid in an amount not greater than 2.5 times the weight of said hexitol monoborate wherein the sum of the weights of said borate and said fatty acid is no more than 60% of the weight of said mixture (*a*).

3. An emulsifier composition as in claim 2 wherein the said hexitol monoborate is sodium sorbitol monoborate—pH 7, and said solid fatty acid is stearic acid.

4. An emulsifier composition as in claim 2 wherein the said lipophilic partial ester is a partial ester of a polyhydroxylic cyclic inner ether of hexitol and a fatty acid of at least 12 carbon atoms, and wherein the said hydroxypolyoxyethylene ether is the hydroxypolyoxyethylene ether of a partial ester of a polyhydroxylic cyclic inner ether of a hexitol and a fatty acid of at least 12 carbon atoms, said ether containing from 10 to 30 oxyethylene groups per mol.

5. An emulsifier composition consisting of (*a*) a mixture of from 40 to 50 per cent of sorbitan monopalmitate and from 60 to 50 per cent of 20-polyoxyethylene sorbitan monopalmitate; (*b*) from 6% to 18%, based on the weight of said mixture, of sodium sorbital monoborate—pH 7; and (*c*) twice as much stearic acid as said sodium sorbitol monoborate.

6. An emulsifier composition consisting of (*a*) a mixture of from 40 to 50 per cent of sorbitan monostearate and from 60 to 50% of 20-oxyethylene sorbitan monostearate; (*b*) from 6% to 18%, based on the weight of said mixture, of sodium sorbitol monoborate—pH 7; and (*c*) twice as much stearic acid as said sodium sorbitol monoborate.

7. An emulsifiable wax consisting essentially of from 70% to 90% paraffin wax and from 30% to 10% of the emulsifier composition of claim 1.

8. An emulsifiable wax consisting essentially of from 70% to 90% paraffin wax and from 30% to 10% of the emulsifier composition of claim 2.

9. An emulsifiable wax consisting essentially of from 70% to 90% paraffin wax and from 30% to 10% of the emulsifier composition of claim 4.

10. An emulsifiable wax consisting essentially of 75% paraffin wax and 25% of the emulsifier composition of claim 5.

11. An aqueous emulsion of paraffin wax, emulsified and stabilized with the emulsifier composition of claim 1.

12. An aqueous emulsion of paraffin wax, emulsified and stabilized with the emulsifier composition of claim 2.

13. An aqueous emulsion of paraffin wax, emulsified and stabilized with the emulsifier composition of claim 4.

14. An aqueous emulsion of paraffin wax, emulsified and stabilized with the emulsifier composition of claim 5.

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