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DescriptionTechnical Field

5 The present invention relates to heavy-duty liquid detergent compositions containing a soil release agent; anionic surfactant (preferably comprising a sulfonate surfactant and alcohol ethoxylate sulfate surfactant); ethoxylated nonionic surfactant; an optional quaternary ammonium, amine, amide, or amine oxide surfactant; preferably, saturated fatty acid and polycarboxylate builders; a neutralization system preferably comprising sodium, potassium and/or low levels of alkanolamines; and a solvent system
10 preferably comprising ethanol, polyol and water. The compositions are isotropic liquids which provide a high level of detergency performance.

There has been considerable demand for liquid detergents capable of providing superior cleaning under a wide variety of laundering conditions. Such compositions generally require a number of ingredients which tend to separate into discrete phases. Isotropic liquid detergents are desired for both consistency of
15 performance and aesthetic reasons. The compositions should remain isotropic during shipping and storage, where temperatures of 55 °F (12.8 °C) or lower are often encountered. They preferably are also formulated to recover, after freezing and thawing, to an isotropic phase prior to consumer use.

Liquid detergents desirably contain a soil release agent to enhance performance. However, soil release agents are difficult to incorporate in liquid detergents. Thus, there is a continuing need for the development
20 of an isotropic liquid detergent with a soil release agent capable of providing superior cleaning, bleach compatibility and product stability.

Background Art

25 US 4 125 370 discloses random ethylene terephthalate polyethylene oxide terephthalate polymers useful as soil release agents.

European Patent Application 0 095 205, Wertz et al, published November 30, 1983, discloses detergent compositions containing anionic surfactants, quaternary ammonium, amine or amine oxide surfactants, and fatty acids, and formulated to provide a near-neutral wash pH. The compositions are preferably liquid
30 detergents which additionally contain ethoxylated nonionic surfactants and polycarboxylate builders.

U.S. Patent 4,285,841, Barrat et al, issued August 25, 1981, discloses liquid detergents containing anionic surfactants, nonionic surfactants and from about 8% to about 20% by weight of a fatty acid. The compositions have a pH of from about 6.0 to about 7.5.

35 U.S. Patent 4,287,082, Tolfo et al, issued September 1, 1981, discloses liquid detergents containing saturated fatty acids, enzymes, enzyme-accessible calcium and short-chain carboxylic acid salts, preferably formates.

EP-A-185 427, Eugene P. Gosselink, published on 25/6/86 discloses liquid detergent compositions of the presently claimed type comprising block polyester soil release agents belonging to the same class as the present soil release agents.
40

Summary of the Invention

The present invention encompasses heavy-duty liquid detergent compositions comprising, by weight:

(a) from 10% to 35%, of an anionic surfactant on an acid basis, preferably:

45 (i) from 5% to 15% of a sulfonate surfactant containing a C₁₀-C₁₆ alkyl or alkenyl group; and
(ii) from 5% to 18%, on an acid basis, of an alcohol ethoxylate sulfate surfactant of the formula RO-(C₂H₄O)_mSO₃M, wherein R is a C₁₀-C₁₆ alkyl or hydroxyalkyl group, m is from 0.5 to 4, and M is a compatible cation;

(b) from 0% to 15% of an ethoxylated nonionic surfactant of the formula R¹(OC₂H₄)_nOH, wherein R¹ is a C₁₀-C₁₆ alkyl group or a C₈-C₁₂ alkyl phenyl group, n averages from 3 to 9, and said nonionic surfactant
50 has an HLB of from 10 to 13;

(c) from 0% to 15% of a cosurfactant selected from the group consisting of:

(i) quaternary ammonium surfactants having the formula:

55 $[R^2(OR^3)_y][R^4(OR^3)_zR^5N^+X^-]$

wherein R² is an alkyl or alkyl benzyl group having from 6 to 16 carbon atoms in the alkyl chain; each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-,

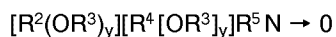
-CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is from 8 to 16; each y averages from 0 to 10 and the sum of the y values is from 0 to 15; and X is any compatible anion;

(ii) amine surfactants having the formula:



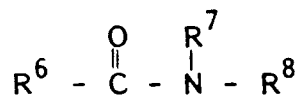
wherein R², R³, R⁴, R⁵ and y are as defined above;

(iii) amine oxide surfactants having the formula:



wherein R², R³, R⁴, R⁵ and y are as defined above;

(iv) an amide surfactant of the formula



wherein R⁶ is an alkyl, hydroxyalkyl or alkenyl radical containing from 8 to 20 carbon atoms, and R⁷ and R⁸ are each selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, and wherein said radicals additionally contain up to 5 ethylene oxide units, and, preferably, at least one of R⁷ and R⁸ contains a hydroxyl group; and

(v) mixtures thereof;

(d) from 5% to 30% of detergent builder, preferably:

(i) from 0% to 20% of a C₁₀-C₁₄ saturated fatty acid, the weight ratio of C₁₀-C₁₂ fatty acid to C₁₄ fatty acid being at least 1; and

(ii) from 3% to 20%, on an acid basis, of a water-soluble polycarboxylate builder material;

(e) a neutralization system, preferably:

(i) from 0 to 0.05 moles per 100 grams of composition of an alkanolamine selected from the group consisting of monoethanolamine, diethanolamine and triethanolamine; and

(ii) potassium and sodium ions in a potassium to sodium molar ratio of from 0.1 to 1.3;

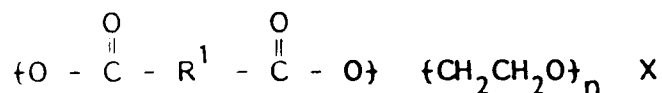
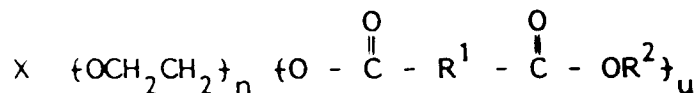
(f) a solvent system, said system not consisting of water only preferably:

(i) from 2% to 10% ethanol;

(ii) from 2% to 15% of a polyol containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups;

(iii) from 25% to 40% water; and

(g) from 0.25% to 4% of a soil release component which is a compound having the formula:



wherein each R¹ moiety is a 1,4-phenylene moiety, ; R² is an ethylene or, preferably, a 1,2-propylene moiety; each n averages 10 to 50; each X is H, and/or an alkyl radical having from 1 to 4 carbon atoms and/or an acyl radical containing from 2 to 4 carbon atoms;

wherein less than 10 mol% of said soil release compound has a u greater than 5, at least 20 mol% of said soil release compound has a u in the range of from 3 to 5 and wherein the average value of u is from 3 to 5.

Said compositions preferably contain from 20% to 40% of (a), (b), (c) and (d); said components being selected to provide an isotropic liquid at 55 °F (12.8 °C) having an initial pH of from 7.5 to 9, preferably from

8.4 to 8.8, at a concentration of 10% by weight in water at 68 °F (20 °C).

Detailed Description of the Invention

5 The liquid detergents of the present invention contain anionic surfactant, preferably a mixture of sulfonate and alcohol ethoxylate sulfate anionic surfactants; ethoxylated nonionic surfactant; optional quaternary ammonium, amine, amide, and/or amine oxide surfactants; builders, preferably saturated fatty acid and/or, polycarboxylate builders; a neutralization system, preferably comprising sodium, potassium and preferably low levels of alkanolamines; and a solvent system said system not consisting of water only, said system preferably comprising ethanol, polyol and water.

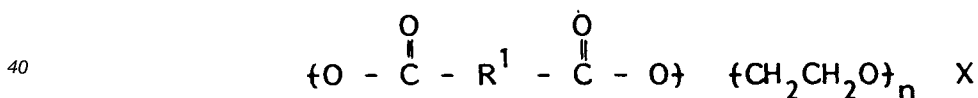
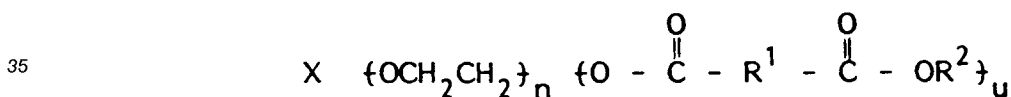
10 The compositions herein are formulated to provide a high level of detergency performance under a wide variety of laundering conditions. Preferred compositions herein are isotropic liquids at 50 °F (10 °C). They preferably also recover, after freezing and thawing, to an isotropic form by 55 °F (12.8 °C), more preferably by 50 °F (10 °C).

15 The present compositions preferably comprise a neutralization system comprising mixed potassium and sodium ions. Complete sodium neutralization tends to cause crystallization of the polycarboxylate builder and poor incorporation of the soil release polymer, whereas all potassium neutralization results in an unacceptably high gel point. The total level of organic and inorganic bases should also be selected to provide a sufficiently high product pH to minimize the level of poorly-soluble free fatty acids, without being so high that pH sensitive stain removal, enzyme stability, soil release polymer stability, and greasy/oily soil removal are compromised.

20 The compositions also preferably have a solvent system comprising water and a mixture of ethanol and polyol. Polyols such as propylene glycol are especially good at solubilizing the soil release polymer. Crystallization occurs without the polyol and unacceptably high gel points tend to occur without the ethanol. The amount of ethanol and polyol must also be sufficient to prevent organic phase separation (i.e., keep free fatty acids and poorly soluble surfactants in solution), and yet not be so high as to cause lye phase separation and/or crystallization by limiting the amount of water available.

The Soil Release Component

30 The soil release component has the generic formula



in which X is selected from the group consisting of H, alkyl groups having from 1 to 4 carbon atoms, preferably 1 to 2 carbon atoms, or acyl groups containing from 2 to 4 carbon atoms preferably alkyl groups. n is selected for water solubility and is a range of values which averages from 10 to 50, preferably from 10 to 25. The selection of u is critical to formulation in a liquid detergent having a relatively high ionic strength. There should be very little material, i.e. less than 10 mol %, preferably less than 5 mol %, more preferably less than 1 mol %, in which u is greater than 5. Furthermore there should be at least 20 mol %, preferably at least 40 mol %, of material in which u ranges from 3 to 5. The average value for u is from 3 to 5.

50 The R¹ moieties are 1,4-phenylene moieties.

For the R² moieties, suitable moieties include ethylene or 1,2-propylene, and mixtures thereof. Although inclusion of a greater percentage of ethylene moieties tends to improve the soil release activity of the compounds, the percentage included is limited by water solubility. Surprisingly, inclusion of a greater percentage of 1,2-propylene moieties tends to improve the water solubility of the compounds and consequently the ability to formulate isotropic aqueous detergent compositions without significantly harming soil release activity.

For this invention, the use of 1,2-propylene moieties is extremely important for maximizing incorporation of a substantial percentage of the soil release component in the heavy duty liquid detergent compositions.

Preferably, from 75% to 100%, more preferably from 90% to 100% of the R² moieties are 1,2-propylene moieties.

In general, soil release components which are soluble in cool (15°C) ethanol are also useful in compositions of the invention.

5 The value for n averages at least 10, but a distribution of n values is present. The value for each n usually ranges from 10 to 50. Preferably, the value for each n averages in the range of from 10 to 25.

A preferred process for making the soil release component comprises the step of extracting a polymer having a typical distribution in which a substantial portion comprises a material in which u is greater than 5 with essentially anhydrous ethanol at low temperatures, e.g. from 10°C to 15°C, preferably less than 13°C.
10 The ethanol soluble fraction is substantially free of the longer polymers and is much easier to incorporate into isotropic heavy duty liquids, especially those with higher builder levels. Although the polymers wherein u is less than 3 are essentially of no value in providing soil release effects, they can be more easily incorporated than higher u values.

A more preferred process for making the soil release component is by direct synthesis.

15 A more comprehensive disclosure of the starting soil release component and methods for making it can be found in European Patent Application EP-A-185 427 filed December 12, 1985 and published on 26/6/88.

The Anionic Surfactant

20 The anionic surfactant herein can comprise any of the synthetic anionic surfactants conventionally used in heavy duty laundry detergents including alkyl benzene sulfonates, alkyl sulfates, alkyl polyethoxylate sulfates, olefin sulfonates, paraffin sulfonates, etc. Mixtures can also be used. Suitable synthetic anionic surfactants are disclosed in detail in U.S. Patent 3,929,678, Laughlin et al, issued December 30, 1975.

Preferred synthetic anionic surfactants include the sulfonates, the alkyl sulfates, and alkylpolyethoxylate ether sulfates discussed more specifically below.
25

Sulfonate Surfactant

The detergent compositions herein preferably contain from 5% to 15%, more preferably from 6% to 12%, by weight (on an acid basis) of an anionic sulfonate surfactant containing a C₁₀-C₁₆ alkyl or alkenyl group. Anionic sulfonate surfactants useful herein are disclosed in U.S. Patent 4,285,841, Barrat et al, issued August 25, 1981, and in U.S. Patent 3,919,678, Laughlin et al, issued December 30, 1975.

Preferred sulfonate surfactants are the water-soluble salts, particularly the alkali metal, and alkanolammonium (e.g., monoethanolammonium or triethanolammonium) salts of alkylbenzene sulfonates in which the alkyl group contains from 10 to 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from 11 to 13.
35

Also useful herein are the water-soluble salts of paraffin sulfonates, olefin sulfonates, alkyl glyceryl ether sulfonates, esters of α-sulfonated fatty acids containing from 1 to 10 carbon atoms in the ester group, 2-acyloxy-alkane-1-sulfonates containing from 2 to 9 carbon atoms in the acyl group, and β-alkyloxy alkane sulfonates containing from 1 to 3 carbon atoms in the alkyl group.
40

Mixtures of the above-described sulfonates, particularly with the C₁₁₋₁₃ linear alkylbenzene sulfonates, can also be used.
45

Alcohol Ethoxylate Sulfate Surfactant

The present compositions also preferably contain an alcohol polyethoxylate ether sulfate surfactant of the formula RO(C₂H₄O)_mSO₃M, wherein R is a C₁₀-C₁₆ alkyl (preferred) or hydroxyalkyl group, m is from 0.5 to 4, and M is a compatible cation. This surfactant preferably represents from 5% to 18%, more preferably from 9% to 14%, by weight (on an acid basis) of the composition.
50

Preferred alcohol ethoxylate sulfate surfactants of the above formula are those wherein the R substituent is a C₁₂₋₁₅ alkyl group and m is from 1.5 to 3. Examples of such materials are C₁₂₋₁₅ alkyl polyethoxylate (2.25) sulfate (C₁₂₋₁₅ E_{2.25}S); C₁₄₋₁₅ E_{2.25}S; C₁₂₋₁₃ E_{1.5}S; C₁₄₋₁₅ E₃S; and mixtures thereof. The sodium, potassium, monoethanolammonium, and triethanolammonium salts of the above are preferred.
55

Ethoxylated Nonionic Surfactant

The compositions also preferably contain from 2% to 15%, more preferably from 4% to 12%, by weight of an ethoxylated nonionic surfactant of the formula $R^1(OC_2H_4)_nOH$, wherein R^1 is a C_{10} - C_{16} alkyl group or a C_8 - C_{12} alkyl phenyl group, n is from 3 to 9, and said nonionic surfactant has an HLB (hydrophile-lipophile balance) of from 10 to 13. These surfactants are more fully described in U.S. Patents 4,285,841, Barrat et al, issued August 25, 1981, and 4,284,532, Leikhim et al, issued August 18, 1981. Particularly preferred are condensation products of C_{12} - C_{14} alcohols with from 3 to 8 moles of ethylene oxide per mole of alcohol, e.g., C_{12} - C_{13} alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

The ethoxylated nonionic surfactants herein have an HLB (hydrophilic-lipophilic balance) of from 5 to 17, preferably from 6 to 13. HLB is defined in detail in Nonionic Surfactants, by M.J. Schick, Marcel Dekker, Inc., 1966, pages 607-613. Suitable ethoxylated nonionic surfactants herein are as follows:

(1) The polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, said ethylene oxide being present in an amount equal to 3 to 25 moles of ethylene oxide per mole of alkyl phenol.

Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecylphenol condensed with about 12 moles of ethylene oxide per mole of phenol; dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol; and diisooctyl phenol condensed with about 15 moles of ethylene oxide per mole of 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.

(2) The condensation products of aliphatic alcohols with from 1 to 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 8 to 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of alcohol; and the condensation product of about 9 moles of ethylene oxide with coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from 10 to 14 carbon atoms). Examples of commercially available nonionic surfactants in this type include Tergitol® 15-S-9, marketed by Union Carbide Corporation, Neodol® 45-9, Neodol® 23-6.5, Neodol® 45-7, and Neodol® 45-4, marketed by Shell Chemical Company, and Kyro® EOB, marketed by The Procter & Gamble Company.

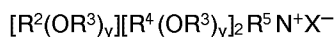
(3) Mixtures of the above.

Preferred ethoxylated nonionic surfactants are of the formula $R^1(OC_2H_4)_nOH$, wherein R^1 is a C_{10} - C_{16} alkyl group or a C_8 - C_{12} alkylphenyl group, n is from 3 to 9, and said nonionic surfactants has an HLB (hydrophile-lipophile balance) of from 9 to 13, preferably from 10 to 13.

Cosurfactant

The compositions herein can also contain from 0% to 15%, preferably from 0.5% to 3%, by weight of a cosurfactant selected from certain quaternary ammonium, amine, amide and/or amine oxide surfactants. The quaternary ammonium and amide surfactants are particularly preferred.

The quaternary ammonium surfactants useful herein are of the formula:



wherein R^2 is an alkyl or alkyl benzyl group having from 6 to 16 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, 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 from 8 to 16; each y is from 0 to 10 and the sum of the y values is from 0 to 15; and X is any compatible anion.

Preferred of the above are the alkyl quaternary ammonium surfactants, especially the mono-long chain alkyl surfactants described in the above formula when R^5 is selected from the same groups as R^4 . The most preferred quaternary ammonium surfactants are the chloride, bromide and methylsulfate C_8 - C_{16} alkyl trimethylammonium salts, C_8 - C_{16} alkyl di(hydroxyethyl)methylammonium salts, the C_8 - C_{16} alkyl hydroxyethyl-dimethylammonium salts, C_8 - C_{16} alkyloxypropyl trimethylammonium salts, and the C_8 - C_{16} alkyloxypropyl dihydroxyethylmethylammonium salts. Of the above, the C_{10} - C_{14} alkyl trimethylammonium salts are preferred, e.g., decyl trimethylammonium methylsulfate, lauryl trimethylammonium chloride, myristyl

trimethylammonium bromide and coconut trimethylammonium chloride and methylsulfate.

Under cold water washing conditions, i.e., less than 65 °F (18.3 °C), the C₈₋₁₀ alkyl trimethylammonium surfactants are particularly preferred since they have lower Kraft boundaries and crystallization temperatures than the longer chain quaternary ammonium surfactants.

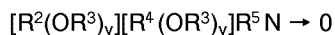
5 Amine surfactants useful herein are of the formula:



wherein the R², R³, R⁴, R⁵ and y substituents are as defined above for the quaternary ammonium surfactants. Particularly preferred are the C₁₂₋₁₆ alkyl dimethyl amines.

10 Amine oxide surfactants useful herein are of the formula:

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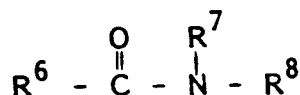


15 wherein the R², R³, R⁴, R⁵ and y substituents are also as defined above for the quaternary ammonium surfactants. Particularly preferred are the C₁₂₋₁₆ alkyl dimethyl amine oxides.

Amine and amine oxide surfactants are preferably used at higher levels than the quaternary ammonium surfactants since they are only partially protonated in the present systems. For example, preferred compositions herein can contain from 0.5% to 1.5% of the quaternary ammonium surfactant, or from 1% to 3% of the amine or amine oxide surfactants.

20 Amide surfactants herein are of the formula

Amide surfactants herein are of the formula



25

wherein R⁶ is an alkyl, hydroxyalkyl or alkenyl radical containing from 8 to 20 carbon atoms, and R⁷ and R⁸ are selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, and said radicals additionally containing up to 5 ethylene oxide units, provided at least one of R⁷ and R⁸ contains a hydroxyl group.

30 provided at least one of R⁷ and R⁸ contains a hydroxyl group.

Preferred amides are the C₈-C₂₀ fatty acid alkylol amides in which each alkylol group contains from 1 to 3 carbon atoms, and additionally can contain up to 2 ethylene oxide units. Particularly preferred are the C₁₂-C₁₆ fatty acid monoethanol and diethanol amides.

35

Fatty Acid

The compositions of the present invention preferably contain from 0% to 20%, more preferably from 8% to 18%, most preferably from 10% to 16%, by weight of a saturated fatty acid containing from 10 to 14 carbon atoms. In addition, the weight ratio of C₁₀-C₁₂ fatty acid to C₁₄ fatty acid is preferably at least 1, more preferably at least 1.5.

40 carbon atoms. In addition, the weight ratio of C₁₀-C₁₂ fatty acid to C₁₄ fatty acid is preferably at least 1, more preferably at least 1.5.

Suitable saturated fatty acids can be obtained from natural sources such as plant or animal esters (e.g., palm kernel oil, palm oil and coconut oil) or synthetically prepared (e.g., via the oxidation of petroleum or by hydrogenation of carbon monoxide via the Fisher-Tropsch process). Examples of suitable saturated fatty acids for use in the compositions of this invention include capric, lauric, myristic, coconut and palm kernel fatty acid. Preferred are saturated coconut fatty acids, from 5:1 to 1:1 (preferably about 3:1) weight ratio mixtures of lauric and myristic acid, mixtures of the above with minor amounts (e.g., 10%-50% of total fatty acid) of oleic acid; and palm kernel fatty acid.

45 acids for use in the compositions of this invention include capric, lauric, myristic, coconut and palm kernel fatty acid. Preferred are saturated coconut fatty acids, from 5:1 to 1:1 (preferably about 3:1) weight ratio mixtures of lauric and myristic acid, mixtures of the above with minor amounts (e.g., 10%-50% of total fatty acid) of oleic acid; and palm kernel fatty acid.

Polycarboxylate Builder

The compositions herein also preferably contain from 3% to 20%, more preferably from 3% to 6%, more preferably from 3.5% to 5% by weight on an acid basis, of a water-soluble polycarboxylate detergent builder material. Polycarboxylate builders are described in U.S. Patent 4,284,532, Leikhim et al, issued August 18, 1981.

55 August 18, 1981.

The various aminopolycarboxylates, cycloalkane polycarboxylates, ether polycarboxylates, alkyl polycarboxylates, epoxy polycarboxylates, tetrahydrofuran polycarboxylates, benzene polycarboxylates, and polyacetal polycarboxylates are suitable for use herein.

Examples of such polycarboxylate builders are sodium and potassium ethylenediaminetetraacetate; sodium and potassium nitrilotriacetate; the water-soluble salts of phytic acid, e.g., sodium and potassium phytates, disclosed in U.S. Patent 1,739,942, Eckey, issued March 27, 1956; the polycarboxylate materials described in U.S. Patent 3,364,103; and the water-soluble salts of polycarboxylate polymers and copolymers described in U.S. Patent 3,308,067, Diehl, issued March 7, 1967.

Useful detergent builders also include the water-soluble salts of polymeric aliphatic polycarboxylic acids having the following structural and physical characteristics: (a) a minimum molecular weight of 350 calculated as to the acid form; (b) an equivalent weight of 50 to 80 calculated as to acid form; (3) at least 45 mole percent of the monomeric species having at least two carboxyl radicals separated from each other by not more than two carbon atoms; (d) the site of attachment of the polymer chain of any carboxyl-containing radical being separated by not more than three carbon atoms along the polymer chain from the site of attachment of the next carboxyl-containing radical. Specific examples of such builders are the polymers and copolymers of itaconic acid, aconitic acid, maleic acid, mesaconic acid, fumaric acid, methylene malonic acid, and citraconic acid.

Other suitable polycarboxylate builders include the water-soluble salts, especially the sodium and potassium salts, of mellitic acid, citric acid, pyromellitic acid, benzene pentacarboxylic acid, oxydiacetic acid, carboxymethyloxysuccinic acid, carboxymethyloxymalonic acid, cis-cyclohexanehexacarboxylic acid, cis-cyclopentanetetracarboxylic acid and oxydisuccinic acid.

Other polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al, and U.S. Patent 4,146,495, issued March 27, 1979 to Crutchfield et al.

Citric acid is a highly preferred polycarboxylate builder.

Neutralization System

The present compositions can contain from 0 to 0.04 moles, preferably from 0.01 to 0.035 moles, more preferably from 0.015 to 0.03 moles, per 100 grams of composition of an alkanolamine selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof. Low levels or none of the alkanolamines, particularly monoethanolamine, are preferred to enhance product stability, detergency performance, and odor. The amount of alkanolamine should be minimized for best chlorine bleach compatibility and stability of the soil release component. While the present compositions can contain mixtures of the alkanolamines, best color stability is obtained using single alkanolamines.

Solvent System

The solvent system for the compositions is preferably comprised of ethanol, a polyol, e.g., propanediol, and water. Ethanol is preferably present at a level of from 2% to 10%, more preferably from 5% to 9%, by weight of the composition.

Any polyol containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups can be used in the present compositions. Examples of such polyols are ethylene glycol, propanediol, propylene glycol and glycerine. Propylene glycol is particularly preferred. The polyol preferably represents from 2% to 15%, more preferably from 3% to 10%, by weight of the composition.

The compositions also preferably contain from 25% to 40%, more preferably from 28% to 37%, by weight of water.

In addition to the above, the ethanol and polyol together preferably represent from 8% to 20%, more preferably 11% to 16%, by weight of the composition. The ethanol, polyol and water preferably total from 35% to 55%, more preferably 40% to 50%, by weight of the composition.

The compositions of the present invention preferably have the following limits, in which all percentages and ratios are calculated on an acid basis where anionic materials are involved. The sulfonate, alcohol ethoxylate sulfate, ethoxylated nonionic and quaternary ammonium, amine, amide and/or amine oxide surfactants, together, preferably represent from 20% to 40%, more preferably from 23% to 30%, by weight of the composition.

The fatty acid and polycarboxylate builder together preferably represent from 5% to 30%, more preferably from 10% to 25%, by weight of the composition. In addition, the fatty acid, polycarboxylate builder and above surfactants preferably represent a total of from 33% to 50%, more preferably from 36% to 48%, by weight of the composition.

Finally, all of the above components are selected to provide an isotropic liquid detergent at 55° F (12.8° C), preferably at 50° F (10° C). The components are also selected to provide an initial pH of from 7.5

to 9.0, preferably from 7.8 to 8.8, at a concentration of 10% by weight in water at 68 ° F (20 ° C).

Optional Components

5 Optional components for use in the liquid detergents herein include enzymes, enzyme stabilizing agents, polyacids, soil removal agents, antiredeposition agents suds regulants, hydrotropes, opacifiers, antioxidants, bactericides, dyes, perfumes, and brighteners described in the U.S. Patent 4,285,841, Barrat et al, issued August 25, 1981. Such optional components generally represent less than 15%, preferably from 2% to about 10%, by weight of the composition.

10 Enzymes are highly preferred optional ingredients and are incorporated in an amount of from 0.025% to 2%, preferably from 0.05% to 1.5%. Preferred proteolytic enzymes should provide a proteolytic activity of at least 5 Anson units (about 1,000,000 Delft units) per liter, preferably from 15 to 70 Anson units per liter, most preferably from 20 to 40 Anson units per liter. A proteolytic activity of from 0.01 to 0.05 Anson units per gram of product is desirable. Other enzymes, including amylolytic enzymes, are also desirably included
15 in the present compositions.

Suitable proteolytic enzymes include the many species known to be adapted for use in detergent compositions. Commercial enzyme preparations such as "Alcalase®" sold by Novo Industries, and "Maxatase®" sold by Gist-Brocades, Delft, The Netherlands, are suitable. Other preferred enzyme compositions include those commercially available under the tradenames SP-72' ("Esperase"®) manufactured and
20 sold by Novo Industries, A/S, Copenhagen, Denmark and "AZ-Protease®" manufactured and sold by Gist-Brocades, Delft, The Netherlands.

Suitable amylases include "Rapidase®" sold by Gist-Brocades and "Termamyl®" sold by Novo Industries.

A more complete disclosure of suitable enzymes can be found in U.S. Patent 4,101,457, Place et al,
25 issued July 18, 1978.

When enzymes are incorporated in the detergent compositions of this invention, they are desirably stabilized by using a mixture of a short chain carboxylic acid salt and calcium ion, such as disclosed in U.S. Patent 4,318,818, Letton et al, issued March 9, 1982.

The short chain carboxylic acid salt is preferably water-soluble, and most preferably is a formate, e.g.,
30 sodium formate. The short chain carboxylic acid salt is used at a level from about 0.25% to about 10%, preferably from 0.3% to 3%, more preferably from 0.5% to 1.5%. Any water-soluble calcium salt can be used as a source of calcium ion, including calcium acetate, calcium formate and calcium propionate. The composition should contain from 0.1 to 30 millimoles of calcium ion per liter, preferably from 0.5 to 15 millimoles of calcium ion per liter. When materials are present which complex calcium ion, it is necessary to
35 use high levels of calcium ion so that there is always some minimum level available for the enzyme.

Enzymes are preferably stabilized in the present compositions by the addition of from 0.25% to 10%, preferably from 0.5% to 5%, more preferably from 0.75% to 3%, by weight of boric acid or a compound capable of forming boric acid in the composition (calculated on the basis of the boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium
40 ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

The combination of boric acid and formate provides improved protease stability, although amylase stability appears to be slightly less than that obtained using boric acid alone.

Preferred compositions also contain from 0.01% to 1% of a polyacid or salt thereof, to enhance
45 pretreatment performance. Preferred polyacids for use herein are ethylenediamine tetramethylenephosphonic acid, diethylene triamine pentamethylenephosphonic acid, and diethylenetriamine pentaacetic acid, or the salts thereof. These polyacids/salts are preferably used in an amount from 0.1% to 0.8%.

Preferred compositions herein further contain from 0.5% to 3%, preferably from 1% to 2%, by weight of
50 a highly ethoxylated polyethyleneamine or polyethyleneimine soil removal and antiredeposition agent. A particularly preferred species of the like soil removal and anti-redeposition agent is tetraethylenepentamine ethoxylated with about 15-18 moles of ethylene oxide at each hydrogen site.

The following examples illustrate the compositions of the present invention.

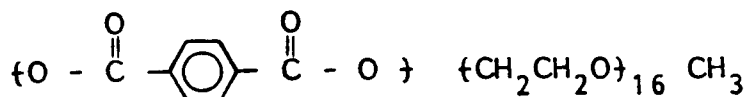
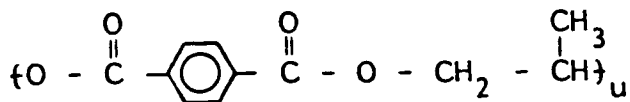
All parts, percentages and ratios used herein are by weight unless otherwise specified.

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EXAMPLE 1

A liquid detergent composition of the present invention is as follows:

A compound having a range of copolymers of the formula:



in which about 20% by weight of the material has a value of u higher than 5 is dissolved at about 15% level
 in anhydrous ethanol; cooled to about 10 °C; the insoluble portion (~ 20%) is filtered; enough ethanol is
 20 distilled to reduce the ethanol level to within the level in the following formula; and the compound is added
 to the formula.

Components	%
C ₁₄₋₁₅ alkyl polyethoxylate (2.25) sulfuric acid half ester	12.0
C ₁₃ alkyl benzene sulfonic acid	8.0
C ₁₂₋₁₃ alkyl polyethoxylate (6.5)	5.0
C ₁₂ alkyl trimethylammonium chloride	0.6
Coconut middle cut fatty acid	7.7
30 Palm kernel oil fatty acids	3.3
Diethylenetriamine pentaacetic acid	0.3
Citric acid	4.0
Ethanol	6.0
1,2 propanediol	8.0
35 Monoethanolamine	1.0
Sodium hydroxide	2.5
Potassium hydroxide	4.7
Tetraethylene pentamine ethoxylated with ~ 16 moles of ethylene oxide at each hydrogen	2.0
The above-identified soil release compound	2.5
40 Water, enzymes, brighteners, etc.	Balance
pH of product ~ 8.3	

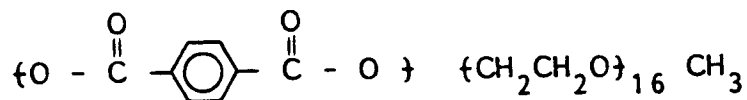
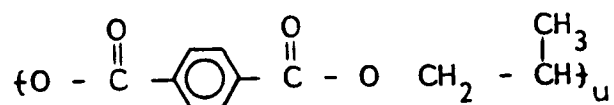
45 EXAMPLE 11

A liquid detergent composition of the present invention is as follows:

A compound having a range of copolymers of the formula:



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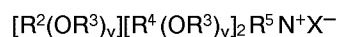


in which about 20% by weight of the material has a value of u higher than 5 is dissolved at about 15% level in anhydrous ethanol; cooled to about 10 °C; the insoluble portion (~ 20%) is filtered; enough ethanol is distilled to reduce the ethanol level to within the level in the following formula; and the compound is added to the formula.

Components	%
C ₁₁₋₁₈ alkyl benzene sulfonic acid	10.3
C ₁₂₋₁₄ alkyl sulfate (acid)	2.6
Triethanolamine	6.5
Sodium hydroxide	3.4
C ₁₃₋₁₅ alkyl polythoxylate (7.0)	11.6
Ethanol	5.7
1,2-propanediol	1.6
Sodium formate (40% solution)	1.0
Calcium chloride	0.02
Diethylenetriamine penta(methylene phosphonic acid)	0.9
Citric acid monohydrate	0.9
Topped whole cut fatty acid	10.7
Oleic acid	3.9
The above-identified soil release compound	0.5
Water, enzymes, brighteners, etc.	Balance

Claims

1. A heavy-duty liquid detergent composition comprising, by weight:
 - (a) from 10% to 35%, of an anionic surfactant on an acid basis;
 - (b) from 0% to 15% of an ethoxylated nonionic surfactant of the formula R¹ (OC₂H₄)_nOH, wherein R¹ is a C₁₀-C₁₆ alkyl group or a C₈-C₁₂ alkyl phenyl group, n averages from 3 to 9, and said nonionic surfactant has an HLB of from 10 to 13;
 - (c) from 0% to 15% of a cosurfactant selected from the group consisting of:
 - (i) quaternary ammonium surfactants having the formula:



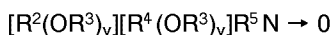
wherein R² is an alkyl or alkyl benzyl group having from 6 to 16 carbon atoms in the alkyl chain; each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is from 8 to 16; each y averages from 0 to 10 and the sum of the y values is from 0 to 15; and X is any compatible anion;

(ii) amine surfactants having the formula:



wherein R², R³, R⁴, R⁵ and y are as defined above;

(iii) amine oxide surfactants having the formula:



5 wherein R^2 , R^3 , R^4 , R^5 and y are as defined above;
 (iv) an amide surfactant of the formula:



15 wherein R^6 is an alkyl, hydroxyalkyl or alkenyl radical containing from 8 to 20 carbon atoms, and R^7 and R^8 are each selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, and wherein said radicals additionally contain up to 5 ethylene oxide units; and

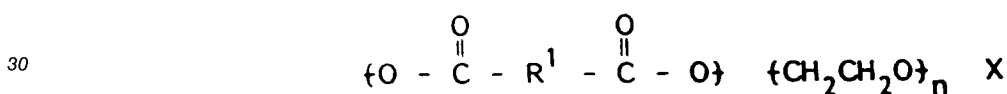
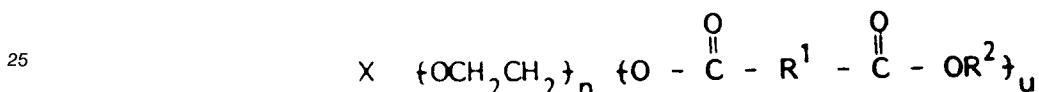
(v) mixtures thereof;

(d) from 5% to 30% of detergent builder;

(e) a neutralization system;

20 (f) an aqueous solvent system, said system not consisting of water only;

(g) from 0.25% to 4% of a soil release component which is a compound having the formula:



35 wherein each R^1 moiety is a 1,4-phenylene moiety, each R^2 is an ethylene or a 1,2-propylene moiety; each n averages from 10 to 50; each X is H, an alkyl radical having from 1 to 4 carbon atoms or an acyl radical containing from 2 to 4 carbon atoms; wherein less than 10 mol% of said soil release compound has a u greater than 5, at least 20 mol% of said soil release compound has a u in the range of from 3 to 5 and wherein the average value of u is from 3 to 5.

40 2. The composition of Claim 1 wherein in component (g), n ranges from 10 to 25 and from 90% to 100% of the R^2 moieties are 1,2-propylene moieties.

3. The composition of Claim 2 wherein X is an alkyl radical containing from 1 to 2 carbon atoms.

45 4. The composition of Claim 2 wherein component (g) is a fraction of polymers soluble in absolute ethanol at a temperature of from 10 °C to 15 °C.

5. The composition of Claim 1 wherein component (g) is a fraction of polymers soluble in absolute ethanol at a temperature of from 10 °C to 15 °C.

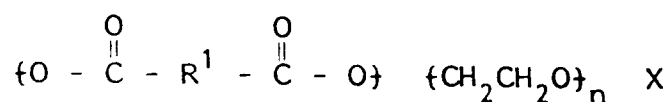
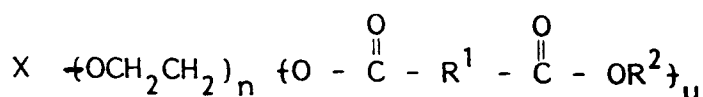
50 6. The composition of Claim 5 wherein the detergent composition comprises by weight:

(a) from 5% to 15%, on an acid basis, of a sulfonate surfactant containing a C_{10} - C_{16} alkyl or alkenyl group;

(b) from 8% to 18%, on an acid basis, of an alcohol ethoxylate sulfate surfactant of the formula $RO-(C_2H_4O)_mSO_3M$ wherein R is a C_{10} - C_{16} alkyl or hydroxyalkyl group, m is from 0.5 to 4, and M is a compatible cation; and

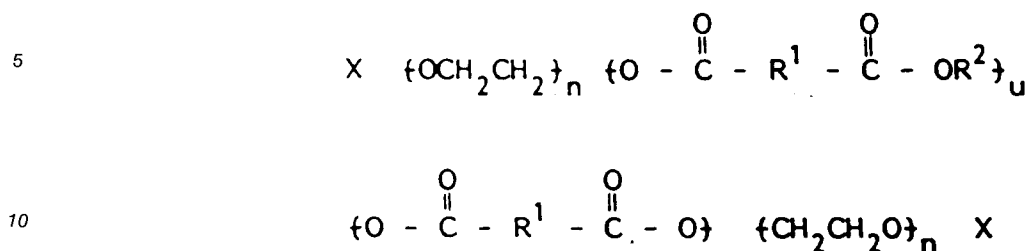
55 (c) from 2% to 15% of an ethoxylated nonionic surfactant of the formula $R^1(OC_2H_4)_nOH$, wherein R^1 is a C_{10} - C_{16} alkyl group or a C_8 - C_{12} alkyl phenyl group, n is from 3 to 9, and said nonionic surfactant has an HLB of from 10 to 13.

7. The composition of Claim 5 wherein the detergent composition comprises by weight:
 (a) from 5% to 15%, on an acid basis, of a sulfonate surfactant containing a C₁₀-C₁₆ alkyl or alkenyl group;
 (b) from 1% to 4%, on an acid basis, of a C₁₀-C₁₆ alkyl sulfate; and
 (c) from 2% to 15% of an ethoxylated nonionic surfactant of the formula R¹(OC₂H₄)_nOH, wherein R¹ is a C₁₀-C₁₆ alkyl group or a C₈-C₁₂ alkyl phenyl group, n is from 3 to 9, and said nonionic surfactant has an HLB of from 10 to 13.
8. The composition of Claim 6 wherein the sulfonate surfactant is a C₁₁-C₁₃ linear alkylbenzene sulfonate; in the alcohol ethoxylate sulfate surfactant, R is a C₁₂-C₁₅ alkyl group and m is from 1.5 to 3; and in the ethoxylated nonionic surfactant, R is a C₁₂-C₁₄ alkyl group and n is from 3 to 7.
9. The composition of Claim 8 comprising from 0.5% to 3% by weight of the cosurfactant, which is a C₁₀-C₁₄ alkyl trimethylammonium chloride, bromide or methylsulfate.
10. The composition of Claim 8 wherein the builder comprises a polycarboxylate builder.
11. The composition of Claim 8 comprising by weight from 6% to 10% of the sulfonate surfactant, from 9% to 14% of the alcohol ethoxylate sulfate surfactant, from 4% to 10% of the ethoxylated nonionic surfactant, and from 0.5% to 1.5% of the cosurfactant, which is a C₁₀-C₁₄ alkyl trimethylammonium chloride, bromide or methylsulfate.
12. The composition of Claim 11 in which the builder comprises by weight of the composition from 10% to 16% of saturated fatty acid and from 3% to 6% of citric acid.
13. The composition of Claim 12 comprising from 0 to 0.035 moles per 100 grams of composition of an alkanolamine, which is monoethanolamine.
14. The composition of Claim 13 comprising by weight from 5% to 9% of ethanol, from 3% to 10% of a polyol, which is propylene glycol, and from 28% to 37% of water.
15. The composition of Claim 14 having an initial pH of from 7.8 to 9.0 at a concentration of 10% by weight in water at 68 °F (20 °C).
16. The process of preparing a soil release component having the formula:



wherein each R₁ is a 1,4-phenylene moiety, each R₂ is an ethylene or a 1,2-propylene moiety; each X is selected from the group consisting of hydrogen, alkyl groups containing from one to four carbon atoms and acyl groups containing from 2 to four carbon atoms; n averages from 10 to 50; wherein less than 10 mol% of said soil release component has a u greater than 5, at least 20 mol% of said soil release component has a u in the range of from 3 to 5 and wherein the average value of u is from 3 to 5; comprising the step of dissolving a soil release component comprising the desired material and a substantial amount of material in which u is greater than five in absolute ethanol at a temperature of from 10 °C to 15 °C and separating the precipitating material.

17. An ethanol soluble soil release component having the formula :



wherein each R¹ moiety is a 1,4-phenylene moiety, each R² is an ethylene or a 1,2-propylene moiety; each n averages from 10 to 50; each X is H, an alkyl radical having from 1 to 4 carbon atoms or an acyl radical containing from 2 to 4 carbon atoms, wherein from 90% to 100% of the R² moieties are 1,2-propylene moieties; and

wherein less than 10 mol% of said soil release compound has a u greater than 5, at least 20 mol% of said soil release compound has a u in the range of from 3 to 5 and wherein the average value of u is from 3 to 5;

obtainable by the process of Claim 16.

18. The component of Claim 17 wherein each X is an alkyl group containing from 1 to 2 carbon atoms.

Patentansprüche

1. Flüssige Vollwaschmittelzusammensetzung, umfassend, bezogen auf das Gewicht:

(a) 10 % bis 35 % eines anionischen grenzflächenaktiven Mittels auf einer Säurebasis;

(b) 0 % bis 15 % eines ethoxylierten nichtionischen grenzflächenaktiven Mittels der Formel R¹-(OC₂H₄)_nOH, worin R¹ eine C₁₀-C₁₆-Alkylgruppe oder eine C₈-C₁₂-Alkylphenylgruppe darstellt, n durchschnittlich von 3 bis 9 beträgt, und die genannte nichtionische grenzflächenaktive Verbindung einen HLB-Wert von 10 bis 13 besitzt;

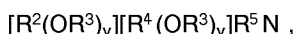
(c) 0 % bis 15 % eines co-grenzflächenaktiven Mittels, welches von der Gruppe ausgewählt ist, die aus:

(i) quaternären Ammonium-grenzflächenaktiven Mitteln der Formel:



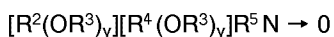
worin R² eine Alkyl- oder Alkylbenzylgruppe mit 6 bis 16 Kohlenstoffatomen in der Alkylkette darstellt; jeder Rest R³ von der Gruppe, welche aus -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂- besteht und aus Gemischen hievon ausgewählt ist; jeder Rest R⁴ von der Gruppe, welche aus C₁-C₄-Alkyl, C₁-C₄-Hydroxyalkyl, Benzyl ausgewählt ist und Wasserstoff bedeutet, wenn y nicht 0 ist; R⁵ die gleiche Bedeutung wie R⁴ besitzt oder eine Alkylkette darstellt, wobei die Gesamtzahl der Kohlenstoffatome von R² plus R⁵ von 8 bis 16 beträgt; jedes y durchschnittlich 0 bis 10 ist und die Summe der y-Werte von 0 bis 15 beträgt; und X für jedes beliebige verträgliche Anion steht;

ii) Amin-grenzflächenaktiven Mitteln der Formel:



worin R², R³, R⁴, R⁵ und y wie vorstehend definiert sind;

iii) Aminoxid-grenzflächenaktiven Mitteln der Formel:



worin R², R³, R⁴, R⁵ und y wie vorstehend definiert sind;

(iv) einem Amid-grenzflächenaktiven Mittel der Formel:



worin R^6 einen Alkyl-, Hydroxyalkyl- oder Alkenylrest mit 8 bis 20 Kohlenstoffatomen darstellt und R^7 und R^8 jeweils von der Gruppe ausgewählt sind, welche aus Wasserstoff, Methyl, Ethyl, Propyl, Isopropyl, 2-Hydroxyethyl, 2-Hydroxypropyl, 3-Hydroxypropyl besteht und worin die genannten Reste zusätzlich bis zu 5 Ethylenoxideinheiten enthalten; und

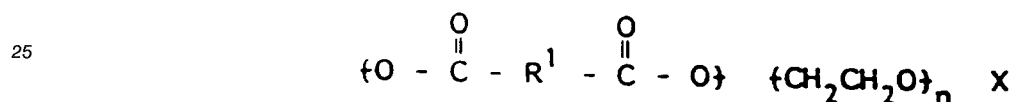
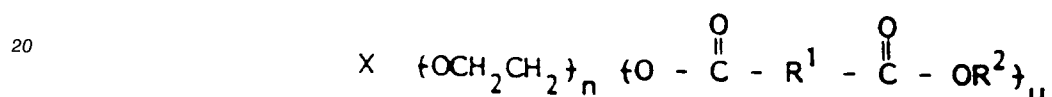
(v) Gemischen hievon besteht;

(d) 5 % bis 30 % an Detergensgerüststoff;

(e) ein Neutralisationssystem;

(f) ein wäßriges Lösungsmittelsystem, wobei das genannte System nicht ausschließlich aus Wasser besteht;

(g) 0,25 % bis 4 % einer Schmutzlösekomponente, welche eine Verbindung der Formel:



ist, worin jeder Rest R^1 ein 1,4-Phenylrest ist, jeder Rest R^2 einen Ethylen- oder einen 1,2-Propylenrest darstellt; jedes n durchschnittlich 10 bis 50 beträgt; jedes X für H, einen Alkylrest mit 1 bis 4 Kohlenstoffatomen oder einen Acylrest mit 2 bis 4 Kohlenstoffatomen steht; wobei in weniger als 10 Mol-% der genannten Schmutzlöseverbindung u mehr als 5 beträgt, in mindestens 20 Mol-% der genannten Schmutzlöseverbindung u im Bereich von 3 bis 5 liegt und worin der durchschnittliche Wert von u von 3 bis 5 ist.

2. Zusammensetzung nach Anspruch 1, worin in der Komponente (g) n von 10 bis 25 beträgt und 90 % bis 100 % der Reste R^2 -1,2-Propylenreste sind.

3. Zusammensetzung nach Anspruch 2, worin X einen Alkylrest mit 1 bis 2 Kohlenstoffatomen darstellt.

4. Zusammensetzung nach Anspruch 2, worin die Komponente (g) eine in absolutem Ethanol bei einer Temperatur von 10 °C bis 15 °C lösliche Polymerenfraction ist.

5. Zusammensetzung nach Anspruch 1, worin die Komponente (g) eine in absolutem Ethanol bei einer Temperatur von 10 °C bis 15 °C lösliche Polymerenfraction ist.

6. Zusammensetzung nach Anspruch 5, worin die Detergenszusammensetzung, bezogen auf das Gewicht: (a) 5 % bis 15 %, auf einer Säurebasis, an einem Sulfonat-grenzflächenaktiven Mittel mit einer C_{10} - C_{16} -Alkyl- oder -Alkenylgruppe;

(b) 8 % bis 18 %, auf einer Säurebasis, an einem Alkoholethoxylat-Sulfat-grenzflächenaktiven Mittel der Formel $\text{RO}(\text{C}_2\text{H}_4\text{O})_m\text{SO}_3\text{M}$, worin R eine C_{10} - C_{16} -Alkyl- oder -Hydroxyalkylgruppe darstellt, m von 0,5 bis 4 beträgt und M ein verträgliches Kation ist; und

(c) 2 % bis 15 % eines ethoxylierten nichtionischen grenzflächenaktiven Mittels der Formel $\text{R}^1(\text{OC}_2\text{H}_4)_n\text{OH}$ umfaßt, worin R^1 eine C_{10} - C_{16} -Alkylgruppe oder eine C_8 - C_{12} -Alkylphenylgruppe ist, n von 3 bis 9 beträgt und das genannte nichtionische grenzflächenaktive Mittel einen HLB-Wert von 10 bis 13 besitzt.

7. Zusammensetzung nach Anspruch 5, worin die Detergenszusammensetzung, bezogen auf das Gewicht,

(a) 5 % bis 15 %, auf einer Säurebasis, an einem Sulfonat-grenzflächenaktiven Mittel mit einer C₁₀-C₁₆-Alkyl oder -Alkenylgruppe;

(b) 1 % bis 4 %, auf einer Säurebasis, an einem C₁₀-C₁₆-Alkylsulfat; und

5 (c) 2 % bis 15 % eines ethoxylierten nichtionischen grenzflächenaktiven Mittels der Formel R¹-(OC₂H₄)_nOH umfaßt, worin R¹ eine C₁₀-C₁₆-Alkylgruppe oder eine C₈-C₁₂-Alkylphenylgruppe darstellt, n von 3 bis 9 beträgt und das genannte nichtionische grenzflächenaktive Mittel einen HLB-Wert von 10 bis 13 aufweist.

8. Zusammensetzung nach Anspruch 6, worin das Sulfonat-grenzflächenaktive Mittel ein lineares C₁₁-C₁₃-Alkylbenzolsulfonat ist; worin im Alkoholethoxylat-Sulfat-grenzflächenaktiven Mittel R für eine C₁₂-C₁₅-Alkylgruppe steht und m von 1,5 bis 3 beträgt, und worin im ethoxylierten nichtionischen grenzflächenaktiven Mittel R für eine C₁₂-C₁₄-Alkylgruppe steht und n von 3 bis 7 beträgt.

9. Zusammensetzung nach Anspruch 8, umfassend 0,5 Gew.-% bis 3 Gew.-% des co-grenzflächenaktiven Mittels, welches ein C₁₀-C₁₄-Alkyltrimethylammoniumchlorid, -bromid oder -methylsulfat ist.

10. Zusammensetzung nach Anspruch 8, worin der Gerüststoff einen Polycarboxylatgerüststoff umfaßt.

11. Zusammensetzung nach Anspruch 8, umfassend, bezogen auf das Gewicht, 6 % bis 10 % des Sulfonat-grenzflächenaktiven Mittels, 9 % bis 14 % des Alkoholethoxylat-Sulfat-grenzflächenaktiven Mittels, 4 % bis 10 % des ethoxylierten nichtionischen grenzflächenaktiven Mittels und 0,5 % bis 1,5 % des co-grenzflächenaktiven Mittels, welches ein C₁₀-C₁₄-Alkyltrimethylammoniumchlorid, -bromid oder -methylsulfat ist.

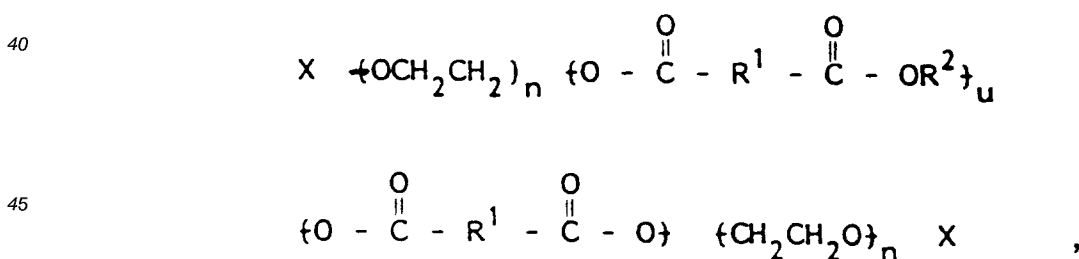
12. Zusammensetzung nach Anspruch 11, worin der Gerüststoff, bezogen auf das Gewicht der Zusammensetzung, 10 % bis 16 % an gesättigter Fettsäure und 3 % bis 6 % an Zitronensäure umfaßt.

13. Zusammensetzung nach Anspruch 12, umfassend 0 bis 0,035 Mol je 100 g an Zusammensetzung von einem Alkanolamin, welches Monoethanolamin ist.

14. Zusammensetzung nach Anspruch 13, umfassend, bezogen auf das Gewicht, 5 % bis 9 % Ethanol, 3 % bis 10 % eines Polyols, welcher Propylenglykol ist, und 28 % bis 37 % Wasser.

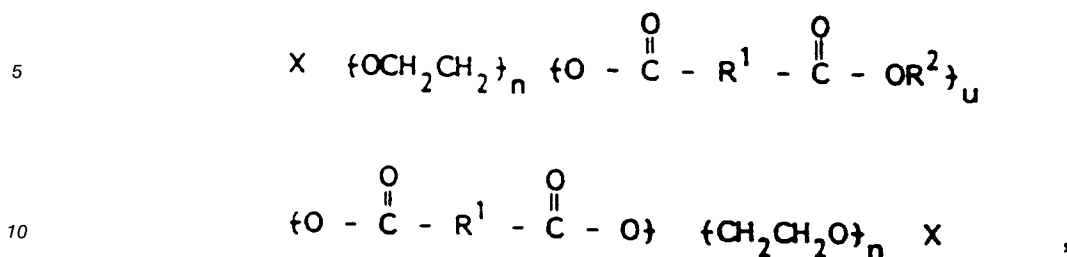
15. Zusammensetzung nach Anspruch 14, mit einem Anfangs-pH-Wert von 7,8 bis 9,0 bei einer Konzentration von 10 Gew.-% in Wasser bei 68° F (20° C).

16. Verfahren zur Herstellung einer Schmutzlösekomponente der Formel:



50 worin jeder Rest R¹ einen 1,4-Phenylrest darstellt, jeder Rest R² einen Ethylen- oder einen 1,2-Propylenrest bedeutet; jeder Rest X von der aus Wasserstoff, Alkylgruppen mit 1 bis 4 Kohlenstoffatomen und Acylgruppen mit 2 bis 4 Kohlenstoffatomen bestehenden Gruppe ausgewählt ist; n durchschnittlich von 10 bis 50 beträgt; worin in weniger als 10 Mol-% der genannten Schmutzlösekomponente u mehr als 5 beträgt, in mindestens 20 Mol-% der genannten Schmutzlösekomponente u im Bereich von 3 bis 5 liegt, und worin der mittlere Wert von u von 3 bis 5 ist; umfassend den Schritt des
 55 Auflösens einer Schmutzlösekomponente, welche das gewünschte Material und eine wesentliche Menge an Material, worin u mehr als 5 beträgt, in absolutem Alkohol bei einer Temperatur von 10° C bis 15° C und das Abtrennen des ausfallenden Materials.

17. Ethanol-lösliche Schmutzlösekomponente der Formel



15 worin jeder Rest R¹ ein 1,4-Phenylrest ist, jeder Rest R² einen Ethylen- oder einen 1,2-Propylenrest darstellt; jedes n durchschnittlich von 10 bis 50 beträgt; jeder Rest X für H, einen Alkylrest mit 1 bis 4 Kohlenstoffatomen oder einen Acylrest mit 2 bis 4 Kohlenstoffatomen steht, worin 90 % bis 100 % der Reste R²- 1,2-Propylenreste sind und worin in weniger als 10 Mol-% der genannten Schmutzlöseverbindung u mehr als 5 beträgt, in mindestens 20 Mol-% der genannten Schmutzlöseverbindung u im Bereich von 3 bis 5 beträgt, und worin der durchschnittliche Wert von u von 3 bis 5 ist; erhältlich durch das Verfahren nach Anspruch 16.

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18. Komponente nach Anspruch 17, worin jeder Rest X eine Alkylgruppe mit 1 bis 2 Kohlenstoffatomen ist.

Revendications

25 1. Composition détergente liquide pour linge très sale, comprenant, en poids :

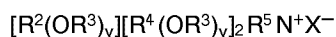
(a) de 10% à 35% d'un tensioactif anionique, sur une base acide;

(b) de 0% à 15% d'un tensioactif non ionique éthoxylé de formule R¹(OC₂H₄)_nOH, dans laquelle R¹ est un groupe alkyle en C₁₀-C₁₆ ou un groupe alkylphényle en C₈-C₁₂, n a une valeur moyenne de 3 à 9, et ledit tensioactif non ionique a un rapport hydrophilophile (HLB) de 10 à 13:

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(c) de 0% à 15% d'un co-tensioactif choisi dans le groupe constitué par :

(i) les tensioactifs ammonium quaternaire de formule :



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dans laquelle R² est un groupe alkyle ou alkylbenzyle comportant de 6 à 16 atomes de carbone dans la chaîne alkyle; chaque R³ est choisi dans le groupe constitué par -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-,

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-CH₂CH₂CH₂-, et des mélanges de ceux-ci; chaque R⁴ est choisi dans le groupe constitué par les groupes alkyle en C₁-C₄, hydroxyalkyle en C₁-C₄, benzyle, et un atome d'hydrogène, lorsque y n'est pas nul; R⁵ est identique à R⁴, ou encore est une chaîne alkyle dans laquelle le nombre total d'atomes de carbone de R² plus R⁵ est de 8 à 16; chaque y est en moyenne de 0 à 10 et la somme des valeurs de y est de 0 à 15; et X est un anion compatible quelconque;

(ii) les tensioactifs amines de formule :

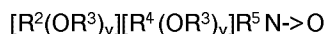
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dans laquelle R², R³, R⁴, R⁵ et y sont tels que définis ci-dessus;

(iii) les tensioactifs oxydes d'amines de formule :

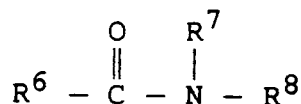
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dans laquelle R², R³, R⁴, R⁵ et y sont tels que définis ci-dessus;

(iv) un tensioactif amide de formule :

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dans laquelle R⁶ est un radical alkyle, hydroxyalkyle ou alcényle contenant de 8 à 20 atomes de carbone, et R⁷ et R⁸ sont chacun choisis dans le groupe constitué par un atome d'hydrogène et les groupes méthyle, éthyle, propyle, isopropyle, 2-hydroxyéthyle, 2-hydroxypropyle, 3-hydroxypropyle, et dans laquelle lesdits radicaux contiennent aussi jusqu'à 5 motifs oxyde d'éthylène; et

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(v) les mélanges de ceux-ci;

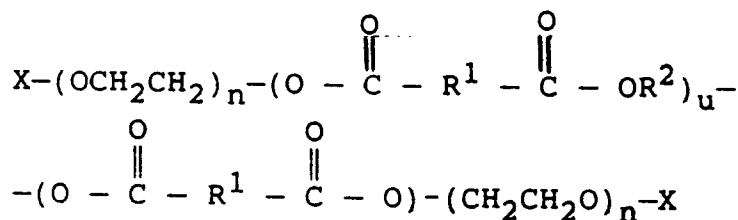
(d) de 5% à 30% d'un adjuvant de détergence;

(e) un système de neutralisation;

(f) un système de solvant aqueux, ledit système n'étant pas seulement constitué d'eau;

(g) de 0,25% à 4% d'un constituant de libération des salissures, qui est un composé de formule :

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dans laquelle chaque groupement R¹ est un groupement 1,4-phénylène, chaque R² est un groupement éthylène ou 1,2-propylène; chaque n a une moyenne de 10 à 50; chaque X est H, un radical alkyle comportant de 1 à 4 atomes de carbone ou un radical acyle contenant de 2 à 4 atomes de carbone; dans laquelle moins de 10% en moles dudit composé de libération des salissures a une valeur de u supérieure à 5, au moins 20% en moles dudit composé de libération des salissures a une valeur de u dans la gamme de 3 à 5 et dans laquelle la valeur moyenne de u est de 3 à 5.

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2. Composition selon la revendication 1, dans laquelle, dans le constituant (g), n s'échelonne de 10 à 25, et de 90% à 100% des groupements R² sont des groupements 1,2-propylène.

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3. Composition selon la revendication 2, dans laquelle X est un radical alkyle contenant de 1 à 2 atomes de carbone.

4. Composition selon la revendication 2, dans laquelle le constituant (g) est une fraction de polymères soluble dans l'éthanol absolu à une température de 10 °C à 15 °C.

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5. Composition selon la revendication 1, dans laquelle le constituant (g) est une fraction de polymères soluble dans l'éthanol absolu à une température de 10 °C à 15 °C.

6. Composition selon la revendication 5, dans laquelle la composition détergente comprend, en poids :

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(a) de 5% à 15%, sur une base acide, d'un tensioactif sulfonate contenant un groupe alkyle ou alcényle en C₁₀-C₁₆;

(b) de 8% à 18%, sur une base acide, d'un tensioactif éthoxysulfate d'alcool de formule RO(C₂H₄O)_mSO₃M, dans laquelle R est un groupe alkyle ou hydroxyalkyle en C₁₀-C₁₆, m est de 0,5 à 4 et M est un cation compatible; et

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(c) de 2% à 15% d'un tensioactif non ionique éthoxylé de formule R¹(OC₂H₄)_nOH, dans laquelle R¹ est un groupe alkyle en C₁₀-C₁₆ ou un groupe alkyphénylène en C₈-C₁₂, n est de 3 à 9, et ledit tensioactif non ionique a un HLB de 10 à 13.

7. Composition selon la revendication 5, dans laquelle la composition détergente comprend, en poids :

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(a) de 5% à 15%, sur une base acide, d'un tensioactif sulfonate contenant un groupe alkyle ou alcényle en C₁₀-C₁₆;

(b) de 1% à 4%, sur une base acide, d'un alkylsulfate en C₁₀-C₁₆; et

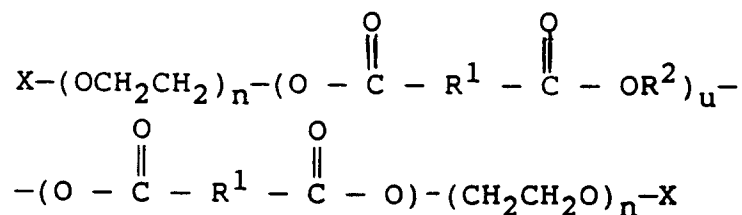
(c) de 2% à 15% d'un tensioactif non ionique éthoxylé de formule R¹(OC₂H₄)_nOH, dans laquelle R¹ est un groupe alkyle en C₁₀-C₁₆ ou un groupe alkyphénylène en C₈-C₁₂, n est de 3 à 9, et ledit tensioactif non ionique a un HLB de 10 à 13.

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8. Composition selon la revendication 6, dans laquelle le tensioactif sulfonate est un alkylbenzènesulfonate où le groupe alkyle est linéaire et en C₁₁-C₁₃; dans le tensioactif éthoxysulfate d'alcool, R est un

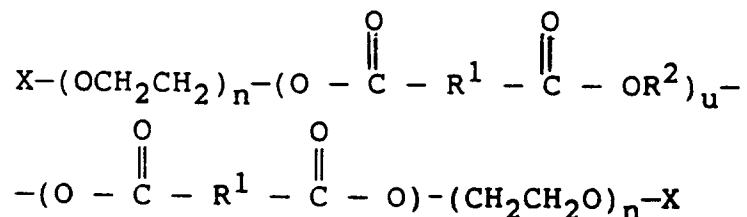
groupe alkyle en C₁₂-C₁₅ et m est de 1,5 à 3; et dans le tensioactif non ionique éthoxylé, R est un groupe alkyle en C₁₂-C₁₄ et n est de 3 à 7.

- 5 9. Composition selon la revendication 8, comprenant de 0,5% à 3% en poids du co-tensioactif, qui est un chlorure, bromure ou méthylsulfate d'alkyl(en C₁₀-C₁₄)triméthylammonium.
- 10 10. Composition selon la revendication 8, dans laquelle l'adjuvant comprend un adjuvant polycarboxylate.
11. Composition selon la revendication 8, comprenant, en poids, de 6% à 10% du tensioactif sulfonate, de 9% à 14% du tensioactif éthoxysulfate d'alcool, de 4% à 10% du tensioactif non ionique éthoxylé et de 0,5% à 1,5% du co-tensioactif, qui est un chlorure, bromure ou méthylsulfate d'alkyl(en C₁₀-C₁₄)-triméthylammonium.
12. Composition selon la revendication 11, dans laquelle l'adjuvant comprend, en poids de la composition, de 10% à 16% d'acide gras saturé et de 3% à 6% d'acide citrique.
13. Composition selon la revendication 12, comprenant de 0 à 0,035 mole, pour 100 g de composition, d'une alcanolamine, qui est la monoéthanolamine.
- 20 14. Composition selon la revendication 13, comprenant, en poids, de 5% à 9% d'éthanol, de 3% à 10% d'un polyol, qui est le propylèneglycol, et de 28% à 37% d'eau.
15. Composition selon la revendication 14, ayant un pH initial de 7,8 à 9,0, à une concentration de 10% en poids dans de l'eau à 68° F (20° C).
- 25 16. Procédé de préparation d'un constituant de libération des salissures de formule :



30 dans laquelle chaque R¹ est un groupement 1,4-phénylène, chaque R² est un groupement éthylène ou 1,2-propylène; chaque X est choisi dans le groupe constitué par un atome d'hydrogène ou les groupes alkyle comportant de 1 à 4 atomes de carbone et les groupes acyle contenant de 2 à 4 atomes de carbone; n a une moyenne de 10 à 50; dans laquelle moins de 10% en moles dudit composé de libération des salissures a une valeur de u supérieure à 5, au moins 20% en moles dudit composé de libération des salissures a une valeur de u dans la gamme de 3 à 5 et dans laquelle la valeur moyenne de u est de 3 à 5; comprenant l'étape consistant à dissoudre un constituant de libération des salissures comprenant la substance voulue et une quantité substantielle de substance dans laquelle u est supérieur à 5 dans de l'éthanol absolu, à une température de 10° C à 15° C, et à séparer le produit précipité.

- 45 17. Constituant de libération des salissures soluble dans l'éthanol de formule :



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dans laquelle chaque R¹ est un groupement 1,4-phénylène, chaque R² est un groupement éthylène ou 1,2-propylène; chaque n a une moyenne de 10 à 50; chaque X est H, un radical alkyle comportant de 1 à 4 atomes de carbone ou un radical acyle contenant de 2 à 4 atomes de carbone; dans laquelle de 90% à 100% des groupements R² sont des groupements 1,2-propylène; et dans laquelle moins de 10% en moles dudit composé de libération des salissures a une valeur de u supérieure à 5, au moins 20% en moles dudit composé de libération des salissures a une valeur de u dans la gamme de 3 à 5 et dans laquelle la valeur moyenne de u est de 3 à 5; que l'on peut obtenir par le procédé de la revendication 16.

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10 **18.** Constituant selon la revendication 17, dans lequel chaque X est un groupe alkyle contenant de 1 à 2 atomes de carbone.

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