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(54) Homogeneous concentrated liquid detergent compositions containing ternary surfactant system.

(57) Homogeneous concentrated liquid detergent compositions with a ternary surfactant system are disclosed. The ternary system contains two anionic surfactants, an alkyl (aryl) - sulfonate and a succinate, and a nonionic surfactant. The compositions exhibit a pH in the neutral to mildly alkaline domain. Preferred compositions additionally contain low level of oleic acid.

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HOMOGENEOUS CONCENTRATED LIQUID DETERGENT COMPOSITIONS CONTAINING TERNARY SURFACTANT SYSTEM

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This invention relates to concentrated homogeneous liquid detergent compositions containing a well-defined surface-active mixture. In more detail, the compositions herein are characterized by the utilization of a ternary surfactant system and contain less than 50% water. The ternary surfactant system contains a majority of an anionic surfactant which is represented by a binary mixture of an alkyl(aryl) sulfonated surface-active agent and an alk(en)yl succinate in a weight ratio of sulfonate to succinate in the range of from 3:1 to 1:4, and a nonionic surfactant component.

The inventive compositions exhibit excellent and highly desirable detergency, they can be manufactured easily and furthermore display excellent stability during prolonged periods of storage.

Homogeneous concentrated heavy duty liquid detergents are well-known in the art and have found commercial application. The like compositions can comprise a ternary active system, namely: synthetic anionic sulfonates or sulfates in combination with nonionic ethoxylates and soaps. Such prior art compositions are difficultly processable, particularly depending upon alkalinity. The prior art concentrated

liquid detergents are in that respect vulnerable to phase separation under neutral to mildly alkaline conditions. As a further consequence of the like matrix criticalities, it is fairly difficult to modify the matrix with a view to increase the performance having regard to certain staining/cleaning situations. From a detergency standpoint, it is known that concentrated liquid compositions of the art, while exhibiting superior cleaning in relation to the majority of fibers, can desirably be improved in relation to cellulosic fiber detergency as compared to the performance derivable from the use of oxygen-bleach containing polyphosphate built granular detergents.

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 manufacture of the like compositions containing less than 50% water requires the utilization of substantial amounts of solvents and/or compatibilizing agents and even under those circumstances, remain of borderline stability having particularly regard to levels and type of nonionics, fatty acids, particularly saturated species, and optional electrolytes such as low levels of organic builders.

The succinate ingredient is well-known in the detergent art and has been disclosed in combination with all kinds of detergent executions, mostly granular compositions. While, the like succinates have been recommended for utilization in liquid compositions, it is well-known that substantial formulation difficulties will originate from their use in such compositions, particularly in presence of low levels of water and substantial amounts of nonionics.

German Patent 17 68 851 relates to the utilization of specific succinate derivatives as suds boosters. These

compositions contain solely anionic surface-active agents and furthermore substantial levels of water in combination with additional hydrotropes.

German Patent 19 56 671 discloses binary liquid preparations containing substantial levels of alk(en)yl succinates in combination with nonionic surface-active agents. German Patent Application 30 13 904 relates to alkaline cleaning agent compositions, solid or liquid, containing a partially neutralized succinic acid derivative which seems to be utilized for its foaming properties.

EP-Patent Application 0 017 951 relates to the utilization of alk(en)yl succinic acid salts or monoesters thereof with polyvalent alcohols for hydrotroping perfumes in liquid detergent compositions containing high levels of electrolytes.

It is a main object of this invention to formulate a homogeneous concentrated liquid detergent composition having outstanding performance characteristics comparable to what can be obtained from polyphosphate built granular detergent compositions containing oxygen bleach.

It is a further object of this invention to formulate homogeneous highly concentrated liquid detergent compositions containing substantial levels of a ternary surfactant system based on anionic sulfonates and succinates in combination with nonionic ethoxylates but containing less than 50% of water.

It is a further object of this invention to define highly concentrated storage stable liquid detergent compositions which have excellent laundry cleaning properties under neutral to mildly alkaline pH conditions.

Summary of the Invention

This invention relates to homogeneous concentrated liquid detergent compositions, having less than about 50% water, containing a ternary surfactant system. In parti-

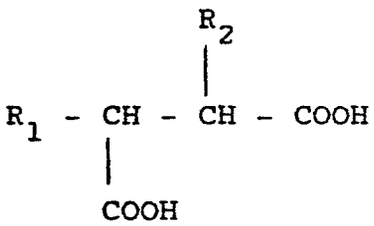
cular the compositions herein are characterized by the presence of:

(a) from 35% to 75% of a ternary surfactant system;

(b) an anionic surfactant component which represents from 50% to 90% of the ternary surfactant system and is represented by a binary mixture of:

(1) an alkyl(aryl)sulfonated surface-active agent; and

(2) 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; the weight ratio of sulfonate to succinate being in the range from 3:1 to 1:4; and

(c) a nonionic surfactant component representing from 50% to 10% of the ternary surfactant system;

said composition having a pH, measured in 1% solution at 20°C, in the range from about 7 to about 9.

Detailed Description of the Invention

The invention herein can be embodied by highly concentrated homogeneous liquid detergent compositions containing a ternary surfactant system and having a pH in the neutral to mildly alkaline range.

The essential parameters qualifying the invention are described in more detail hereinafter.

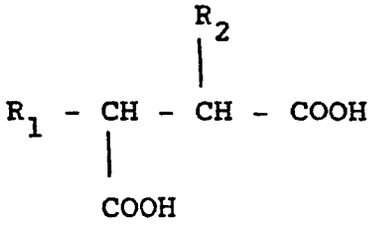
Unless stated to the contrary, the "percent-indications" stand for "percent by weight" of the composition.

The anionic surfactant component amounts to from 50% to

90% of the ternary surfactant system and is represented by a binary combination of:

(1) an alkyl(aryl) sulfonated surface-active agent; and

(2) 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; the weight ratio of sulfonate to succinate being in the range from 3:1 to 1:4.

The anionic sulfonate surfactant can be represented by all alkyl(aryl) sulfonated surface-active agents which are known to be suitable for use in liquid detergent compositions and have been used in fact, extensively, in commercial detergent executions.

The like anionic synthetic sulfonates can be represented by the general formula R^1SO^3M wherein R^1 represents a hydrocarbon moiety selected from the group consisting of straight or branched alkyl radicals containing from about 8 to about 24 carbon atoms and alkyl phenyl radicals containing from about 10 to about 18 carbon atoms in the alkyl group. M is a salt forming cation which typically is selected from the group consisting of sodium, potassium, magnesium, ammonium, monoalkanolammonium, dialkanolammonium, trialkanolammonium and mixtures thereof.

A preferred synthetic anionic sulfonate surfactant is a water-soluble salt of an alkylbenzene sulfonic acid containing from about 10 to about 18 carbon atoms in the alkyl group, the most preferred species for use herein having from C_{12} to C_{16} carbon atoms in the alkyl chain.

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.

The weight ratio of sulfonate to succinate surfactant in the binary mixture is in the range from 3:1 to 1:4, preferably from 2:1 to 1:2.

The ternary surfactant system represents usually from 35% to 75% of the composition. The anionic surfactant component is defined in the salt form.

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 conden- sation 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.

Preferred nonionic ethoxylated components can also be represented by a mixture of 2 separately ethoxylated nonionic surfactants having a different degree of ethoxylation. For example, the nonionic ethoxylate can be represented by mixtures of a first ethoxylated surfactant containing from 3 to 7 moles of ethylene oxide per mole of hydrophobic moiety and a second ethoxylated species having from 8 to 14 moles of ethylene oxide per mole of hydrophobic moiety. A preferred nonionic ethoxylated mixture contains a lower ethoxylate which is the condensation product of a C_{12}-C_{15} oxo-alcohol, with up to 50% (wt) branching, and from about 3 to 7 moles of ethylene oxide per mole of fatty oxo-alcohol, and a higher ethoxylate which is the condensation product of a C_{16}-C_{19} oxo-alcohol with more than 50% (wt) branching

and from about 8 to 14 moles of ethylene oxide per mole of branched oxo-alcohol.

The nonionic surfactant component represents from 50% to 10%, preferably from 15% to 40% of the ternary surfactant system.

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

The claimed compositions are further characterized by 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, 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, e.g. in levels not exceeding 25% of the ternary surfactant system. 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, cellulase, 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 2%. Suitable polyacids are those having one pK value of at least 5. Preferred polyacid species for use herein can be represented by 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 are disclosed in European Patent Application 83201776.8.

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-m-cresol) 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. Patent Application Serial Number 684.511, filed December 21, 1984, incorporated herein by reference.

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.

EXAMPLE I

A liquid detergent composition in accordance with the invention is prepared by mixing the listed ingredients in the stated proportions.

Ingredients		% by weight
Dodecylbenzene sulfonate acid		10.-
C_{10}-C_{15}-oxoalcohol condensed with 7 moles of ethylene oxide per mole of fatty alcohol		11.5
2-Dodecenyl-succinic acid		15.-
C_{12}-C_{14} alcohol sulfate-triethanol-amine salt		4.-
Oleic acid		4.-
Triethanolamine	]	5.-
	] neutralizing agents	
Sodium hydroxide	] to yield pH 7.6	6.-
Ethanol		7.-
Water		32.-
Miscellaneous-Minors		balance to 100

The preceeding composition is, from a detergency performance standpoint, compared to ARIEL,[R] a granular tripolyphos- phate built detergent containing oxygen bleach. The tests are carried out in a horizontal drum washing machine in an up-to-60°C cycle. Comparative performances are measured on cotton strips, stained with various types of artificial soils inclusive of bleach-builder sensitive soils, enzyme- sensitive soils, particulate soils and greasy-oily soils. It is found that the composition in accordance with this invention provides textile cleaning performance on all types of soils comparable to what is obtained from ARIEL.

It was also found that the liquid composition of Example I remained homogeneous and stable after at least 2 weeks

storage at temperatures varying from 4°C to 50°C and also following exposure to several freeze-thaw cycles.

The following examples illustrate additional executions of this invention. The abbreviations for the individual ingredients of the examples have the following meaning:

C_{12}HLAS	linear dodecyl benzene sulfonic acid
C_{16}HLAS	linear hexadecyl benzene sulfonic acid
C_{20}AS	sodium salt of eicosene α sulfonate
TEA CnAS	triethanolamine coconut(C_{12-14}) alcohol sulfate
$C_{x-y}EO_n$	C_{x-y} alcohol ethoxylated with n moles of ethylene oxide
$C_{x-y}EO_nS$	sodium salt of sulfated $C_{x-y}EO_n$
DSA	2-dodecenyl succinic acid
HDSA	dodecyl succinic acid
TSA	2-tetradecenyl succinic acid
C_{12-14}FA	coconut fatty acid
DETPMP	diethylene triamino pentamethyl phosphonic acid
TEA	triethanolamine
TPG-EO_{30}	poly(terephthalate propylene glycol ester) ethoxylated with about 30 moles of ethylene oxide.

	EXAMPLES											
	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII
	in % by weight											
C_{12}HLAS	8.5	15	10	-	11	10	6	8	11	-	14	8
C_{16}HLAS				12.5								
C_{20}ES										12		
$C_{16-18}EO_{11}$					7							
$C_{13-15}EO_7$				11.5		6	15	12	12	12	10	
$C_{13-15}EO_5$	13		11									14
$C_{13-15}EO_4$		7			7	6						
$C_{16-18}EO_2S$								5				
DSA	15	15	12.5	15			15	15	10	15	8	15
HDSA					7							
TSA						17						
TEA CnAS	4		4	3			3					4
$C_{12-14}FA$									5		5	
Oleic acid	4		5	4	4		8		3		3	4
Citric acid	0.9	1.0	0.2	1.0	0.2	1.0	0.2	1.0	0.2	1.0	1.0	0.5
DETPMP	0.8	0.9	0.9	0.6	0.9	0.6	0.9	0.6	0.9	0.9	0.9	0.8
TPG-EO	0.5		0.5									
Ethanol	8	8	6	5	8	10	6	6	8	5	10	8
TEA	5	5	4	5	6	5	4	4	4	5	5	8
NaOH	to neutralize acid components up to pH 7.5 to 7.8 as is											
Water	30	38	36	32	39	35	32	31	35	39	33	30
Miscellaneous incl.brightener, enzyme,aesthetic	up to 100											
pH(1% sol.)	7.9	7.9	7.7	7.9	7.5	8.0	7.9	7.9	7.7	7.9	7.5	7.7

CLAIMS

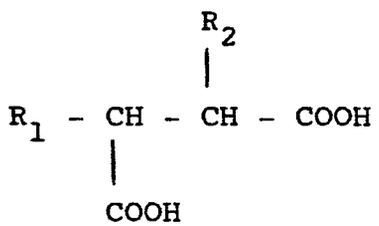
1. Homogeneous concentrated aqueous liquid detergent composition containing less than 50% by weight water, a ternary anionic-nonionic surfactant system, and if desired, conventional additives, characterized in that,

(a) the ternary surfactant system represents from 35% to 75% by weight (of the composition);

(b) the anionic surfactant component amounts to 50% to 90% by weight of the ternary surfactant system and is represented by a binary mixture of:

(1) an alkyl(aryl)sulfonated surface-active agent; and

(2) 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; the weight ratio of sulfonate to succinate being in the range from 3:1 to 1:4; and

(c) the nonionic surfactant component represents from 50% to 10% of the ternary surfactant system;

said composition having a pH, measured in 1% solution at 20°C, in the range from about 7 to about 9.

2. The composition in accordance with Claim 1 wherein the alkyl(aryl)sulfonate is an alkylbenzene sulfonate salt having from 10 to 18 carbon atoms in the alkylgroup, the salt forming cation being, sodium, potassium, magnesium, ammonium, monoalkanolammonium, dialkanolammonium, trialkanolammonium and mixtures thereof.

3. The composition in accordance with Claim 1 wherein the alk(en)yl succinate is selected from the group of 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.

4. The composition in accordance with Claim 3 wherein the alk(en)yl group is a straightchain moiety and wherein the weight ratio of the sulfonate surfactant to the succinate surfactant is in the range from 2:1 to 1:2.

5. The composition in accordance with Claim 3 wherein the nonionic surfactant component represents from 15% to 40% by weight of the ternary surfactant system.

6. The composition in accordance with Claim 1 which contains from 15% to 40% by weight of water.

7. The composition in accordance with Claim 1 which, in addition, contains from 1% to 8% by weight of a C_{10}-C_{18} fatty acid.

8. The composition in accordance with Claim 7 which in addition contains from 0.01% to 0.25% by weight of an antioxidant.

9. The composition in accordance with Claim 8 wherein the fatty acid is oleic acid.