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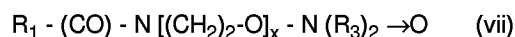
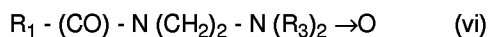
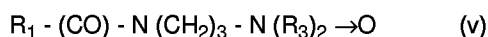
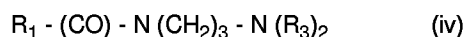
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1350 Jauche (BE)(74) Representative: **Engisch, Gautier et al****Procter & Gamble****European Technical Center N.V.****Temselaan 100****1853 Strombeek-Bever (BE)**(54) **Low sudsing liquid detergent compositions**

(57) A liquid detergent comprising a silicone suds suppressor and a short chain length amine surfactant selected from the formulas (i)-(viii) :



wherein R_1 is a linear, branched, cyclic, saturated or unsaturated alkyl group having 6 to 10 carbons atoms; R_2 is a hydrogen or methyl group; R_3 is independently selected from a hydrogen, methyl, CH_2CH_2OH , polyethoxy or polypropoxy group and x is between 1 to 5.

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DescriptionField of the invention

5 The present invention relates to detergent compositions having controlled sudsing profile. More in particular, the invention relates to liquid detergent compositions comprising a suds suppressing system, said suds suppressing system comprising a silicone suds suppressor and a specific short chain length amine surfactant.

Background of the invention

10 The effective and uniform control of the quantity of suds formed during the laundry operation is a long-standing and well-known product formulation aspect which desires additional improvement. Excessive sudsing can affect the overall textile cleaning and fabric benefits frequently conferred by modern detergent compositions, particularly when the washing treatment is carried out in drum washing machine. Too much sudsing in the washing machine is undesirable because not only it does interfere - diminish - the action of the laundry liquor upon fabrics but also residual suds in the washing machine can be carried over to the rinse cycle. This will not only increase the amount of suds in the rinse with the inherent difficulties of suppressing it but also can interfere with active agents to the rinsing step such as textile softeners.

20 This problem has been often addressed in the prior art by the incorporation of suds suppressing systems in conventional surfactant detergent mixture compositions. Suds suppressing systems include for example suds suppressing agents such as silicone. However, suds suppressing systems such as silicone can be difficult to maintain as a dispersion in liquid compositions and are difficult to process. In addition silicone suds suppressors are expensive.

25 In such context, European patent application No. 94922023.0 filed June 28, 1993 discloses low sudsing liquid detergent compositions comprising a conventional anionic surfactant in combination with a α -branched anionic surfactant. European patent application No. 94307794.1 filed October 24, 1994 describes concentrated detergent compositions comprising branched nonionic surfactants derived from 2-alkyl-alkanols and having controlled sudsing profile. A suds suppressor system comprising a specific mixture of fatty acids and silicone anti-foam agent and capable of providing a suds controlling profile for concentrated liquid detergent has been proposed in European patent application No. 94307979.8 filed October 28, 1994.

30 It has been now surprisingly found that the addition of a specific short chain length $C_6 - C_{10}$ amine surfactant to a silicone suds suppressor in a liquid detergent composition, provide a synergistic enhancement in the suds-suppression effectiveness of the silicone suds suppressor. This finding allows us to reduce the level of silicone suds suppressor while maintaining the suds controlling profile of silicone-containing liquid detergents.

35 Therefore, it is an object of the present invention to provide a suds suppressors system having an effective suds controlling profile for liquid detergents.

It is another object of this invention to provide homogeneous liquid detergent compositions which will remain stable, particularly upon prolonged storage.

The above objectives have been met by a suds suppressing system comprising silicone suds suppressors in combination with a specific short chain length $C_6 - C_{10}$ amine surfactant.

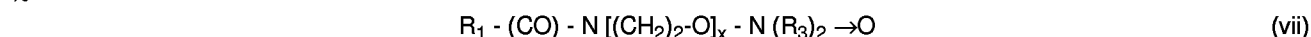
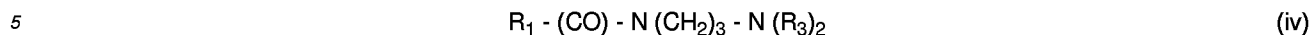
40 WO 95/05440 discloses granular automatic dishwashing compositions comprising long-chain ($>12C$) amines oxides and silicone suds suppressors. Shorter-chain amines oxides are therein recognised to foam less but provide poorer cleaning. Short chain length are known in the art to be lower foaming than long chain surfactants (*J. Coll. Int. Sci.*, 159, pp 214-225 (1993) - Kirk-Othner's Enc. Chem. Techn., p 359). Indeed, European patent application No. 93870050.7 filed March 19, 1993 discloses that the following nonionic surfactants - short chain alkoxyated alcohols - are particularly efficient in cleaning and are low foaming and mild to the skin.

45 Amineoxides are extensively described in general detergent formulations (J 04 011 698, GB 2 229 460), in dishwashing (WO 95/20026, WO 95/07971) and in personal cleansing applications (GB 2 160 541, US 5 290 471, DE 4 020 500). $C_{10} - C_{18}$ amineoxides (J 59 196 395, J 56087000), betaines are generally described as suds enhancing agents (WO 94/05758, WO 92/06161, US 4 879 051). WO 95/20028 indeed states that the inclusion of relatively high levels of long chain amineoxides substantially enhances the grease and oil removal of the detergent compositions and allows the formulation of reasonably low sudsing, stable and homogeneous detergent compositions.

Summary of the invention

55 The present invention relates to liquid detergents comprising a suds suppressing system, said system comprising a silicone suds suppressor and a specific short chain length amine surfactant selected from the formulas (i)-(viii):



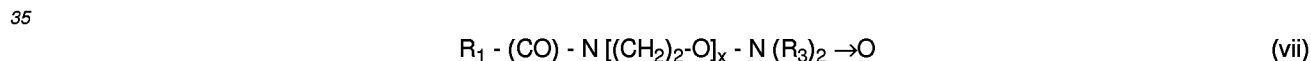
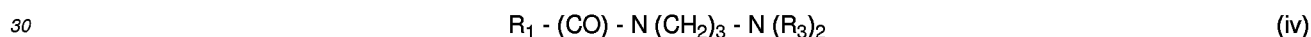
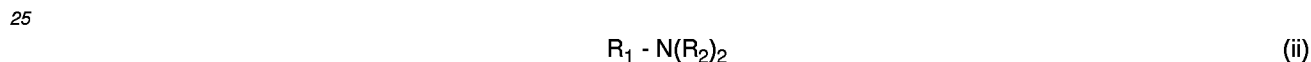


and mixtures thereof (viii)

15 wherein R₁ is a linear, branched, cyclic, saturated or unsaturated alkyl group with 6 to 10 carbons atoms; R₂ is a hydrogen or methyl group; R₃ is independently selected from a hydrogen, methyl, CH₂CH₂OH, polyethoxy or polypropoxy group and x is between 1 to 5.

Detailed description of the invention

20 The liquid detergent of present invention comprise a suds suppressing system consisting of a silicone suds suppressor and a short chain length amine surfactant selected from the formulas (i)-(viii):



and mixtures thereof (viii)

40 wherein R₁ is a linear, branched, cyclic, saturated or unsaturated alkyl group with 6 to 10 carbons atoms; R₂ is a hydrogen or methyl group; R₃ is a hydrogen, methyl, CH₂CH₂OH, polyethoxy or polypropoxy group and x is between 1 to 5.

Preferred short chain length amine surfactants are selected from the group of amidopropylamines, dimethylamines, trimethylammonium salts, hydroxyethyl dimethylammonium salts, bishydroxyethyl methylammonium salts, dimethylamine oxides, betaines, amidopropylbetaines; more preferred short length C₆ - C₁₀ amine surfactant are amine oxides and amido-propyldimethylamines; most preferred are ethylhexyl amine, octylamine and hexylamine.

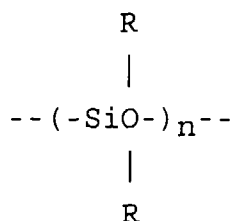
The level of short chain length amine surfactant will vary depending on the particular characteristics desired in the final detergent composition. It will generally be comprised between 0.2 to 10% by weight of the total detergent composition

50 For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilised, are preferably present in a "suds suppressing amount". By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

55 Preferably, the weight ratio of the short chain length amine surfactant to the silicone ranges from 0.1 to 250, more preferably from 0.5 to 150, and most preferably from 1 to 50.

It has been found that the short chain length amine surfactants according to the present invention synergistically enhance the suds suppressing activity of the silicone suds suppressor. The silicone/short chain length amine surfactant combination according to the present invention gives a statistically significant better suds suppressing activity which is better than the sum of the individual suds suppressing activity of both ingredients.

In industrial practice, the term "silicone suds suppressor" has become a generic term which encompasses a variety of relatively high-molecular-weight polymers containing siloxane units and hydrocarbyl groups of various types. Generally, the silicone suds controllers can be described as siloxanes having the general structure:



wherein n is from 20 to 2,000, and where each R independently can be an alkyl or an aryl radical. Examples of such substituents are methyl, ethyl, propyl, isobutyl, and phenyl. Preferred polydiorganosiloxanes are polydimethylsiloxanes having trimethylsilyl endblocking units and having a viscosity at 25°C of from 5×10^{-5} m²/s to 0.1 m²/s i.e. a value of n in the range 40 to 1500. These are preferred because of their ready availability and their relatively low cost.

Other suitable silicone oils that can be used for the present invention are functional silicone oils. Preferred functional silicone oils are anionic or cationic type of silicone oils.

Other silicone include combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica.

Silicone suds suppressors are well-known in the art and are, for example, disclosed in U.S. Patent 4,265,779, and European Patent Application No. 89307851.9, published February 7, 1990, by Starch, M.S.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839, which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672 and in U.S. Patent 4,652,392.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of :

- (i) polydimethylsiloxane fluid having a viscosity of from about 20 cs. to about 1,500cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of (CH₃)₃SiO_{1/2} units of SiO₂ units in a ratio of from (CH₃)₃SiO_{1/2} units and to SiO₂ units of from about 0.6:1 to about 1.2:1, and
- (iii) from about 1 to about 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The preferred primary silicone suds suppressor is branched/crosslinked.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from about 0.001 to about 2, preferably from about 0.01 to about 0.7, most preferably from about 0.05 to about 0.5 weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant, and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than about 2 weight % and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471 and 4,983,316, U.S. Patent 5,288,431 and U.S. Patents 4,639,489 and 4,749,740.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene glycol/polypropylene glycol, all having an average molecular weight of less than about 1,000, preferably between about 100 and 800. The polyethylene glycol and polyethylene/ polypropylene copolymers herein have a solubility in water at room temperature of more than about 2 weight %, preferably more than about 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than about 1,000, preferably between about 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between about 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like

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Silicone suds suppressors are typically utilized in amounts up to about 2.0% by weight of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.05% to about 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized.

In terms of processing, the silicone/short chain length amine surfactant being cationic at low pH can be added to the liquid detergent composition as a premix as such or as a mixture with other detergent ingredients.

Adjunct detergent ingredients

In another embodiment of the present invention, the liquid detergent composition is provided comprising the surfactant system of the present invention mixed with detergent ingredients. A wide range of surfactants can be used in the detergent composition of the present invention.

A typical listing of anionic, nonionic, ampholytic and zwitterionic classes, and species of these surfactants, is given in US Patent 3,664,961 issued to Norris on May 23, 1972.

ANIONIC SURFACTANTS

Suitable anionic surfactants include alkyl alkoxyated sulfate surfactants hereof are water soluble salts or acids of the formula $RO(A)_mSO_3M$ wherein R is an unsubstituted $C_{10}-C_{24}$ alkyl or hydroxyalkyl group having a $C_{10}-C_{24}$ alkyl component, preferably a $C_{12}-C_{20}$ alkyl or hydroxyalkyl, more preferably $C_{12}-C_{18}$ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are $C_{12}-C_{18}$ alkyl polyethoxylate (1.0) sulfate ($C_{12}-C_{18}E(1.0)M$), $C_{12}-C_{18}$ alkyl polyethoxylate (2.25) sulfate ($C_{12}-C_{18}E(2.25)M$), $C_{12}-C_{18}$ alkyl polyethoxylate (3.0) sulfate ($C_{12}-C_{18}E(3.0)M$), and $C_{12}-C_{18}$ alkyl polyethoxylate (4.0) sulfate ($C_{12}-C_{18}E(4.0)M$), wherein M is conveniently selected from sodium and potassium.

Suitable anionic surfactants to be used are alkyl ester sulfonate surfactants including linear esters of C_8-C_{20} carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO_3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula :



wherein R^3 is a C_8-C_{20} hydrocarbyl, preferably an alkyl, or combination thereof, R^4 is a C_1-C_6 hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R^3 is $C_{10}-C_{16}$ alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R^3 is $C_{10}-C_{16}$ alkyl.

Other suitable anionic surfactants include the alkyl sulfate surfactants hereof are water soluble salts or acids of the formula $ROSO_3M$ wherein R preferably is a $C_{10}-C_{24}$ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a $C_{10}-C_{20}$ alkyl component, more preferably a $C_{12}-C_{18}$ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of $C_{12}-C_{16}$ are preferred for lower wash temperatures (e.g. below about $50^\circ C$) and $C_{16}-C_{18}$ alkyl chains are preferred for higher wash temperatures (e.g. above about $50^\circ C$).

Other anionic surfactants useful for deterative purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9-C_{20} linear alkylbenzenesulfonates, C_8-C_{22} primary or secondary alkanesulfonates, C_8-C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No.

1,082,179, C₈-C₂₄ alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide) ; alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C₁₂-C₁₈ monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C₆-C₁₂ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those of the formula RO(CH₂CH₂O)_k-CH₂COO-M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.

NONIONICS

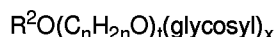
Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms, preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal™ CO-630, marketed by the GAF Corporation; and Triton™ X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about 10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol™ 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), Tergitol™ 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol™ 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), Neodol™ 23-6.5 (the condensation product of C₁₂-C₁₃ linear alcohol with 6.5 moles of ethylene oxide), Neodol™ 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), Neodol™ 45-4 (the condensation product of C₁₄-C₁₅ linear alcohol with 4 moles of ethylene oxide) marketed by Shell Chemical Company, and Kryo™ EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company.

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

Optionally, and less desirably, there can be a polyalkylene-oxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecyldodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexagluco-sides, galactosides, lactosides, glucoses, fructosides, fructoses and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentagluco-sides and tallow alkyl tetra-, penta-, and hexagluco-sides.

The preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

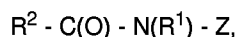
Although not preferred, the condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant of the nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C_8 - C_{14} alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C_8 - C_{18} alcohol ethoxylates (preferably C_{10} avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants.

Also suitable as nonionic surfactants are poly hydroxy fatty acid amide surfactants of the formula

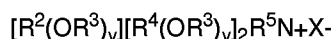


wherein R^1 is H, or R^1 is C_{1-4} hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R^2 is C_{5-31} hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof. Preferably, R^1 is methyl, R^2 is a straight C_{11-15} alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

When included in such laundry detergent compositions, the nonionic surfactant systems of the present invention act to improve the greasy/oily stain removal properties of such laundry detergent compositions across a broad range of laundry conditions.

The laundry detergent compositions of the present invention may also contain nonionic, ampholytic, zwitterionic, and semi-polar surfactants, as well as cationic surfactants other than those already described herein.

Preferred other cationic surfactant systems include nonionic and ampholytic surfactants. Other cationic deterative surfactants suitable for use in the laundry detergent compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula :



wherein R^2 is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R^3 is selected from the group consisting of $-CH_2CH_2-$, $-CH_2CH(CH_3)-$, $-CH_2CH(CH_2OH)-$, $-CH_2CH_2CH_2-$, and mixtures thereof; each R^4 is selected from the group consisting of C_1 - C_4 alkyl, C_1 - C_4 hydroxyalkyl, benzyl ring structures formed by joining the two R^4 groups, $-CH_2CHOH-CHOHCOR^6CHOHCH_2OH$ wherein R^6 is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R^5 is the same as R^4 or is an alkyl chain

wherein the total number of carbon atoms of R^2 plus R^5 is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



wherein R_1 is C_8 - C_{16} alkyl, each of R_2 , R_3 and R_4 is independently C_1 - C_4 alkyl, C_1 - C_4 hydroxy alkyl, benzyl, and - $(C_2H_4O)_xH$ where x has a value from 2 to 5, and X is an anion. Not more than one of R_2 , R_3 or R_4 should be benzyl. The preferred alkyl chain length for R_1 is C_{12} - C_{15} particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R_2R_3 and R_4 are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

coconut trimethyl ammonium chloride or bromide;
 coconut methyl dihydroxyethyl ammonium chloride or bromide;
 decyl triethyl ammonium chloride;
 decyl dimethyl hydroxyethyl ammonium chloride or bromide;
 C_{12-15} dimethyl hydroxyethyl ammonium chloride or bromide;
 coconut dimethyl hydroxyethyl ammonium chloride or bromide;
 myristyl trimethyl ammonium methyl sulphate;
 lauryl dimethyl benzyl ammonium chloride or bromide;
 lauryl dimethyl (ethenoxy) $_4$ ammonium chloride or bromide;
 choline esters (compounds of formula (i) wherein R_1 is - $CH_2-O-C(O)-C_{12-14}$ alkyl and $R_2R_3R_4$ are methyl).

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 25%, preferably from about 3% to about 15% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the laundry detergent compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

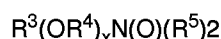
When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

Zwitterionic surfactants are also suitable for use in laundry detergent compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof;

x is from 0 to about 3; and each R⁵ is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R⁵ groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxy ethyl amine oxides.

When included therein, the laundry detergent compositions of the present invention typically comprise from 0% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

The present invention further provides laundry detergent compositions comprising at least 1% by weight, preferably from about 3% to about 65%, more preferably from about 10% to about 25% by weight of total surfactants.

BUILDER

The compositions according to the present invention may further comprise a builder system. Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyposphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Though less preferred for obvious environmental reasons, phosphate builders can also be used herein.

Suitable polycarboxylates builders for use herein include citric acid, preferably in the form of a water-soluble salt, derivatives of succinic acid of the formula R-CH(COOH)CH₂(COOH) wherein R is C₁₀-20 alkyl or alkenyl, preferably C₁₂-16, or wherein R can be substituted with hydroxyl, sulfo sulfoxyl or sulfone substituents. Specific examples include lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenylnsuccinate, 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid such as described in US 4,663,071.

Especially for the liquid execution herein, suitable fatty acid builders for use herein are saturated or unsaturated C₁₀-18 fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. Another preferred builder system for liquid compositions is based on dodecenyl succinic acid and citric acid.

Detergency builder salts are normally included in amounts of from 10% to 80% by weight of the composition preferably from 20% to 70% and most usually from 30% to 60% by weight.

Other components used in detergent compositions may be employed, such as enzymes and stabilizers or activators therefore, soil-suspending agents, abrasives, bactericides, tarnish inhibitors, coloring agents, corrosion inhibitors and perfumes. Especially preferred are combinations with enzyme technologies which also provide a type of color care benefit. Examples are cellulase for color maintenance/rejuvenation. Other examples are the polymers disclosed in EP 92870017.8 filed January 31, 1992 and enzyme oxidation scavengers disclosed in EP 92870018.6 filed January 31, 1992.

Also particularly suitable are amine base catalyst stabilizers disclosed in EP 92870019.4 filed January 31, 1992.

The detergent compositions of the present invention can also be used as detergent additive products. Such additive products are intended to supplement or boost the performance of conventional detergent compositions.

The detergent compositions according to the present invention include compositions which are to be used for cleaning of substrates, such as fabrics, fibers, hard surfaces, etc., for example laundry detergent compositions and automatic and non-automatic dishwashing compositions, hard surface cleaners.

The following examples are meant to exemplify compositions of the present inventions, but are not necessarily meant to limit the scope of the invention.

Example I :

Aqueous liquid detergent compositions were prepared in accord with the present invention and were found to be very efficient in controlling suds while remaining stable upon prolonged periods of storage.

	I	II	III	IV	V
5 Alkylsulphate	15.75	15.75	15.75	15.75	15.75
Alkylethoxylate	3.0	3.0	3.0	3.0	3.0
C ₁₃₋₁₅ mixed etoxylated/propoxylated fatty alcohol	2.5	2.5	2.5	2.5	2.5
Polyhydroxy fatty acid amide	6.8	6.8	6.8	6.8	6.8
10 Silicone	0.1	0.1	0.1	0.1	0.1
Ethylhexylamine	-	1.0	-	-	0.5
Hexylamine	0.5	-	1.0	-	-
15 Octylamine	0.5	-	-	1.0	0.5
Topped palm kernel fatty acid	-	10.0	10.0	10.0	2.0
Rapeseed fatty acid	10.0	-	-	-	8.0
Citric acid	1.6	1.6	1.6	1.6	1.6
20 Protease	1.5	1.5	1.5	1.0	1.5
Amylase	-	0.8	0.8	1.0	-
Lipase	0.5	-	-	0.1	0.5
25 Cellulase	-	0.1	0.2	0.1	0.2
Calcium chloride	0.1	0.1	0.1	0.1	0.1
Boric acid	2.0	-	2.0	-	1.0
Minors (including ethanol, propanediol, monoethylamine and NaOH)	Up to 100%				
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Example II :

35 Non-aqueous liquid detergent compositions were prepared in accord with the present invention and were found to be very efficient in controlling suds while remaining stable upon prolonged periods of storage.

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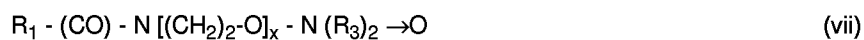
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	I	II	III	IV	V
5 Linear alkyl benzene sulfonate	20.0	20.0	20.0	20.0	20.0
C ₁₃₋₁₅ mixed etoxylated/propoxylated fatty alcohol	18.0	18.0	18.0	18.0	18.0
Butoxy propoxy propanol	18.0	18.0	18.0	18.0	18.0
Silicone	0.9	0.9	0.9	0.9	0.9
10 Hexamethylenediamine tetra-E24 ethoxylate	0.9	0.9	0.9	0.9	0.9
Ethylhexylamine	-	1.0	-	-	0.5
Hexylamine	0.5	-	1.0	-	-
15 Octylamine	0.5	-	-	1.0	0.5
Acrylic acid/maleic acid copolymer	3.3	3.3	3.3	3.3	3.3
Citric acid	1.4	1.4	1.4	1.4	1.4
Na ₂ CO ₃	3.4	3.4	3.4	3.4	3.4
20 1,1-hydroxyethane diphosphonic acid	1.8	1.8	1.8	1.8	1.8
TiO ₂	0.4	0.4	0.04	0.4	0.4
Protease	1.5	1.5	1.5	1.0	1.5
25 Amylase	-	0.8	0.8	1.0	-
Lipase	0.5	-	-	0.1	0.5
Cellulase	-	0.1	0.2	0.1	0.2
Percarbonate	19.0	19.0	19.0	19.0	19.0
30 Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid	6.9	6.9	6.9	6.9	6.9
Minors Up to 100%					

Claims

1. A liquid detergent comprising a silicone suds suppressor and a short chain length amine surfactant selected from the formulas (i)-(viii) :



wherein R₁ is a linear, branched, cyclic, saturated or unsaturated alkyl group having 6 to 10 carbons atoms; R₂ is a hydrogen or methyl group; R₃ is independently selected from a hydrogen, methyl, CH₂CH₂OH, polyethoxy or poly-

propoxy group and x is between 1 to 5.

2. A liquid detergent composition according to claim 1 wherein the weight ratio of said amine surfactant to the silicone suds suppressor is from 1 to 250, more preferably from 0.5 to 150 and most preferably from 1 to 50.

3. A liquid detergent composition according to claims 1-2 wherein said amine surfactant is selected from ethylamine, octylamine and hexylamine.

4. A detergent composition according to claims 1-3 further comprising surfactants, builders, enzymes and other conventional detergent ingredients.

5. A detergent composition according to Claims 1-4 further comprising an anionic surfactant selected from an alkyl ethoxylated sulfate and/or alkyl sulfate surfactant.

6. A detergent composition according to claims 1-5 which is in the form of an additive.

7. Use of a detergent composition according to claims 1-6 for the cleaning of fabrics, dishes and hard surfaces.

8. Use of a detergent composition according to Claims 1-6 for pretreatment of fabrics, dishes and hard surfaces.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 96 87 0038

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	CA-A-2 144 781 (PROCTER & GAMBLE) 1 October 1995 * page 3, line 17 - page 5, line 18; claims; example 1; tables 1,2 * ---	1,2,4,7,8	C11D3/30 C11D1/75
D,A	WO-A-95 20028 (PROCTER & GAMBLE) 27 July 1995 * claims * ---	1,2,4-8	
A	US-A-4 584 125 (GRISWOLD ROY M ET AL) 22 April 1986 * column 4, line 3 - line 9 * * column 10, line 5 - line 16; claim 1 * -----	1-3,7	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 August 1996	Examiner Grittern, A
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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