(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 223 306**
A2

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **86202001.3**

(22) Date of filing: **14.11.86**

(51) Int. Cl.⁴: **C 11 D 1/37**, C 11 D 1/08

(30) Priority: **20.11.85 GB 8528521**

(43) Date of publication of application: **27.05.87**
Bulletin 87/22

(84) Designated Contracting States: **AT BE CH DE FR GB IT LI NL**

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(84) Designated Contracting States: **CH GB LI AT**

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(84) Designated Contracting States: **BE DE FR IT NL**

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(54) **Liquid detergent compositions containing binary anionic surfactant system.**

(57) Homogeneous concentrated liquid detergent compositions are disclosed, containing a binary anionic surfactant system.

The binary anionic surfactant system is represented by a mixture, in well-defined ratios, of an alk(en)yl succinate and a specific class of sulfonated surface-active agents with a critical micellar concentration in the range of from 10^{-5} to 10^{-3} mole/l.

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LIQUID DETERGENT COMPOSITIONS CONTAINING BINARY ANIONIC SURFACTANT SYSTEM

Jean-Pol BOUTIQUE

Technical Field

The present invention relates to homogeneous, concentrated, liquid detergent compositions containing a binary anionic surfactant system, together with desirable detergent ingredients. The binary anionic surfactant system is represented by a mixture, in well-defined ratios, of an alk(en)yl succinate and a specific class of sulfonated surface-active agents, said sulfonated surface-active agents having a critical micellar concentration in the range of from 10^{-5} to 10^{-3} mole/l.

Preferred sulfonated surface-active agents for use in the binary system of the invention are linear alkyl arene sulfonates, containing from 13 to 17 carbon atoms in their alkyl group, and dialkyl sulfosuccinates, having from 9 to 12 carbon atoms in each alkyl group.

The compositions of the invention exhibit excellent cleaning properties on all types of stains.

Background of the invention

The prior art relative to concentrated homogeneous heavy duty liquid detergent compositions is crowded and diverse. As an example U.S. Patent 4.285.841 discloses builder-free concentrated homogeneous liquid compositions containing a combination of anionic synthetic surface-active compounds, nonionic surface-active compounds and fatty acids.

The succinate ingredient is well-known in the detergent art and has been disclosed in combination with all kinds of detergent executions.

Succinate derivatives have been used for several purposes as surfactants in U.S. Patent 2.283.214, as builders in U.S. Patent 2.562.758, as suds-boosters in U.K. Patent 1.293.753, and as ingredients of liquid cleaners in U.S. Patent 4.277.378.

Linear alkyl-arene sulfonates, such as linear ortho-xylene sulfonates, are known surfactants, mainly for Enhanced Oil Recovery Applications. In European Patent 0 111 354, their use in detergents is mentioned.

Dialkyl sulfosuccinates are also known as surfactants; they have been disclosed frequently in high-foaming dishwashing compositions; U.K. Patents 2.130.235 and 2.130.238, disclose combination of dialkyl sulfosuccinates with linear alkyl sulfonates and ethoxylated nonionic surfactants.

European Patent Application n° 86200690.5 discloses liquid detergent compositions containing a ternary surfactant system of succinates, anionic surface-active agents and nonionic surface-active agents.

European Patent Application n° 86201319.0 relates to liquid detergent compositions containing a mixture of citrates and succinates as detergency builders.

However, the incorporation of high levels of alk(en)yl succinates in concentrated liquid detergent compositions is

known to adversely affect overall detergency benefits, such as greasy stain removal performance.

It is a major objective of the present invention to provide liquid detergent compositions containing high levels of alk(en)yl succinates, which exhibit excellent cleaning benefits on all types of stains, especially on greasy stains.

The above and other objectives can now be met by means of a combination, in well-defined ratios, of alk(en)yl succinates and sulfonated surface-active agents having a narrowly-defined critical micelle concentration. Linear alkyl-arene sulfonates containing from 13 to 17 carbon atoms in their alkyl group, and di-alkyl sulfosuccinates having from 9 to 12 carbon atoms in each alkyl group, are especially useful in that respect.

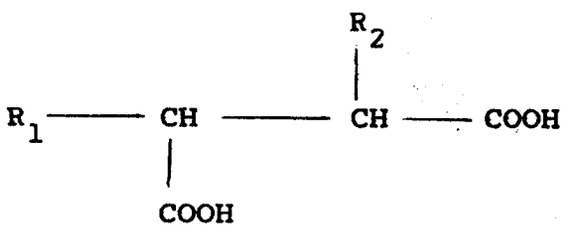
Summary of the invention

The present invention relates to homogeneous concentrated aqueous liquid detergent compositions containing less than 50% by weight of water, and a binary anionic surfactant system, together with conventional additives, characterized in that,

(a) the binary anionic surfactant system represents from 12% to 50% by weight of the composition;

(b) the anionic surfactant system is represented by a mixture of

(1) an alk(en)yl succinate having the formula



wherein R_1 is an alk(en)yl radical, having from 10 to 20 C-atoms, and R_2 is hydrogen or C_1-C_4 alkyl; and

(2) a sulfonated surface-active agent having a critical micelle concentration in the range of from 10^{-3} to 10^{-5} mole/l;

the weight ratio of sulfonate to succinate being in the range from 2:1 to 1:4.

Preferred sulfonated surface-active agents are:

- linear alkyl-arene sulfonates containing from 13 to 17 carbon atoms in the alkyl group; and
- di-alkyl sulfosuccinates, having from 9 to 12 carbon atoms in each alkyl group.

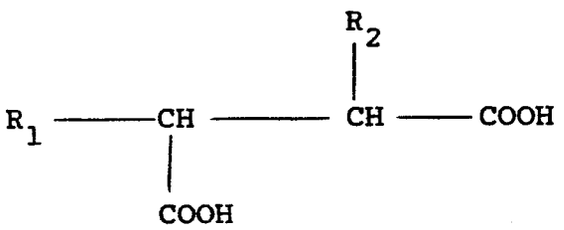
Most preferred are C_{13}-C_{14} linear alkyl ortho-xylene sulfonate and di-C_{10} alkyl sulfosuccinate

Detailed description of the invention

Unless stated to the contrary, the "percent-indications" stand for "percent by weight" of the compositions.

The anionic surfactant binary mixture amounts to from 12% to 50% preferably from 15% to 35% of the total composition and is represented by a binary composition of:

(1) an alk(en)yl succinate having the formula:



wherein R_1 is an alk(en)yl radical, having from 10 to 20 C-atoms, and R_2 is hydrogen or C_1-C_4 alkyl; and

(2) a sulfonated surface-active agent having a critical micellar concentration in the range of from 10^{-5} to 10^{-3} mole/l;

(1) The alk(en)yl succinate has the formula referred to hereinbefore wherein R_1 is either a saturated or unsaturated radical having from 10 to 20 carbon atoms, preferably an unsaturated derivative having from 12 to 16 carbon atoms in the alkenyl moiety. R_2 can be hydrogen or C_1-C_4 alkyl, although hydrogen is preferred. The terms "succinate" and "succinic acid" are used interchangeably. Suitable succinic acid salts include the sodium, potassium, lithium, ammonium, mono-, di- and tri-alkanol amine salts and mixtures thereof.

Preferred succinic acid derivatives for use herein include 2-dodecenylsuccinic acid, 2-tetradecenylsuccinic acid, 2-hexadecenylsuccinic acid, decyl succinic acid, dodecyl succinic acid and tetradecyl succinic acid and the water-soluble salts thereof. The alkyl or alkenyl chain attached to succinic acid can be either straight or branched. Preferred are the straight-chain alk(en)yl moieties. For any practical purpose, the alk(en)yl succinates are used at levels above 4% of the total composition.

(2) The sulfonated surface-active agent for use in the present invention must have a critical micelle concentration, measured on the sodium salt form, in the range of from 10^{-5} to 10^{-3} mole/l.

The critical micellar concentration (hereinafter referred to as cmc) of a compound is the concentration above which the molecules of the compound begin to aggregate to form micelles.

Several methods of determination of the cmc have been described in the literature. The method used in the context of the present invention is the surface-tension-log concentration plot method, which can be found e.g. in "Critical Micelle Concentrations of Aqueous Surfactant Systems", by P. Mukerjee and K.J. Mysels, published by the United States Department of Commerce. The cmc is determined

with the aid of solutions in distilled water. The temperature of measurement is superior to the Kraft temperature.

Particularly suitable for use herein are sulfonated surface-active agents inclusive of:

A. Linear alkyl arene sulfonates containing from 13 to 17 carbon atoms in the alkyl group, preferably toluene or xylene derived sulfonates. Especially preferred are C_{13-14} linear orthoxylene sulfonate, C_{13-14} linear paraxylene sulfonate, and C_{14} linear toluene sulfonate;

B. Di-alkyl sulfosuccinates, having from 9 to 12 carbon atoms in each alkyl group. Particularly preferred are di-C_{10} alkyl sulfosuccinates.

The sulfonate component can be represented by individual sulfonates having the specified cmc's or by mixtures of sulfonate surfactants provided the sulfonate mixture has a cmc within the claimed range. It is possible that specific sulfonate mixtures meet the cmc requirement even though the individual sulfonates of the mixture can have cmc's which are outside of the claimed range.

Consequently, conventional sulfonate surface-active agents such as water-soluble salts of alkylbenzene sulfonic acid containing from 10 to 18 carbon atoms in the alkyl groups can be present in the above mixtures.

The weight ratio of sulfonate to succinate surfactant in the binary mixture is in the range from 2:1 to 1:4.

In addition to the binary anionic surfactant system, the compositions therein can contain, as an optional but preferred ingredient, a nonionic surface-active agent.

The nonionic surfactant can be present at levels of from 3% to 35%, preferably from 8% to 20% of the total composition.

The nonionic surfactant component contains a hydrophobic organic radical condensed with an ethylene oxide hydrophilic

moiety. All ethoxylated nonionic surfactants which are known to be suitable for use in detergent application can be used in the compositions of this invention. Preferred nonionic species herein are polyethoxylates derived from primary and secondary aliphatic alcohols having from 8 to 24 carbon atoms, and having a HLB (hydrophilic lipophilic balance) in the range from about 8 to 15. These preferred ethoxylates frequently contain from 2 to about 14 moles of ethylene oxide per mole of hydrophobic moiety. The hydrocarbyl chain (hydrophobic moiety) can be represented by linear or branched fatty alcohols.

A preferred class of nonionic ethoxylates is represented by the condensation product of a fatty alcohol having from 12 to 15 carbon atoms and from about 4 to 10 moles of ethylene oxide per mole of fatty alcohol. Suitable species of this class of ethoxylates include: the condensation product of C_{12}-C_{15} oxo-alcohols and 7 moles of ethylene oxide per mole of alcohol; the condensation product of C_{13-15} oxoalcohols and 5 moles of ethylene oxide; the condensation product of narrow cut C_{14}-C_{15} oxo-alcohols and 7 or 9 moles of ethylene oxide per mole of fatty (oxo)alcohol; the condensation product of a narrow cut C_{12}-C_{13} fatty (oxo)alcohol and 6.5 moles of ethylene oxide per mole of fatty alcohol; and the condensation products of a C_{10}-C_{14} coconut fatty alcohol with a degree of ethoxylation (moles EO/mole fatty alcohol) in the range from 5 to 8. The fatty oxo alcohols while mainly linear can have, depending upon the processing conditions and raw material olefins, a certain degree of branching, particularly short chain such as methyl branching. A degree of branching in the range from 15% to 50% (weight %) is frequently found in commercial oxo-alcohols.

Nonionic ethoxylated components can also be represented by a mixture of 2 separately ethoxylated nonionic surfactants having a different degree of ethoxylation.

The compositions herein contain less than 50%, usually from 15% to 40% water.

The claimed compositions have a pH, measured in 1% aqueous solution at 20°C, in the range from about 7 to about 9. This pH range implies that the anionic surfactant component, i.e., the binary mixture of sulfonate and succinate, particularly the succinate, is substantially completely (i.e., more than 90%) neutralized in the claimed composition as is.

In addition to the essential ingredients described hereinbefore, the compositions herein frequently contain a series of optional ingredients which are used for their known functionality in conventional quantities.

Examples of the like optional ingredients can include fatty acids, saturated and/or unsaturated, and the corresponding soaps, synthetic anionic surfactants which are different from sulfonates (non-sulfonate anionics), water-insoluble solvents, enzymes, enzyme stabilizers, polyacids, polyaminopolyalkylene ethoxylate polymers, suds regulants, brighteners, perfumes, dyes, antioxidants, bactericides, corrosion inhibitors, fabric-softening agents, phase regulants and the like.

Suitable fatty acids, saturated or unsaturated, have from 10 to 18 carbon atoms in the alkyl chain. Preferred are unsaturated species having from 14 to 18 carbon atoms in the alkyl chain, most preferably oleic acid. The corresponding soaps can equally be used. The optional fatty acid/soaps are used in levels up to 10%, preferably from 1% to 8%, (of the composition). The fatty acids/soaps, among others, act as suds modifiers/regulants.

Synthetic non-sulfonate anionics can also be used in the composition in relatively minor levels. Examples of suitable non-sulfonate anionics include the salts of sulfated fatty alcohols having from 12 to 20 carbon atoms in the alcohol chain.

Water-insoluble solvents such as terpenes, phthalic acid esters and liquid paraffins can also be used in levels generally below 5%.

Detergent enzymes generally aid and augment the removal of specific stains. Suitable enzymes can be represented by proteases, amylases, lipases, glucose-oxidases, or mixtures thereof. Proteases and amylases are preferred in the claimed liquid concentrated compositions. They are frequently employed in a level from about 0.01% to about 1%.

All generally known enzyme stabilizing systems can be used in the compositions herein in the art established level. Examples of suitable stabilizing systems include short C_{1-4} chain carboxylic acid, particularly formic acid in combination with low level of calcium, boric acid and the water-soluble salts thereof possibly in combination with polyols.

Another preferred optional ingredient is represented by a polyacid or mixture of polyacids in an amount from about 0.05% to about 4%. Suitable polyacids are those having one pK value of at least 5. Preferred polyacid species for use herein can be represented by citric acid, and organo-phosphonic acids, particularly alkylene-polyamino-polyalkylene phosphonic acids such as ethylene diamine tetramethylenephosphonic acid, and diethylene triaminepentamethylenephosphonic acid or the salts thereof. Suitable polyamino-polyalkylene ethoxylate polymers, disclosed in published European Patent Application N° 112 593, are present at levels of from 0.2 to 1.2%.

Non-fatty acid detergent suds regulants can also be used. Preferred species include alkylated polysiloxanes such as dimethylpolysiloxane also frequently termed silicone. The silicones are frequently used in a level not exceeding 0.5%, most preferably between 0.01% to 0.2%.

The compositions herein can also contain known antioxidants for their known utility, frequently radical

scavengers, in the art established levels i.e. 0.01% to 0.25% (by reference to total composition). These antioxidants are frequently introduced in conjunction with unsaturated organic acids. While many suitable antioxidants are readily known and available for that purpose, especially preferred for use in the compositions herein are: 2,6 ditertiary butyl-p-cresol, more commonly known as butylated hydroxytoluene, BHT, and 2-tertiarybutyl-4-hydroxyanisole. Other suitable antioxidants are: 4,4'thiobis(6-ter-butyl-mcresol) and 2-methyl-4,6-dinonyl phenol.

Soil release polymers can also be incorporated in the compositions herein. Suitable species of such release polymers are described in U.S. copending Patent Application Serial Number 684.511, filed December 21, 1984.

The phase regulant is a further optional ingredient in the compositions herein. This component together with water can constitute the solvent matrix for the claimed concentrated liquid compositions. Suitable ingredient classes include lower aliphatic alcohols having from 2 to 6 carbon atoms and from 1 to 3 hydroxyl groups, ethers of diethyleneglycol and lower aliphatic monoalcohols having from 1 to 4 carbon atoms. Specific examples of phase regulants are: ethanol; n-propanol; isopropanol; butanol; 1,2-propanediol; 1,3-propanediol; monomethyl-, ethyl-, propyl-, and monobutyl ethers of di-ethylene glycol.

The claimed invention is illustrated and clarified with the aid of the following examples.

Concentrated liquid detergent compositions are prepared by mixing the individual ingredients listed hereinafter in the stated proportions.

Ingredients	Comp.A	Comp.B	Ex.1	Ex.2
Dodecylbenzene sulfonic acid	10.3	10.3	-	-
Ethoxylated C_{13-15} alcohol condensed with 7 moles of ethylene oxide per mole of fatty alcohol *	11.6	11.6	11.6	11.6
C_{13-14} linear ortho xylene sulfonic acid (1)	-	-	11.8	-
Di-isodecyl sulfosuccinate Na salt * (2)	-	-	-	12.0
Topped Whole Cut fatty acid **	10.7	-	-	-
2-Dodecenyl succinate	-	15.0	15.0	15.0
Citric acid	0.9	0.9	0.9	0.9
Oleic acid	3.9	3.9	3.9	3.9
Diethylenetriamine pentamethylene phosphonic acid	0.85	0.85	0.8	0.8
Triethanolamine	5.0	5.0	6.3	6.3
Coconut alkyl sulfate TEA salt	3.9	3.9	3.9	3.9
Soil release polymer ***	-	0.5	-	-
Ethanol	6.2	9.0	9.0	9.0
1,2-Propanediol	1.5	-	-	-
Formate (Na)	1.0	1.0	1.0	1.0
Enzymes	0.43	0.69	0.15	0.15
Water, NaOH $CaCl_2$ and minors	balance to 100			
pH	7.7	7.6	7.6	7.6

(1) cmc (surface tension-log concentration plot method) = $4.7\ 10^{-4}$ mole/l
(2) cmc (surface tension-log concentration plot method) = $1.9\ 10^{-4}$ mole/l

* 70% by weight solution in propylene glycol

** Fatty acid chain distribution:50% lauric, 20% myristic, 15% palmitic, 10% oleic, 2% stearic

*** Prepared by esterifying 1,4 phtalic acid (chloride) with 1,2-propane diol and ethoxylating the polymer with ethylene oxide. The resulting polymer mix is fractionated in cold (15°C) ethanol to provide a cold-ethanol soluble fraction with an average ethoxylation value in the range from 12-43.

The above compositions were used for comparative laundry tests. A MIELE W423 washing machine was used thereby selecting a main-wash step.

Cotton and polyester/cotton (polycotton) strips stained as indicated below were used to measure the comparative performance. Additional testing parameters were, temperature 60°C, product usage 180 g/18 l. of city water having an average water hardness of about 3 mmoles/l.; laundering treatment in presence of 3 kgs soiled clothes (no-pretreatment on test strips); stains : greasy type, i.e., make-up, lipstick, and dirty motor oil (DMO).

After having been subjected to the above washing treatment the dried stained cotton strips were visually graded by two expert judges thereby using a 0-4 scale whereby:

0 = see no difference between the swatches
1 = believe there is a difference between the swatches
2 = there is a difference between the swatches
3 = am sure there is a difference between the swatches
4 = very important difference between the swatches.

The stain removal readings were pooled and averaged on 8 replicates with the following results. The swatches treated with prior art composition A were used for reference purposes:

Type of stains	Comp.B vs.Comp.A Cotton/Poly-cotton	Ex.1 vs.Comp.A Cotton/Poly-cotton	Ex.2 vs.Comp.A Cotton/Poly-cotton
GREASY	-1.1*/-1.0*	+0.8*/+0.7*	+0.1/+1.0*
. Makeup	-2.4*/-2.6*	+1.8*/+1.4*	+0.9/+1.2*
. Lipstick	-2.3*/-2.1*	+0.2/-0.2	-0.1/+1.0*
. DMO	-1.5*/+0.8*	-0.3/+0.8*	-1.5*/+1.0*

* Readings statistically significant at 95°% confidence limit.

The above data shows significant performance superiority on greasy stains of the compositions of Examples 1 and 2 in accordance with this invention vs. a commercial heavy duty liquid, termed composition A. The performance superiority is equally applicable vs. a succinate containing liquid detergent, termed composition B.

On other types of stains (bleachable, enzymatic, particulate) the performance of the compositions of Example 1 and 2 is at least as good as the performance of composition B, with composition A as a reference.

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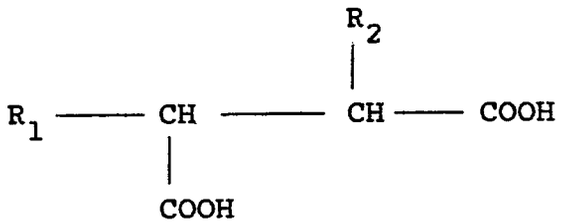
CLAIMS

1. A homogeneous concentrated aqueous liquid detergent composition containing less than 50% by weight of water, and a binary anionic surfactant system, together with conventional additives, characterized in that,

(a) the binary anionic surfactant system represents from 12% to 50% by weight of the composition;

(b) the anionic surfactant system is represented by a mixture of

(1) an alk(en)yl succinate having the formula



wherein R_1 is an alk(en)yl radical, having from 10 to 20 C-atoms, and R_2 is hydrogen or C_1-C_4 alkyl; and

(2) a sulfonated surface-active agent having a critical micelle concentration in the range of from 10^{-3} to 10^{-5} mole/l;

the weight ratio of sulfonate to succinate being in the range from 2:1 to 1:4.

2. The composition in accordance with Claim 1 wherein the sulfonated surface-active agent is selected from linear alkyl xylene sulfonates containing from 13 to 17 carbon atoms in the alkyl group, linear alkyl toluene sulfonates containing from 13 to 17 carbon atoms in the alkyl group, and dialkyl sulfosuccinates having from 9 to 12 carbon atoms in each alkyl group, and mixtures thereof.

3. The composition in accordance with Claim 2 wherein the sulfonated surface-active agent is selected from C_{13-15} linear ortho xylene sulfonates and di-C_{10} alkyl sulfosuccinates.

4. The composition in accordance with Claim 1 wherein the binary anionic surfactant system represents from 15% to 35% by weight of the total composition.

5. The composition in accordance with Claim 1 which in addition contains from 3% to 35% by weight of a nonionic surfactant.

6. The composition in accordance with Claim 1 which in addition contains from 1% to 8% by weight of a fatty acid having from 10 to 18 carbon atoms in the alkyl chain.

7. The composition in accordance with Claim 1 wherein the alkenyl succinate has from 12 to 16 carbon atoms in the alkenyl moiety and R_2 is hydrogen.

8. The composition in accordance with Claim 6 wherein the fatty acid is represented by oleic acid.