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EUROPEAN PATENT APPLICATION

21 Application number: **89870064.6**

22 Date of filing: **10.05.89**

51 Int. Cl.4: **C 11 D 1/83**
C 11 D 3/20, C 11 D 3/37,
C 11 D 3/386, C 11 D 3/30

30 Priority: **12.05.88 US 193320 22.12.88 US 288738**
26.04.89 US 341918

43 Date of publication of application:
15.11.89 Bulletin 89/46

84 Designated Contracting States:
AT BE CH DE FR GB GR IT LI LU NL SE

71 Applicant: **THE PROCTER & GAMBLE COMPANY**
One Procter & Gamble Plaza
Cincinnati Ohio 45202 (US)

72 Inventor: **Showell, Michael Stanford**
810 Finney Trail
Cincinnati Ohio 45224 (US)

Wertz, William Conrad
23800 Salt-Fork Rd.
Lawrenceburg Indiana 47025 (US)

7A Representative: **Canonici, Jean-Jacques et al**
Procter & Gamble European Technical Center N.V.
Temselaan 100
B-1820 Strombeek-Bever (BE)

54 **Heavy duty liquid laundry detergents containing anionic and nonionic surfactant, builder and proteolytic enzyme.**

57 Heavy duty liquid laundry detergent compositions containing synthetic anionic and ethoxylated nonionic surfactant, detergency builder, specific proteolytic enzyme, an enzyme stabilization system, and water are disclosed. The compositions have a pH in a 10% by weight solution in water at 20°C of between about 7.0 and 9.0, a Critical Micelle Concentration of less than or equal to about 200 ppm, and an air/water Interfacial Tension above the Critical Micelle Concentration of less than or equal to about 32 dynes/cm at 35°C in distilled water. The compositions are preferably clear, homogeneous, stable and provide good cleaning performance, particularly through-the-wash on enzyme-sensitive stains.

EP 0 342 177 A2

Description**HEAVY DUTY LIQUID LAUNDRY DETERGENTS CONTAINING ANIONIC AND NONIONIC SURFACTANT, BUILDER AND PROTEOLYTIC ENZYME**

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TECHNICAL FIELD

10 The present invention relates to heavy duty liquid laundry detergent compositions containing synthetic anionic and ethoxylated nonionic surfactant, detergency builder, specific proteolytic enzyme, an enzyme stabilization system, and water. The compositions have a pH in a 10% by weight solution in water at 20°C of between about 7.0 and 9.0, a Critical Micelle Concentration of less than or equal to about 200 ppm, and an air/water Interfacial Tension above the Critical Micelle Concentration of less than or equal to about 32 dynes/cm at 35°C in distilled water. The compositions are preferably clear, homogeneous, and stable and provide good cleaning performance, particularly through-the-wash on enzyme-sensitive stains.

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BACKGROUND OF THE INVENTION

20 Laundry detergents containing high levels of anionic surfactant and builder, and capable of providing superior cleaning performance, are currently on the market. Some of these compositions contain enzymes to enhance removal of enzyme-sensitive stains. The stabilization of enzymes is particularly difficult in these compositions because anionic surfactants, especially alkyl sulfates, tend to denature enzymes and render them inactive. Detergency builders can also sequester the calcium ion needed for enzyme activity and/or stability.

25 There is a continuing need for the development of new enzymes that provide improved performance and better stability in heavy duty liquid detergent compositions, particularly those containing high levels of anionic surfactant and builder. Once these enzymes are developed, it is then difficult to formulate a composition containing them that is clear, homogeneous and phase stable, maintains enzyme stability over time in product, and is an excellent fabric cleaner.

30 European Patent Application 130,756, Bott et al., published January 9, 1985, discloses specific proteolytic enzymes and methods for their preparation. The enzymes of this reference are said to be useful in laundry detergents, but liquid and granular. They can be combined with surfactants (including anionics), builders, bleach and/or fluorescent whitening agents.

35 European Patent Application Serial No. 199,404, Venegas, published October 29, 1986, discloses heavy duty liquid laundry detergents containing a specific protease referred to as "Protease A", anionic surfactant, detergency builder, and calcium ion. The compositions provide improved cleaning performance, particularly through-the-wash, of enzyme-sensitive stains such as grass, blood, gravy and chocolate pudding.

40 European Patent Application Serial No. 199,405, Venegas, published October 29, 1986, discloses liquid detergent compositions containing synthetic surfactant, the same Protease A, boric acid or a boron compound capable of forming boric acid in the composition, and calcium ion. The compositions exhibit improved enzyme stability because the boric acid stabilizes the Protease A to a greater degree than it does other proteolytic enzymes. Preferred laundry detergent compositions containing anionic surfactant and detergency builder also provide improved cleaning performance, particularly through-the-wash, on enzyme-sensitive stains.

45 An improved proteolytic enzyme referred to herein as "Protease B" is described in European Patent Application Serial Number 87303761.8, filed April 28, 1987, on pages 17, 24, and 98. Protease B differs from the above cited Protease A in that it has a leucine substituted for the tyrosine in position 217 on the protein backbone.

50 U.S. Patent 4,507,219, Hughes, issued March 26, 1985, discloses heavy duty liquid laundry detergents which may contain proteolytic enzyme along with anionic surfactant, optional quaternary ammonium, amine or amine oxide surfactants, saturated fatty acid, polycarboxylate builder, a neutralization system, and a solvent system. The compositions are isotropic liquids.

55 International Patent Publication No. WO87/04461, Stabinsky, published July 30, 1987, discloses a specific enzyme and methods for its preparation. The difference between the European application enzyme structure and the present enzyme structure is replacement of the asparagine residue in the 218 position on the protein backbone with serine, valine, threonine, cysteine, glutamine or isoleucine. Said replacement is claimed to impart improved pH and heat stability to the enzyme.

60 U.S. Patent 4,670,179, Inamorato et al., issued June 2, 1987; UK Patent Application 2,178,054, published February 4, 1987; UK Patent Application 2178055, published February 4, 1987; U.S. Patent 4,661,287, Crossin, issued April 28, 1987; U.S. Patent 4,529,525, Dormal et al., issued July 16, 1985; and U.S. Patent 4,652,394, Inamorato et al., issued March 24, 1987, disclose stabilized, single-phase liquid detergent compositions containing proteolytic enzymes, an enzyme stabilization system, nonphosphate builder salts, and/or polymeric soil removal/release systems.

U.S. Patent 4,608,189, Koch et al., issued August 26, 1986, discloses aqueous detergent compositions, essentially free of inorganic builder salts which contain proteolytic enzymes and polyoxyethylene surfactants.

The following references disclose various stabilization systems in liquid detergent compositions containing enzymes: U.S. Patent 4,261,868, Hora et al, issued April 14, 1981; U.S. Patent 4,404,115, Tai, issued September 13, 1983; U.S. Patent 4,318,818, Letton et al., issued March 9, 1982; U.S. Patent 4,243,543, Guilbert et al, issued January 6, 1981, U.S. Patent 4,529,525, Dormal et al., issued July 16, 1985; and U.S. Patents 4,537,706 and 4,537,707, both Severson, Jr., issued August 27, 1985.

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It is an object of this invention to provide heavy duty liquid detergent compositions comprising a proteolytic enzyme which have improved cleaning performance.

It is also an object of this invention to provide heavy duty liquid detergent compositions comprising a proteolytic enzyme which are clear, homogeneous suspensions that are stable at room temperature.

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It is further an object of this invention to provide heavy duty liquid detergent compositions comprising a proteolytic enzyme which have improved enzyme stability.

It is yet another object of this invention to provide heavy duty liquid detergent compositions comprising a proteolytic enzyme which clean enzyme-sensitive stains, such as grass, blood, gravy and chocolate pudding stains, as well as or better than currently available heavy duty liquid detergent compositions comprising proteolytic enzymes.

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These and other objects are attained as a result of formulating certain levels of Protease B, synthetic anionic surfactant, ethoxylated nonionic surfactant, detergency builder, a conventional enzyme stabilization system, and water at a pH in a 10% by weight solution in water at 20°C of between about 8.0 and 8.5. This composition is preferably clear, homogeneous, and phase stable, and has good cleaning performance and enzyme stability.

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SUMMARY OF THE INVENTION

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The present invention relates to a heavy duty liquid laundry detergent composition comprising, by weight:

- (a) from about 10% to about 50% of a synthetic anionic surfactant;
- (b) from about 2% to about 14% of an ethoxylated nonionic surfactant;
- (c) from about 5% to about 20% of a detergency builder;
- (d) from about 0.01% to about 5% of the proteolytic enzyme characterized by the following amino acid sequence:

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Pro His Val Ala Gly Ala Ala Ala Leu Ile Leu Ser Lys His

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Pro Asn Trp Thr Asn Thr Gln Val Arg Ser Ser Leu Glu Asn

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Thr Thr Thr Lys Leu Gly Asp Ser Phe Tyr Tyr Gly Lys Gly

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Leu Ile Asn Val Gln Ala Ala Ala Gln; (referred to herein as
Protease B)

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(e) from about 0.5% to about 15% of an enzyme stabilization system; and

(f) from about 30% to about 80% of water; said composition containing (a) and (b) in a ratio of from 1:1 to 5:1; having a pH, in a 10% by weight solution in water at 20° C, of from about 7.0 to about 9.0; and having a Critical Micelle Concentration of less than or equal to about 200 ppm, and an air/water Interfacial Tension above the Critical Micelle Concentration of less than or equal to about 32 dynes/cm at 35° C in distilled water.

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DESCRIPTION OF THE INVENTION

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The instant compositions contain six essential ingredients which are: (1) synthetic anionic surfactant, (2) ethoxylated nonionic surfactant, (3) detergency builder, (4) a specific proteolytic enzyme, (5) an enzyme stabilization system, and (6) water. The weight ratio of synthetic anionic surfactant to ethoxylated nonionic surfactant is from about 1:1 to about 5:1. The compositions have a pH in a 10% by weight solution in water at 20° C of from about 7.0 to about 9.0, a Critical Micelle Concentration of less than or equal to about 200 ppm, and an air/water Interfacial Tension at the Critical Micelle Concentration of less than or equal to about 32 dynes/cm at 35° C in distilled water. The compositions are preferably clear, homogeneous and phase stable, and have good cleaning performance and enzyme stability.

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A. Synthetic Anionic Surfactant

The compositions of the present invention contain from about 10% to about 50%, preferably from about 15% to about 50%, more preferably from about 20% to about 40%, and most preferably from about 20% to about 30%, by weight of a synthetic anionic surfactant. Suitable synthetic anionic surfactants are disclosed in U.S. Patent 4,285,841, Barrat et al., issued August 25, 1981, and in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, both incorporated herein by reference.

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Useful anionic surfactants include the water-soluble salts, particularly the alkali metal, ammonium and alkylammonium (e.g., monoethanolammonium or triethanolammonium) salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of aryl groups.) Examples of this group of synthetic surfactants are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C₈-C₁₈ carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; and the alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 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 about 11 to 14.

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Other anionic surfactants herein are the water-soluble salts of: paraffin sulfonates containing from about 8 to about 24 (preferably about 12 to 18) carbon atoms; alkyl glyceryl ether sulfonates, especially those ethers of C₈-18 alcohols (e.g., those derived from tallow and coconut oil); alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 4 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group; and alkyl ethylene oxide ether sulfates containing about 1 to about 4 units of ethylene oxide per molecule and from about 10 to about 20 carbon atoms in the alkyl group.

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Other useful anionic surfactants include the water-soluble salts of esters of alpha-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

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Preferred anionic surfactants are the C₁₀-C₁₈ alkyl sulfates and alkyl ethoxy sulfates containing an average of up to about 4 ethylene oxide units per mole of alkyl sulfate, C₁₁-C₁₃ linear alkylbenzene sulfonates, and

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mixtures thereof.

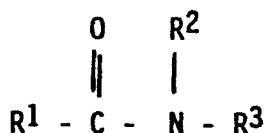
B. Ethoxylated Nonionic Surfactant

A second essential ingredient is from about 2% to about 14%, preferably from about 2% to about 8%, most preferably from about 3% to about 5% by weight, of an ethoxylated nonionic surfactant. The weight ratio of synthetic anionic surfactant (on an acid basis) to nonionic surfactant is from about 1:1 to about 5:1, preferably from about 2:1 to about 5:1, most preferably from about 3:1 to about 4:1. This is to ensure the formation and adsorption of sufficient hardness surfactants at the air/water interface to provide good greasy/oily soil removal.

the ethoxylated nonionic surfactant is 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 about 3 to about 9, and said nonionic surfactant has an HLB (Hydrophilic-Lipophilic Balance) of from about 6 to about 14, preferably from about 10 to about 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, both incorporated herein by reference. Particularly preferred are condensation products of C_{12} - C_{15} alcohols with from about 3 to about 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.

C. Optional Cosurfactants

Optional cosurfactants for use with the above ethoxylated nonionic surfactants include amides of the formula



wherein R^1 is an alkyl, hydroxyalkyl or alkenyl radical containing from about 8 to about 20 carbon atoms, and R^2 and R^3 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 about 5 ethylene oxide units, provided at least one of R^2 and R^3 contains a hydroxyl group.

Preferred amides are the C_8 - C_{20} fatty acid alkylol amides in which each alkylol group contains from 1 to 3 carbon atoms, and additionally can contain up to about 2 ethylene oxide units. Particularly preferred are the C_{12} - C_{16} fatty acid monoethanol and diethanol amides.

If used, amides are preferably present at a level such that the above ethoxylated nonionic surfactant and amide surfactant is in a weight ratio of from about 4:1 to 1:4, preferably from about 3:1 to about 1:3.

Preferred and optional cosurfactants, used at a level of from about 0.15% to about 1%, are the quaternary ammonium, amine and amine oxide surfactants described in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, incorporated herein by reference.

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. From about 0.2% to about 0.8% of monoalkyl trimethylammonium chloride is preferred.

D. Detergency Builder

The compositions herein contain from about 5% to about 20%, preferably from about 10% to about 15%, by weight of a detergency builder which can be a fatty acid containing from about 10 to about 18 carbon atoms and/or a polycarboxylate, polyphosphonate and/or polyphosphate builder. Preferred are from 0 to about 10% (more preferably from about 3% to about 10%) by weight of saturated fatty acids containing from about 12 to about 14 carbon atoms, along with from 0 to about 10%, more preferably from about 2% to about 8%, most preferably from about 2% to about 5%, by weight of a polycarboxylate builder, most preferably citric acid, in a weight ratio of from 1:1 to 3:1.

Since the proteolytic enzymes herein appear to provide optimum performance benefits versus other enzymes when the builder to water hardness ratio is close to one, the compositions preferably contain sufficient builder to sequester from about 2 to about 10, preferably from about 3 to about 8, grains per gallon of hardness.

Suitable saturated fatty acid 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 about 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., 1%-30% of total fatty acid) of oleic acid; and palm kernel fatty acid.

The compositions herein preferably also contain the polycarboxylate, polyphosphonate and polyphosphate builders described in U.S. Patent 4,284,532, Leikhim et al., issued August 18, 1981, incorporated herein by reference. Water-soluble polycarboxylate builders, particularly citrates, are preferred of this group. Suitable

polycarboxylate builders include the various aminopolycarboxylates, cycloalkane polycarboxylates, ether polycarboxylates, alkyl polycarboxylates, epoxy polycarboxylates, tetrahydrofuran polycarboxylates, benzene polycarboxylates, and polyacetal polycarboxylates.

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, incorporated herein by reference; the polycarboxylate materials described in U.S. Patent 3,364,103, incorporated herein by reference; and the water-soluble salts of polycarboxylate polymers and copolymers described in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, incorporated herein by reference.

Other useful detergency builders include the water-soluble salts of polymeric aliphatic polycarboxylic acids having the following structural and physical characteristics: (a) a minimum molecular weight of about 350 calculated as to the acid from; (b) an equivalent weight of about 50 to about 80 calculated as to acid forms; (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-cyclopentanetetra-carboxylic acid and oxydisuccinic acid.

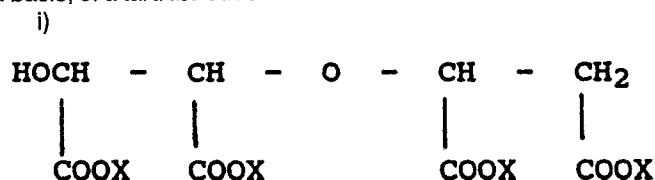
Other polycarboxylates are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al., and U.S. Patent 4,146,495, issued March 27, 1979 to Crutchfield et al., both incorporated herein by reference.

Other detergency builders include the aluminosilicate ion exchange material described in U.S. Patent 4,405,483, Kuzel et al., issued September 20, 1983, incorporated herein by reference.

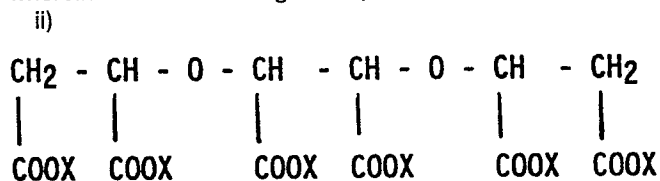
Other preferred builders are those of the general formula $R-CH(COOH)CH_2(COOH)$, i.e. derivatives of succinic acid, wherein R is C_{10} - C_{20} alkyl or alkenyl, preferably C_{12} - C_{16} , or wherein R may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents. These succinate builders are preferably used in the form of their water soluble salts, including the sodium, potassium and alkanolammonium salts. Specific examples of succinate builders include: lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenyly succinate, and the like.

E. Tartrate Succinate Builder

The positions herein preferably contain from 0 to about 10%, preferably from 0 to about 6%, by weight on an acid basis, of a tartrate succinate builder material selected from the group consisting of:



wherein X is a salt-forming cation;



wherein X is a salt-forming cation; and

iii) mixtures thereof.

The tartrate succinate compounds used herein are described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, incorporated herein by reference.

F. Neutralization System

The present compositions can also optionally contain from about 0 to about 0.04 moles, preferably from about 0.01 to about 0.035 moles, more preferably from about 0.015 to about 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 of the alkanolamines, particularly monoethanolamine, are preferred to enhance product stability, detergency performance, and odor. However, the amount of alkanolamine should be minimized for best chlorine bleach compatibility.

In addition, the compositions contain sodium ions, and preferably potassium ions, at a level sufficient to

neutralize the anionic species and provide the desired product pH.

G. Proteolytic Enzyme

The compositions of the present invention contain from about 0.01% to about 5%, preferably from about 0.1% to about 2%, by weight of the proteolytic enzyme referred to herein as Protease B.

This proteolytic enzyme, and methods for its preparation, is described in European Patent Application Serial Number 87303761.8, filed April 28, 1987, incorporated herein by reference. Methods for its preparation are also described in European Patent Application 130,756, Bott et al., published January 9, 1985, incorporated herein by reference.

The described proteolytic enzyme is preferably included in an amount sufficient to provide an activity of from about 0.05 to about 1.0, more preferably from about 0.1 to about 0.75, most preferably from about 0.125 to about 0.5, mg of active enzyme per gram of composition.

H. Enzyme Stabilization System

An enzyme stabilization system, comprising calcium ion, boric acid, propylene glycol and/or short chain carboxylic acids, is the fifth essential element of the instant heavy duty liquid detergent composition. The enzyme stabilization system comprises from about 0.5% to about 15% by weight of the composition.

The composition preferably contains from about 0.01 to about 50, preferably from about 0.1 to about 30, more preferably from about 1 to about 20, millimoles of calcium ion per liter. The level of calcium ion should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, etc., in the composition. Any water-soluble calcium salt can be used as the source of calcium ion, including calcium chloride, calcium formate, and calcium acetate. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. From about 0.03% to about 0.6% of calcium formate is preferred.

A second preferred enzyme stabilizer is polyols containing only carbon, hydrogen and oxygen atoms. They preferably contain from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups. Examples include propylene glycol (especially 1,2 propanediol, which is preferred), ethylene glycol, glycerol, sorbitol, mannitol, and glucose. The polyol generally represents from about 0.5% to about 15%, preferably from about 1.5% to about 8%, by weight of the composition. Preferably, the weight ratio of polyol to any boric acid added is at least 1, more preferably at least about 1.3.

The compositions preferably also contain the water-soluble, short chain carboxylates described in U.S. Patent 4,318,818, Letton et al., issued March 9, 1982, incorporated herein by reference. The formates are preferred and can be used at levels of from about 0.05% to about 5%, preferably from about 0.2% to about 2%, most preferably from about 0.4% to about 1.5%, by weight of the composition. Sodium formate is preferred.

The compositions herein also optionally contain from about 0.25% to about 5%, most preferably from about 0.5% to about 3%, by weight of boric acid. The boric acid may be, but is preferably not, formed by a compound capable of forming boric acid in the composition. Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium 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.

I. Water

Finally, the compositions herein contain from about 30% to about 80%, preferably from about 35% to about 60%, by weight of water.

J. Suds Suppressor

Another optional component for use in the liquid detergents herein is from 0 to about 1.5%, preferably from about 0.5% to about 1.0%, by weight of silicone based suds suppressor agent.

Silicones are widely known and taught for use as highly effective suds controlling agents. For example, U.S. Patent 3,455,839 relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Useful suds controlling silicones are mixtures of silicone and silanated silica as described, for instance, in German Patent Application DOS 2,124,526.

Silicone defoamers and suds controlling agents have been successfully incorporated into granular detergent compositions by protecting them from detergent surfactants as in U.S. Patent 3,933,672, Bartolatta et al., and in U.S. Patent 4,652,392, Baginski et al., issued March 24, 1987.

A preferred 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 1500 cs. at 25°C;
- (ii) from about 5 to about 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and SiO_2 units in a ratio of from $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and to SiO_2 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;

By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this

suds controlling agent that will control the suds to the extent desired. The amount of suds control will vary with the detergent surfactant selected. For example, with high sudsing surfactants, relatively more of the suds controlling agent is used to achieve the desired suds control than with low foaming surfactants.

K. Other Optional Components

Other optional components for use in the liquid detergents herein include soil removal agents, soil release polymers, antiredeposition agents such as tetraethylene pentamine ethoxylate (from about 0.5% to about 30%, preferably from about 1% to about 3%, by weight), suds regulants, hydrotropes such as sodium cumene sulfonate, opacifiers, antioxidants, bactericides, dyes, perfumes, and brighteners known in the art. Such optional components generally represent less than about 15%, preferably from about 0.5% to about 10%, more preferably from about 1% to about 10%, by weight of the composition.

The compositions may contain from 0% to about 8%, preferably from 0% to about 5%, by weight of a C₁₂-C₁₄ alkenyl succinic acid or salt thereof. These materials are of the general formula R-CH(COOX)CH₂(COOX), wherein R is a C₁₂-C₁₄ alkenyl group and each X is H or a suitable cation, such as sodium, potassium, ammonium or alkanolammonium (e.g., mono-, di-, or tri-ethanolammonium). Specific examples are 2-dodecanyl succinate (preferred) and 2-tetradecanyl succinate.

The compositions herein optionally contain from about 0.1% to about 1%, preferably from about 0.2% to about 0.6%, by weight of water-soluble salts of ethylenediamine tetramethylenephosphonic acid, diethylenetriamine pentamethylenephosphonic acid, ethylenediamine tetraacetic acid (preferred), or diethylenetriamine pentaacetic acid (most preferred) to enhance cleaning performance when pretreating fabrics.

The compositions herein preferably contain up to about 10% of ethanol.

L. Other Requirements

The instant composition has a pH, in a 10% by weight solution in water at 20° C, of from about 7.0 to about 9.0, preferably from about 8.0 to about 8.5.

The instant compositions also have a Critical Micelle Concentration (CMC) of less than or equal to about 200 parts per million (ppm), and an air/water Interfacial Tension above the CMC of less than or equal to about 32, preferably less than or equal to about 30, dynes per centimeter at 30° C in distilled water. These measurements are described in "Measurement of Interfacial Tension and Surface Tension - General Review for Practical Man", C. Weser, GIT Fachzeitschrift für das Laboratorium, 24 (1980) 642-648 and 734-742, FIT Verlag Ernst Giebeler, Darmstadt, and Interfacial Phenomena - Equilibrium and Dynamic Effects, C.A. Miller and P. Neogi, Chapter 1, pp. 29-36 (1985), Marcel Dekker, Inc. New York.

Enzyme activity can be measured using the PNA assay, according to reaction with the soluble substrate succinyl-alanine-alanine-proline-phenylalanine-para-nitrophenol, which is described in the Journal of American Oil Chemists Society, Rothgeb, T.M., Goodlander, B.D., Garrison, P.H., and Smith, L.A., in press (1988).

The following examples illustrate the compositions of the present invention. All parts, percentages and ratios used herein are by weight unless otherwise specified.

EXAMPLE I

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

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	<u>Component</u>	<u>Active Weight %</u>
	C ₁₃ linear alkylbenzene sulfonic acid	8.00
5	C ₁₄₋₁₅ alkyl polyethoxylate (2.25) sulfonic acid	12.00
	1,2 Propanediol	3.50
	Sodium diethylenetriamine pentaacetate	0.30
10	Monoethanolamine	2.00
	C ₁₂₋₁₃ alcohol polyethoxylate (6.5) *	5.00
15	Ethanol	8.50
	Sodium hydroxide	3.85
	Potassium hydroxide	1.80
	C ₁₂₋₁₄ fatty acid	10.00
20	Citric acid	4.00
	Calcium formate	0.12
	Sodium formate	0.86
	C ₁₂ alkyltrimethylammonium chloride	0.50
25	Tetraethylene pentamine ethoxylate (15-18)	2.00
	Water	37.14
30	Dye	0.08
	Perfume	0.25
	Protease B**	0.099
35	* Alcohol and monoethoxylated alcohol removed.	
	** mg active enzyme/g (@ 27 mg active enzyme/g stock)	

The ingredients listed above are added to a mixing tank with a single agitator in the order in which they appear below. Before the proteolytic enzyme, dye and perfume are added, the pH of the mix is adjusted so that a 10% by weight solution in water at 20°C has a pH of about 8.5.

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<u>Stock Material</u>	<u>Weight Percent</u>	
C ₁₃ linear alkyl benzene sulfonic acid (96%)	8.33	
Alkyl polyethoxylate paste mixture	<u>24.80</u>	5
C ₁₄₋₁₅ alkyl polyethoxylate (2-25) sulfonic acid	48.38	
Ethanol (92%)	16.20	10
Sodium hydroxide	5.12	
Water	<u>30.30</u>	
1,2 Propanediol	3.50	
Sodium diethylenetriamine pentaacetate (41%)	0.73	15
Brightener premix	<u>6.70</u>	
Brightener	3.07	
Monoethanolamine	7.46	20
C ₁₂₋₁₃ alcohol polyethoxylate (6.5) *	29.82	
Water	<u>59.65</u>	
Monoethanolamine	1.50	
C ₁₂₋₁₃ alcohol polyethoxylate (6.5) *	2.93	25
Sodium hydroxide (50%)	5.16	
Potassium hydroxide (45%)	4.00	30
C ₁₂₋₁₄ fatty acid	10.00	
Citric acid (50%)	8.00	
Ethanol (92%)	4.87	
Calcium formate (10%)	1.20	35
Sodium formate (30%)	2.87	
C ₁₂ alkyltrimethylammonium chloride (37%)	1.62	
Tetraethylene pentamine ethoxylate (15-18)(80%)	2.50	40
Water	10.86	
Dye	0.08	
Perfume	0.25	45
Protease B**	0.099	

*Alcohol and monoethoxylated alcohol removed.

**mg active enzyme/g (27 mg active enzyme/g stock)

This formula is clear, homogeneous, and stable, and has a Critical Micelle Concentration of about 220 ppm and an air/water Interfacial Tension above this CMC of about 25 dynes/cm at 35°C in distilled water. The composition with Protease B provides superior cleaning of enzyme-sensitive stains, even when compared to Protease A (described above) at 0.25 mg active enzyme/g product in a 60°F (15.6°C) wash at 5 grains per gallon (gpg) hardness (3:1 Ca/Mg).

Protease B also shows superior enzyme stability in the composition of Example I versus other proteolytic enzymes such as Protease A and Alcalase B (Novo Industries, Copenhagen, Denmark):

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Enzyme Activity* (after 1 week storage at 37.8° C)

	<u>% Activity</u>	<u>Half Life (days)</u>
5 Protease B	58.4	9.1
Protease A	33.6	4.5
Alcalase B	13.7	2.5

*PNA assay

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EXAMPLE II

A heavy duty liquid composition of the present invention is as follows:

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<u>Component</u>	<u>Active Weight %</u>
C ₁₃ linear alkylbenzene sulfonic acid	3.80
20 C ₁₁₋₈ linear alkylbenzene sulfonic acid	3.80
C ₁₄₋₁₅ alkyl polyethoxylate (2.25) sulfonic acid	11.41
25 C ₁₂₋₁₃ alkyl polyethoxylate (6.5)*	3.80
C ₁₂ alkyl trimethyl ammonium chloride	0.28
30 Sodium cumene sulfonate	2.38
Ethanol	2.61
1,2 Propanediol	2.85
Brightener	0.12
35 Monoethanolamine	1.66
Potassium hydroxide	0.19
Sodium hydroxide	3.85
C ₁₂₋₁₄ fatty acid	3.33
Citric acid	3.80
40 Tartrate succinate	3.80
Sodium formate	0.92
Calcium formate	0.04
Tetraethylene pentamine ethoxylate (15-18)	1.66
45 Water	48.04
Soil release polymer	1.10
Dye	0.08
50 Perfume	0.30
Protease B**	0.175

Alcohol and monoethoxylated alcohol removed
 ** mg active enzyme/g (@ 27 mg active enzyme/g stock)

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The ingredients listed above are added to a mixing tank with a single agitator in the order which they appear below. Before addition of soil release polymer, dye, perfume, and proteolytic enzyme, the pH of the mixture is adjusted such that a 10% by weight solution in water has a pH of about 8.5.

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<u>Stock Material</u>	<u>Weight Percent</u>
Alkyl polyethoxylate paste mixture	<u>28.28</u>
C ₁₄₋₁₅ alkyl polyethoxylate (2.25)	40.34
sulfonic acid	
Ethanol 40-b	4.98
Sodium hydroxide	5.13
1,2 Propanediol	6.89
Monoethanolamine	2.84
Sodium formate	1.65
Water	<u>38.17</u>
Sodium amine sulfonate (45%)	5.29
Ethanol (92%)	1.31
1,2 Propanediol	0.90
Brightener premix	<u>2.59</u>
Brightener	4.63
Monoethanolamine	10.62
C ₁₂₋₁₃ alcohol polyethoxylate (6.5)*	42.38
Water	<u>42.37</u>
C ₁₂₋₁₃ alcohol polyethoxylate (6.5)*	2.70

	Monoethanolamine	0.58
	Potassium hydroxide (45%)	0.42
5	Sodium hydroxide (50%)	4.80
	C ₁₃ linear alkyl benzene sulfonic acid (96%)	3.96
	C _{11.8} linear alkyl benzene sulfonic acid (97%)	3.92
10	C ₁₂₋₁₄ fatty acid	3.33
	Citric acid	6.96
	Tartrate succinates (34.3%)	11.08
15	Sodium formate (30%)	3.08
	Calcium formate (10%)	0.38
	C ₁₂ alkyl trimethylammonium chloride (37%)	0.76
20	Tetraethylene pentamine ethoxylate (15-18) (80%)	2.08
	Water	15.92
	Soil release polymer	1.10
25	Dye	0.08
	Perfume	0.30
	Protease B**	0.175
30	*Alcohol and monoethoxylated alcohol removed	
	** mg active enzyme/g (@ 27 mg active enzyme/g stock)	

35 The above formula is clear, stable, and homogeneous, and has a Critical Micelle Concentration of about 100 ppm and an air/water Interfacial Tension above the CMC of about 30 dynes/cm at 35°C in distilled water. The composition with Protease B provides protease-sensitive stain removal equal to that achieved with the same formula using 0.35 mg active enzyme/g product of Protease A (described above).

40 Protease B also shows superior enzyme stability in the composition of Example II versus other proteolytic enzymes such as Protease A and Alcalase B (Novo Industries, Copenhagen Denmark).

Enzyme Activity* (After 4 weeks storage at 37.8°C)

45	<u>% Activity</u>	<u>Half Life (days)</u>
	Protease B	16.2
	Protease A	4.2
	Alcalase B	0.00

50 *PNA assay

55 EXAMPLE III

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

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<u>Component</u>	<u>Active Weight %</u>	
C ₁₃ linear alkylbenzene sulfonic acid	13.00	
C ₁₃₋₁₄ alkyl sulfuric acid	13.00	5
C ₁₂₋₁₃ alcohol polyethoxylate (6.5)*	6.00	
Sodium cumene sulfonate	6.30	
Ethanol (92%)	2.50	10
1,2 Propanediol	7.50	
Brightener	0.12	
Monoethanolamine	2.00	
Potassium hydroxide	0.15	15
Sodium hydroxide	4.29	
C ₁₂₋₁₄ fatty acid	1.0	
Tartrate succinate	10.0	
Citric acid	4.0	
Calcium formate	0.04	20
Sodium formate	0.86	
C ₁₂ alkyltrimethylammonium chloride	0.50	
Tetraethylene pentamine ethoxylate (15-18)	1.65	25
Water	25.36	
Soil release polymer	1.00	30
Dye	0.08	
Perfume	0.25	
Protease B**	0.397	
*Alcohol and monoethoxylated alcohol removed.		35
**mg active enzyme/g (@ 27 mg active enzyme/g stock)		

The composition is prepared as in Example II.

EXAMPLE IV

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

	<u>Component</u>	<u>Active Weight %</u>
	C ₁₃ linear alkylbenzene sulfonic acid	4.23
5	C _{11.8} alkylbenzene sulfonic acid	4.23
	C ₁₄₋₁₅ alkyl polyethoxylate (2.25) sulfonic acid	8.46
10	C ₁₂₋₁₃ alkyl polyethoxylate (6.5)*	3.39
	Sodium cumene sulfonate	5.45
	Ethanol (92%)	1.18
15	Propanediol	2.89
	Brightener	0.11
	Monoethanolamine	1.57
	Tartrate succinate	9.62
20	Calcium formate	0.102
	Formic acid	0.51
	C ₁₂ Trimethylammonium chloride	0.51
25	Tetraethylene pentamine ethoxylate (15-18)	0.96
	Water	55.57
	Soil release polymer	0.90
30	Silicone suds suppressor	0.10
	Protease B**	0.221
	*Alcohol and monoethoxylated alcohol removed.	
35	**mg active enzyme/g (@ 27 mg active enzyme/g stock)	

The composition is prepared as in Example II.

40 The above formula is clear, stable, and homogeneous, and has a Critical Micelle Concentration of about 100 ppm and an air/water Interfacial Tension above that CMC of about 30 dynes/cm at 35°C in distilled water. The composition with Protease B provides protease-sensitive stain removal equal to that achieved with the same formula using 0.35 mg active enzyme/g product of Protease A (described above).

Protease B also shows superior enzyme stability in the composition of Example IV versus other proteolytic enzymes such as Protease A and Alcalase B (Novo Industries, Copenhagen, Denmark).

	<u>Enzyme Activity*</u> (After 2 weeks storage at 37.8°C)	
	<u>% Activity</u>	<u>Half Life (days)</u>
50	Protease B	64.0
	Protease A	50.0
	Alcalase B	---

55 *PNA assay

EXAMPLE V

60 A heavy duty liquid laundry detergent composition of the present invention is as follows:

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<u>Component</u>	<u>Active Weight %</u>	
C ₁₀₋₁₅ Linear alkylbenzene sulfonic acid	12.86	5
Sodium C ₁₂₋₁₄ alkyl sulfate	2.00	
1,2 Propanediol	2.00	
Diethylenetriamine pentamethylene phosphonic acid	0.70	10
C ₁₄₋₁₅ alcohol polyethoxylate (E07)	7.77	
Ethanol	4.60	15
Sodium hydroxide	7.00	
Soil release polymer	0.46	
C ₁₂₋₁₄ alkenyl succinic acid	11.44	
Brightener	0.163	20
Oleic acid	1.80	
Citric acid (monohydrate)	2.90	
Calcium chloride	0.014	
Boric acid	1.00	25
Silane	0.03	
Water & miscellaneous	Balance	
Protease B*	0.28	
*41g active enzyme/liter of enzyme		30

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Stock Material

Premix 1

Water	23.68
Sodium hydroxide	11.50
Citric acid	5.674
Ethanol	4.00
C12-14 alkenyl succinic acid	10.74
C10-15 Linear alkylbenzene sulfonic acid	<u>6.70</u>
	62.294

Premix 2

1,2 Propanediol	0.493
Brightener	0.163
C14-15 alcohol polyethoxylate (E07)	<u>1.70</u>
	2.356

Premix 3

Water	4.44
Boric acid	1.0
Sodium hydroxide	2.4
Diethylene triamine pentamethylene phosphonic acid	<u>1.4</u>
	9.244

Premix 4

Citric acid	0.126
Calcium chloride	<u>0.015</u>
	0.141

Premix 5

Soil release polymer	0.46
Water	<u>0.46</u>
	0.92

Finished Product

Premix 1	62.294
1,2 Propanediol	1.507
C10-15 Linear alkyl benzene sulfonate	6.70
C14-15 alcohol polyethoxylate (E07)	6.07
Premix 2	2.356

Premix 3	9.244	
Sodium C ₁₂₋₁₄ alkyl sulfate	6.66	
Oleic acid	1.80	5
Premix 4	0.141	
Premix 5	0.92	
Silane	0.03	10
Protease B	0.28	
Water	Balance	

The ingredients listed above in "Finished Product" are added to a mixing tank with a single agitator in the order in which they appear. The pH of the mix is adjusted so that the pH is from 7.5 to 7.8.

The composition with Protease B provides 61% retained protease activity after three weeks storage at 35°C.

EXAMPLE VI

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

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	<u>Component</u>	<u>Active Weight %</u>
	C ₁₀₋₁₅ Linear alkylbenzene sulfonic acid	10.25
5	Triethanolamine C ₁₂₋₁₄ alkyl sulfate	3.88
	1,2 Propanediol	1.50
10	Diethylenetriamine pentamethylene phosphonic acid	0.765
	Triethanolamine (free)	4.335
	C ₁₄₋₁₅ alcohol polyethoxylate (E07)	11.620
15	Ethanol	5.510
	Sodium hydroxide	3.400
	C ₈₋₁₈ fatty acid	10.68
	Oleic acid	3.88
20	Citric acid (anhydrous)	0.83
	Calcium chloride	0.0167
	Sodium formate	0.972
	Tetraethylene pentamine ethoxylate (15-18)	0.30
25	Dye	0.0032
	Opacifier	0.224
	Perfume	0.30
	Soil release polymer	0.50
30	N-(ethylene diaminoethyl) aminopropyltrimethoxy silane	0.030
35	Silicone suds suppressor	0.0025
	Brightener	0.148
	Water & miscellaneous	Balance
	Protease B*	0.28
40	Amylase**	0.183

*41g active enzyme/liter of enzyme.

** 125 PGU active enzyme/gram amylase solution.

45 The ingredients listed above are added to a mixing tank with a single agitator. The pH of the mix is adjusted so that it is between about 8.0 and 8.5.

Claims

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1. A heavy duty liquid laundry detergent composition comprising by weight:

(a) from about 10% to 50% of a synthetic anionic surfactant; preferably from 15% to 40% by weight of anionic surfactant selected from the group consisting of alkyl sulfates containing from 10 to 18 carbon atoms, alkyl ethoxy sulfates containing from 10 to 18 carbon atoms and an average of up to 4 ethylene oxide units per mole or alkyl sulfate, linear alkylbenzene sulfonates containing from 11 to 13 carbon atoms, and mixtures thereof;

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(b) from 2% to 14% of an ethoxylated nonionic surfactant; preferably 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, wherein said nonionic surfactant has an HLB (Hydrophilic-Lipophilic Balance) of from 6 to 14; most preferably from 3% to 5% of an ethoxylated nonionic surfactant which is a condensation product of C₁₂-C₁₅ alcohols with from 3 to 8 moles of ethylene oxide per mole of alcohol;

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(c) from 5% to 20% of a detergency builder; preferably from 0% to 10% by weight of a saturated fatty acid builder containing from 12 to 14 carbon atoms along with from 0% to 10% by weight of water-soluble polycarboxylate builder, preferably citric acid.

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Ala Val Ile Asp Ser Gly Ile Asp Ser Ser His Pro Asp Leu
 50
 Lys Val Ala Gly Gly Ala Ser Met Val Pro Ser Glu Thr Asn
 60 70
 Pro Phe Gln Asp Asn Asn Ser His Gly Thr His Val Ala Gly
 80
 Thr Val Ala Ala Leu Asn Asn Ser Ile Gly Val Leu Gly Val
 90
 Ala Pro Ser Ala Ser Leu Tyr Ala Val Lys Val Leu Gly Ala
 100 110
 Asp Gly Ser Gly Gln Tyr Ser Trp Ile Ile Asn Gly Ile Glu
 120
 Trp Ala Ile Ala Asn Asn Met Asp Val Ile Asn Met Ser Leu
 130 140
 Gly Gly Pro Ser Gly Ser Ala Ala Leu Lys Ala Ala Val Asp
 150
 Lys Ala Val Ala Ser Gly Val Val Val Val Ala Ala Ala Gly
 160
 Asn Glu Gly Thr Ser Gly Ser Ser Ser Thr Val Gly Tyr Pro
 170 180
 Gly Lys Tyr Pro Ser Val Ile Ala Val Gly Ala Val Asp Ser
 190
 Ser Asn Gln Arg Ala Ser Phe Ser Ser Val Gly Pro Glu Leu
 200 210
 Asp Val Met Ala Pro Gly Val Ser Ile Gln Ser Thr Leu Pro
 220
 Gly Asn Lys Tyr Gly Ala Leu Asn Gly Thr Ser Met Ala Ser
 230
 Pro His Val Ala Gly Ala Ala Ala Leu Ile Leu Ser Lys His
 240 250
 Pro Asn Trp Thr Asn Thr Gln Val Arg Ser Ser Leu Glu Asn
 260
 Thr Thr Thr Lys Leu Gly Asp Ser Phe Tyr Tyr Gly Lys Gly
 270 275
 Leu Ile Asn Val Gln Ala Ala Ala Gln;

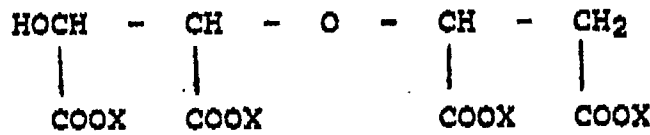
(e) from 0.5% to 15% of an enzyme stabilization system;
 preferably including from 0.5% to 15% by weight of a polyol containing only carbon, hydrogen and oxygen atoms, most preferably from about 1.5% to about 8% by weight of propylene glycol; and
 (f) from 30% to 80% of water;

said composition containing (a) and (b) in a ratio of from 1:1 to 5:1; having a pH, in a 10% by weight solution in water at 20° C, of from 7.0 to 9.0; and having a Critical Micelle Concentration of less than or equal to 200 ppm, and an air/water Interfacial Tension above the Critical Micelle Concentration of less than or equal to 32 dynes/cm at 35° C in distilled water.

2. A heavy duty liquid laundry detergent composition according to Claim 1 further comprising from 0.15% to 1% by weight of a surfactant selected from the group consisting of quaternary ammonium, amine and amine oxide surfactants and mixtures thereof; preferably from 0.2% to 0.8% of monoalkyl trimethylammonium chloride.

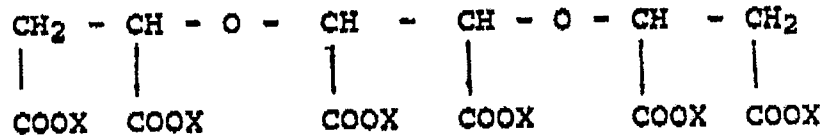
3. A heavy duty liquid laundry detergent composition according to Claims 1 or 2 further comprising from 0% to 10% by weight of an acid basis of a tartrate succinate builder material selected from the group consisting of:

i)



wherein X is a salt-forming cation;

ii)



wherein X is a salt-forming cation; and

iii) mixtures thereof.

4. A heavy duty liquid laundry detergent composition according to Claims 1, 2 or 3 additionally comprising from 0.2% to 0.6% by weight of water-soluble salts of ethylenediamine tetraacetic acid or diethylenetriamine pentaacetic acid.

5. A heavy duty liquid laundry detergent composition according to Claims 1, 2, 3 or 4 comprising from 0.01 to 50 millimoles of calcium ion per liter of composition.

6. A heavy duty liquid laundry detergent composition according to Claims 1, 2, 3, 4 or 5 comprising from 0.03% to 0.6% by weight of calcium formate.

7. A heavy duty liquid laundry detergent composition according to Claims 1, 2, 3, 4, 5 or 6 further comprising from 0.05% to 5% by weight of formate, preferably from 0.4% to 1.5% by weight of sodium formate.

8. A heavy duty liquid laundry detergent composition according to Claims 1, 2, 3, 4, 5, 6 or 7 further comprising from 0.5% to 3% by weight of tetraethylene pentamine ethoxylate.

9. A heavy duty liquid laundry detergent composition according to Claims 1, 2, 3, 4, 5, 6, 7, or 8 further comprising from 0 to 0.04 moles per 100 grams of composition of an alkanolamine selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, and mixtures thereof.

10. A heavy duty liquid laundry detergent composition according to Claims 1, 2, 3, 4, 5, 6, 7, 8 or 9 further comprising from 0% to 15% by weight of a silicone based suds suppressor agent.