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EMULSION CLEANER

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ABSTRACT OF THE DISCLOSURE

Stable emulsion cleaners comprising (a) water-immiscible organic solvent emulsified into (b) an approximately 5 to 18% aqueous solution of at least one water-soluble inorganic salt builder, said solution containing from 5 to 15% of a mono-alkyl benzene sulfonate in which not less than about 35% by weight of the alkyl contains from 8 to 10 carbon atoms, the volume ratio of (a) to (b) being in the range of about 1:1 to about 10:1.

Our invention is directed to emulsion cleaners.

It has heretofore been known to prepare emulsion cleaners which contain an organic water-insoluble cleaning solvent such as Stoddard solvent emulsified into aqueous solutions of inorganic builders, including salts such as alkali metal silicates, polyphosphates, sodium carbonate, and sodium sulfate. A typical emulsion cleaner of this type is one which comprises (a) several volumes of Stoddard solvent emulsified into (b) an approximately 12½% aqueous solution containing sodium metasilicate, sodium carbonate, sodium tripolyphosphate and sodium sulfate. Compositions of such character are required to maintain emulsion stability for several hours, as, for example, with not more than 2 ml. of free water separating out after 6 hours from 40 ml. of the emulsion. Unfortunately, it is difficult to produce emulsion cleaners of this type with stabilities of this character. Thus, for example, numerous emulsifiers or combinations of emulsifiers, which are known to be useful in the production of relatively stable oleaginous-aqueous emulsions of various types, are of no value in producing stable emulsions of the character referred to above. Illustrative of such ineffective emulsifiers are sodium lauryl sulfate, dodecyl benzene sodium sulfonate, tetradecyl benzene sodium sulfonate, hexadecyl benzene sodium sulfonate, alone or in conjunction with alkanolamides such as lauric diethanolamide, lauric diisopropanolamide, oleic diethanolamide and oleic diisopropanolamide; alginates, polyvinyl methyl ether; and phosphoric acid esters of linear ethoxylated alcohols alone and in combination with octadecyl benzene sulfonic acid or salts thereof such as the sodium and triethanolamine salts.

We have discovered that a certain limited group of substantially monoalkyl benzene sulfonates, in which the alkyl radical (or mixture of alkyl radicals) is of certain restricted character, as set out below, have the surprising property of producing stable emulsions of the character referred to above. To achieve the desired results, the alkyl radical is especially desirably a straight chain alkyl radical containing essentially 8 carbon atoms. Certain mixtures of straight chain alkyl radicals are also effective for the production of substantially monoalkyl benzene sulfonates which produce stable emulsions in the environments with which our present invention deals. Such mixed straight chain alkyl radicals are, generally speaking, those in which not less than about 35% thereof contain from 8 to 10 carbon atoms. Typical examples of useful mixed straight chain alkyl radicals which have been found to be satisfactory, when said mixed radicals repre-

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sent the alkyl radicals of alkyl benzene sulfonates, are the following:

(1) C₆-C₉ alkyl radicals fraction in which the C₆ alkyl content is 25%, the C₇ alkyl content is 40%, the C₈ alkyl content is 20%, and the C₉ alkyl content is 15%.

(2) C₇-C₉ alkyl radicals fraction in which the C₇ alkyl content is 30%, the C₈ alkyl content is 40%, and the C₉ alkyl content is 30%.

(3) C₈-C₉ alkyl radicals fraction in which the C₈ and the C₉ alkyl contents are each approximately 50%.

(4) C₉-C₁₀ alkyl radicals fraction in which the C₉ and C₁₀ alkyl contents are each approximately 50%.

On the other hand, for instance, monoalkyl benzene sulfonates in which in one case (a) the alkyl radicals fraction comprised a C₆-C₇ mixture of alkyl radicals in which the C₆ and C₇ alkyl contents were each approximately 50%; and in which in another case (b) the alkyl radicals fraction comprised a C₁₀-C₁₃ mixture of alkyl radicals in which the C₁₀ alkyl content was 20%, the C₁₁ alkyl content was 35%, the C₁₂ alkyl content was 30% and the C₁₃ alkyl content was 10%, were inoperative to produce stable emulsion cleaners.

The aforesaid monoalkyl benzene sulfonates can be used, in the practice of our invention, in the form of the free sulfonic acid or in the form of alkali metal or monovalent metal salts or amine salts such as monoethanolamine, diethanolamine, triethanolamine, isopropanolamine, propylamine, isopropylamine, butylamine or isobutylamine salts. In general, for economic reasons, they will generally be employed in the form of their sodium salts. It is particularly preferred to use sodium octylbenzene sulfonate, which is a free-flowing powder or flake up to 100% active (preferably at 95% minimum active). It is rapidly soluble in water and does not cake or become tacky on exposure to commonly encountered humidities, is convenient to handle and can be dry blended with combinations of powdered builders and still retain a free-flowing character.

The aqueous phase of the emulsion cleaners of our present invention, as indicated above, comprises an aqueous solution of detergent builders. Such builders, which are generally inorganic water-soluble alkaline salts, are, per se, well known to the art and include such compounds as alkali metal (including ammonium) carbonates and bicarbonates, particularly sodium carbonate, sodium sesquicarbonate, potassium carbonate and sodium bicarbonate; alkali metal silicates such as sodium silicate and sodium metasilicate; alkali metal phosphates and polyphosphates such as trisodium phosphate, disodium orthophosphate, sodium tripolyphosphate, tetrasodium pyrophosphate, tetrapotassium pyrophosphate, potassium tripolyphosphate, sodium hexametaphosphate; and alkali metal borates such as borax and potassium pentaborate. The builders, or mixtures of two or more thereof, are dissolved in water to produce varying concentrations, and together with the aforesaid alkyl benzene sulfonates are added to or admixed with the water-immiscible organic solvent, under conditions of stirring or agitation, until the final, homogeneous stable emulsion results. The concentration of the builder or builders will, in general, range from about 5% or slightly less to about 18%, by weight of the aqueous solution, with from 10% to 15% being an especially preferred range. If the concentration is too high or too low, emulsion stability is not obtained. Where mixtures of builders are utilized, which include sodium carbonate and sodium sulfate in conjunction with sodium silicate or sodium metasilicate and sodium or potassium tripolyphosphate or tetrasodium pyrophosphate or tetrapotassium phosphate, the proportions of the sodium carbonate and the sodium sulfate will advantageously exceed the proportions of the other inorganic builders.

The water-immiscible organic solvent which is utilized in the production of the emulsion cleaners of the present invention is most advantageously Stoddard solvent. However, other water-immiscible organic solvents, particularly hydrocarbons, which are useful in dry cleaning operations, can be employed as, for example, halogenated and especially chlorinated solvents such as methylene chloride and perchlorethylene, and naphtha, benzene, gasoline and other normally liquid hydrocarbon fractions.

The proportions of the aforesaid monoalkyl benzene sulfonates employed in the production of the emulsion cleaners is somewhat variable. Generally speaking, they should not be less than 0.5% by weight of the aqueous phase containing the builder and said sulfonates, and it will not be necessary to employ more than 1.5%. A range of 0.8% to 1.2% is particularly useful and approximately 1% will be close to optimum in most cases. Based on the weight of the finished emulsion, the said monoalkyl benzene sulfonates will generally constitute from about 0.2% to about 0.5% with a good average of 0.3% to 0.4%.

The relative proportions of the aqueous and water-immiscible organic solvent phases of the emulsion cleaners of the present invention are variable. Generally speaking, for most purposes, the volume ratio of the water-immiscible organic solvent phase to the aqueous phase will be in the range of 1:1 to 10:1 and will usually fall within the range of 2:1 to 5:1 with a distinctly preferred range of 2.5:1 to 3.5:1, a volume ratio of about 3:1 being especially satisfactory; and, in general, the higher the aforesaid ratio, the thicker will be the emulsion. Again, generally speaking, with ratios above 6:1, the emulsion tends to invert from an oil-in-water emulsion to a water-in-oil emulsion, but without any noticeable adverse effect on the stability of the emulsion. While, from the standpoint of emulsion stability, the volume ratios may be even less than 1:1, it will not usually be desired to produce such emulsions since, as a general rule, it will be desired to have present in the emulsion an appreciably greater volume of Stoddard solvent or the like than the volume of the aqueous phase.

The following table shows the amount of sulfonic acid emulsifier in the aqueous phase or solution of Example 1, the first five examples involving the use of n-octyl benzene sulfonic acid as the emulsifier, and examples (f) and (g) involving the use of a C₇-C₉ alkyl benzene sulfonic acid in which the C₇ alkyl content is 30%, the C₈ alkyl content is 40%, and the C₉ alkyl content is 30%. In each example, 3 volumes of Stoddard solvent were utilized.

Example No.	Volume of aqueous phase	Relative amount sulfonic acid	Parts inorganic salts	Parts water
(a)-----	1	0.0125	0.1125	0.875
(b)-----	0.503	0.0063	0.1125	0.875
(c)-----	0.400	0.0050	0.1125	0.875
(d)-----	0.304	0.0038	0.1125	0.875
(e)-----	0.136	0.0017	0.1125	0.875
(f)-----	0.52	0.0065	0.1125	0.875
(g)-----	0.48	0.0060	0.1125	0.875

In all cases [(a)-(g)], stable emulsions were formed.

The following examples are illustrative of the practice of our invention. It will be understood that various changes may be made in the character and proportions of the inorganic builder or builders, the character of the water-immiscible organic solvent, and the proportions of the water and aqueous phase in relation to the organic solvent phase, without departing from the principles of our invention in the light of the guiding teachings disclosed herein. All parts listed are by weight.

EXAMPLE 1

10 parts sodium metasilicate, 40 parts sodium carbonate, 10 parts sodium tripolyphosphate, 30 parts sodium sulfate, and 10 parts n-octyl benzene sulfonic acid are dissolved in water to form a 12½% solution of said mixture of salts. Then, 1 volume of said aqueous solution is added to

3 volumes of Stoddard solvent, with stirring, until a homogeneous emulsion is obtained.

EXAMPLE 2

10 parts sodium metasilicate, 38 parts sodium carbonate, 11 parts sodium tripolyphosphate, 31 parts sodium sulfate, and 10 parts triethanolamine salt of a C₈-C₉ alkyl benzene sulfonic acid (in which the C₈ and C₉ alkyl radicals are each approximately 50%) are dissolved in water to form a 12% solution of said mixture of salts. Then, 1 volume of said aqueous solution is added to 3 volumes of Stoddard solvent, with stirring, until a homogeneous emulsion is obtained.

EXAMPLE 3

10 parts sodium metasilicate, 40 parts sodium carbonate, 10 parts sodium tripolyphosphate, 30 parts sodium sulfate, and 10 parts n-octyl benzene sulfonic acid (sodium salt) are dissolved in water to form an 8% solution. Then, 1 volume of said aqueous solution is added to 4 volumes of Stoddard solvent, with stirring, until a homogeneous emulsion is obtained.

EXAMPLE 4

10 parts sodium metasilicate, 40 parts sodium carbonate, 10 parts sodium tripolyphosphate, 30 parts sodium sulfate, and 10 parts n-octyl benzene sulfonic acid are dissolved in water to form a 12½% solution of said mixture of salts. Then, 1 volume of said aqueous solution is added to 3 volumes of methylene chloride or perchlorethylene, with stirring, until a homogeneous emulsion is obtained.

While, in the broader aspects of our invention, the alkyl radicals need not be linear or straight chain but may be branched chain, the use of the latter is less satisfactory. Similarly, while the optimum results achieved pursuant to the present invention are based upon the utilization of the particular straight chain alkyl benzene sulfonates described above, certain straight chain and branched chain alkyl naphthalene sulfonates, in the form of the free sulfonic acids or alkali metal or monovalent metal or amine salts, can be used with fairly good results. The alkyl radicals of said alkyl naphthalene sulfonic acids should contain from 3 to 4 carbon atoms and representative examples thereof are isopropyl naphthalene sulfonic acid, diisopropyl naphthalene sulfonic acid and the sodium and ethanalamine (mono-, di- and triethanolamine) salts thereof.

We claim:

1. A stable emulsion cleaner consisting essentially of (a) a water-immiscible dry cleaning organic solvent emulsified into (b) an approximately 5 to 18% aqueous solution of at least one water-soluble inorganic alkaline builder salt, said solution containing from 5 to 15% of a member selected from the group consisting of a monoalkyl benzene sulfonic acid and the monovalent salts and mono-amine salts thereof, in which no less than about 35% by weight of the alkyl or alkyls contains from 8 to 10 carbon atoms, the volume ratio of (a) to (b) being in the range of about 1:1 to about 10:1.

2. A stable emulsion cleaner according to claim 1, wherein the alkyl radical is a straight chain alkyl.

3. A stable emulsion cleaner according to claim 2, wherein (b) consists essentially of a 10 to 15% aqueous solution of a mixture of inorganic alkaline builder salts which comprise at least sodium carbonate and sodium sulfate, said sodium carbonate and sodium sulfate together exceeding the proportions of such other inorganic alkaline builder salts present in said aqueous solution.

4. A stable emulsion cleaner according to claim 3, in which (a) is Stoddard solvent.

5. A stable emulsion cleaner according to claim 4, in which the member of the group consisting of a monoalkyl benzene sulfonic acid and salts thereof is a member selected from the group consisting of mono-n-octyl benzene sulfonic acid and the sodium and ethanalamine salts thereof.

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6. A stable emulsion cleaner according to claim 5, in which the volume ratio of (a) to (b) is in the range of 2.5:1 to 3.5:1.

7. A stable emulsion cleaner according to claim 1, in which (b) consists essentially of a 10 to 15% aqueous solution of a mixture of approximately 10% sodium metasilicate, 40% sodium carbonate, 10% sodium tripolyphosphate, 30% sodium sulfate, and 10% of a member selected from the group consisting of a straight chain mono-alkyl benzene sulfonic acid and the monovalent and mono-amine salts thereof and in which at least about 35% by weight of the alkyl radical or mixture of radicals contains from 8 to 10 carbon atoms.

8. A stable emulsion cleaner according to claim 1, in which (b) consists essentially of an approximately 12½% aqueous solution of a mixture of approximately 10% sodium metasilicate, 40% sodium carbonate, 10% sodium tripolyphosphate, 30% sodium sulfate, and 10% of a member selected from the group consisting of mono-n-octyl benzene sulfonic acid and its sodium salt, and in which (a) is Stoddard solvent.

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9. A stable emulsion cleaner according to claim 8, in which the volume ratio of (a) to (b) is about 3:1.

10. A stable emulsion cleaner according to claim 3, in which (a) is a dry cleaning chlorinated hydrocarbon, said chlorinated hydrocarbon containing no substituents other than said chlorine.

11. A stable emulsion cleaner according to claim 7, in which (a) is a member selected from the group consisting of methylene chloride and perchlorethylene.

References Cited

UNITED STATES PATENTS

3,310,499	3/1967	Michaels et al.	252—152
3,320,174	5/1967	Rubinfeld	252—137 X
3,336,232	8/1967	Bauer et al.	252—153

MAYER WEINBLATT, Primary Examiner

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