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PATENT REQUEST: STANDARD PATENT

We, COLGATE-PALMOLIVE COMPANY, being the person(s) identified below as the Applicant, request the grant of a standard patent to the person identified below as the Nominated Person, for an invention described in the accompanying complete specification.

Full application details follow.

Applicant:	COLGATE-PALMOLIVE COMPANY a Delaware Corporation
Address:	300 Park Avenue New York New York 10022 United States of America
Nominated Person:	COLGATE-PALMOLIVE COMPANY a Delaware Corporation
Address:	300 Park Avenue New York New York 10022 United States of America
Invention Title:	"High foaming nonionic surfactant based liquid detergent"
Name(s) of Actual Inventor(s):	Stephen T REPINEC; Gilbert S GOMES; Rita ERILLI; Ronald KERN
Address for service is:	F.B. RICE & CO., 28A Montague St, Balmain N.S.W. 2041
Attorney Code: RI	

BASIC CONVENTION APPLICATION(S) DETAILS

Application No	Country	Country Code	Date of Application
8/091518	U S A	US	9 July 1993

Applicant(s):Stephen T REPINEC; Gilbert S GOMES; Rita ERILLI; Ronald KERN

We are not an eligible person described in Section 33 - 36 of the Act.

Dated this 23 day of June 1994

COLGATE-PALMOLIVE COMPANY

S 047203 230694

By: _____
Registered Patent Attorney

PW/FS/WAW4/64181

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P/00/008
Section 29(1)
Regulation 3.1(2)

NOTICE OF ENTITLEMENT

(To be filed before acceptance)

I, Gwendoline Ruth Bentley being authorised by COLGATE-PALMOLIVE COMPANY of 300 Park Avenue, New York, New York 10022 United States Of America, the applicant in respect of an application for a patent for an invention entitled "High foaming nonionic surfactant based liquid detergent" filed under Australian Application No 65918/94, state the following:-

The person(s) nominated for the grant of the patent have, for the following reasons, gained entitlement from the actual inventor(s):-

The nominated person(s) is the assignee of the invention from the actual inventor(s).

The person(s) nominated for the grant of the patent are entitled to rely on the basic application(s) listed on the Patent Request Form by reason of the following:-

The nominated person(s) is the assignee of the basic application(s) from the basic applicant(s).

The basic application listed on the Patent Request Form is the first application made in a convention country in respect of the invention.

Signed: GRBentley.....Date: 28 November 1996

Status: Registered Patent Attorney

64181k28.grb/dkc

F.B. RICE & CO. PATENT ATTORNEYS

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(12) PATENT ABRIDGMENT (11) Document No. AU-B-65918/94
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(54) Title
HIGH FOAMING NONIONIC SURFACTANT BASED LIQUID DETERGENT

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(57) Claim

1. A high foaming light duty, liquid detergent comprising approximately, by weight:

(a) 6% to 12% of a water soluble nonionic surfactant selected from the group consisting of primary and secondary C_8-C_{18} alkanol condensates with 5 to 30 moles of ethylene oxide, condensates of C_8-C_{18} alkylphenol with 5 to 30 moles of ethylene oxide, condensates of C_8-C_{20} alkanol with a heteric mixture of ethylene oxide and propylene oxide having a weight ration of ethylene oxide to propylene oxide from 2.5:1 to 4:1 and a total alkylene oxide content of 60% to 85% by weight and condensates of 2 to 30 moles of ethylene oxide with sorbitan mono and tri-C_{10}-C_{20} alkanoic acid esters having an HLB of 8 to 15;

(b) 4% to 9% of a water-soluble anionic detergent which is selected from the group consisting of a C_8-C_{18} alkyl sulfates, C_8-C_{18} alkyl benzene sulfonate and C_{10}-20 paraffin sulfonate;

(c) 1% to 6% of a water-soluble betaine; and

(d) balance being water as an aqueous medium in which said nonionic surfactant, said anionic detergent and said betaine are solubilised in said water;

wherein the weight ratio of the water-soluble nonionic surfactant to the water soluble anionic detergent is from 3:1 to 1:1;

with the proviso that the composition does not contain any amine oxides, fatty acid alkanolamides, alkali metal carbonate, polymeric or clay

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thickeners, abrasives, clays, silicas or more than 3 wt % of a fatty acid or a metal salt of the fatty acid.

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COLGATE-PALMOLIVE COMPANY

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Invention Title:

"High foaming nonionic surfactant based liquid detergent"

The following statement is a full description of this invention including the best method of performing it known to us:-

Background Of The Invention

The present invention relates to novel light duty liquid detergent compositions with high foaming properties, containing a nonionic surfactant, an alkali metal or ammonium sulfate surfactant in a weight ratio of nonionic surfactant to sulfate surfactant of 3:1 to 1:1 and supplemented with lesser amounts of a Zwitterionic betaine surfactant, wherein the surfactants are dissolved in an aqueous medium.

Nonionic surfactants are in general chemically inert and stable toward pH change and are therefore well suited for mixing and formulation with other materials. The superior performance of nonionic surfactants on the removal of oily soil is well recognized. Nonionic surfactants are also known to be mild to human skin. However, as a class, nonionic surfactants are known to be low or moderate foamers. Consequently, for detergents which require copious and stable foam, the application of nonionic surfactants is limited.

The prior art is replete with light duty liquid detergent compositions containing nonionic surfactants in combination with anionic and/or betaine surfactants. As shown in U.S. Patent No. 3,658,985 wherein an anionic based shampoo contains a minor amount of a fatty acid alkanolamide. U.S. Patent No. 3,769,398 discloses a betaine-based shampoo containing minor amounts of nonionic surfactants. This patent states that the low-foaming properties of nonionic detergents renders its use in shampoo compositions non-preferred. U.S. Patent No. 4,329,335 also discloses a shampoo containing a betaine surfactant as the major ingredient and minor amounts of a nonionic surfactant and of a fatty acid mono- or di-ethanolamide. U.S. Patent No. 4,259,204 discloses a shampoo comprising 0.8-20% by weight of an anionic phosphoric acid ester and one additional surfactant which may be either anionic, amphoteric, or nonionic. U.S. Patent No. 4,329,334 discloses an anionic-amphoteric based shampoo containing a major amount of anionic surfactant and lesser amounts of a betaine and nonionic surfactants.

U.S. Patent No. 3,935,129 discloses a liquid cleaning composition based on the alkali metal silicate content and containing five basic ingredients, namely, urea, glycerin, triethanolamine, an anionic detergent and a nonionic detergent. The silicate content determines the amount of anionic and/or nonionic detergent in the liquid cleaning composition. However, the foaming property of these detergent compositions is not discussed therein.

U.S. Patent No. 4,129,515 discloses a heavy duty liquid detergent for laundering fabrics comprising a mixture of substantially equal amounts of anionic and nonionic surfactants, alkanolamines and magnesium salts, and, optionally, zwitterionic surfactants as suds modifiers.

U.S. Patent No. 4,224,195 discloses an aqueous detergent composition for laundering socks or stockings comprising a specific group of nonionic detergents, namely, an ethylene oxide of a secondary alcohol, a specific group of anionic detergents, namely, a sulfuric ester salt of an ethylene oxide adduct of a secondary alcohol, and an amphoteric surfactant which may be a betaine, wherein either the anionic or nonionic surfactant may be the major ingredient.

The prior art also discloses detergent compositions containing all nonionic surfactants as shown in U.S. Patent Nos. 4,154,706 and 4,329,336 wherein the shampoo compositions contain a plurality of particular nonionic surfactants in order to effect desirable foaming and detersive properties despite the fact that nonionic surfactants are usually deficient in such properties.

U.S. Patent No. 4,013,787 discloses a piperazine based polymer in conditioning and shampoo compositions which may contain all nonionic surfactant or all anionic surfactant.

U.S. Patent No. 4,450,091 discloses high viscosity shampoo compositions containing a blend of an amphoteric betaine surfactant, a polyoxybutylene polyoxyethylene nonionic detergent, an anionic surfactant, a fatty acid alkanolamide and a polyoxyalkylene glycol fatty ester. But, none of the exemplified compositions contains an active ingredient mixture wherein the nonionic detergent is present in

major proportion, probably due to the low foaming properties of the polyoxybutylene polyoxyethylene nonionic detergent.

U.S. Patent No. 4,595,526 describes a composition comprising a nonionic surfactant, a betaine surfactant, an anionic surfacant and a C_{12}-C_{14} fatty acid monethanolamide foam stabilizer.

However, none of the above-cited patents discloses a high foaming, liquid detergent composition containing a nonionic surfactant and a sulfate surfactant in a ratio of nonionic surfactant to sulfate surfactant of 3:1 to 1:1 and minor amounts of a supplementary foaming zwitterionic surfactant selected from betaine type surfactants as the three essential ingredients, wherein the nonionic ingredient preferably constitutes more than 50% of the total surfactant content and the composition does not contain any amine oxides, fatty acid alkanolamides, clays, silicas, alkali or alkaline earth metal carbonates, clay or polymeric thickeners, alkyl glycine surfactant, cyclic imidinium surfactant, or more than 3 wt. % of a fatty acid or salt thereof.

Summary Of The Invention

It has now been found that a high foaming liquid detergent can be formulated with a nonionic surfactant which has desirable cleaning properties, mildness to the human skin and avoids the dioxane toxicity problem associated with the sulfation process of manufacturing anionic ethoxylated alcohol ether sulfates.

Accordingly, one object of the invention is to provide novel, high foaming, nonionic based, light duty liquid detergent compositions containing a nonionic surfactant at a concentration of 6 to 12 wt. %.

Another object of this invention is to provide novel liquid detergent compositions containing a nonionic surfactant supplemented with lesser amounts of an alkyl sulfate anionic surfactant, and a zwitterionic betaine surfactant, wherein the composition does not contain any amine oxide, fatty acid alkanolamides, silica, clay, abrasive, alkali or alkaline earth metal carbonate, clay or polymeric thickener, alkyl glycine surfactant, cyclic imidinium surfactant, or more than 3 wt. % of a fatty acid or salt thereof.

Still another object of this invention is to provide a novel, nonionic based, liquid detergent with desirable high foaming and cleaning properties which is mild to the human skin.

Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the combinations particularly pointed out in the appended claims.

To achieve the foregoing and other objects and in accordance with the purpose of the present invention, as embodied and broadly described herein the novel, high foaming, light duty liquid detergent of this invention comprises three essential surfactants: a water soluble, ethoxylated, nonionic surfactant, a supplemental amount of a foaming anionic surfactant excluding the ethoxylated alkyl ether sulfate; a lesser amount of a zwitterionic surfactant selected from the class of betaines wherein the surfactants are dissolved in an aqueous vehicle

More specifically, the present invention relates to a high foaming liquid detergent containing preferably more than 50% by weight of the total surfactant content of a nonionic surfactant selected from the group consisting of water soluble primary aliphatic alcohol ethoxylates secondary aliphatic alcohol ethoxylates, alkyl phenol ethoxylates and alcohol ethylene oxide propylene oxide condensates; a supplementary amount of an anionic surfactant which is a water soluble salts of C_8-C_{18} alkyl sulfates; and a water soluble zwitterionic betaine surfactant.

Detailed Description Of The Invention

The high foaming light duty liquid detergent compositions of the instant invention comprise approximately by weight: 6 to 12 wt. % of a water soluble nonionic surfactant; 4 to 9 wt. % of a water soluble or dispersible anionic sulfate surfactant; 3 to 6 wt. percent of a water soluble betaine surfactant; and 70 to 90 wt. % of water, wherein the compositions do not contain any amine oxides, fatty acid alkanolamides

(for example - coco diethanol amides), alkali metal carbonate, polymeric or clay thickeners, abrasives, clays, silicas or more than 3 wt. % of a fatty acid or a metal salt of the fatty acid.

The nonionic surfactant is present in amounts of 6 to 12%, preferably 7 to 10% by weight of the composition and provides superior performance in the removal of oily soil and mildness to human skin.

The water soluble nonionic surfactants utilized in this invention are commercially well known and include the primary aliphatic alcohol ethoxylates, secondary aliphatic alcohol ethoxylates, alkylphenol ethoxylates and ethylene-oxide-propylene oxide condensates on primary alkanols, such a Plurafacs (BASF) and condensates of ethylene oxide with sorbitan fatty acid esters such as the Tweens (ICI). The nonionic synthetic organic detergents generally are the condensation products of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic ethylene oxide groups. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a water-soluble nonionic detergent. Further, the length of the polyethenoxy chain can be adjusted to achieve the desired balance between the hydrophobic and hydrophilic elements.

The nonionic detergent class includes the condensation products of a higher alcohol (e.g., an alkanol containing 8 to 18 carbon atoms in a straight or branched chain configuration) condensed with 5 to 30 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with 16 moles of ethylene oxide (EO), tridecanol condensed with 6 to moles of EO, myristyl alcohol condensed with 10 moles of EO per mole of myristyl alcohol, the condensation product of EO with a cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms in length and wherein the condensate contains either 6 moles of EO per mole of total alcohol or 9 moles of EO per mole of alcohol and tallow alcohol ethoxylates containing 6 EO to 11 EO per mole of alcohol.

A preferred group of the foregoing nonionic surfactants are the Neodol ethoxylates (Shell Co.), which are higher aliphatic, primary alcohol containing 9-15 carbon atoms, such as C_9-C_{11} alkanol condensed with 7 to 10 moles of ethylene oxide (Neodol 91-8), C_{12-13} alkanol condensed with 6.5 moles ethylene oxide (Neodol 23-6.5), C_{12-15} alkanol condensed with 12 moles ethylene oxide (Neodol 25-12), C_{14-15} alkanol condensed with 13 moles ethylene oxide (Neodol 45-13), and the like. Such ethoxamers have an HLB (hydrophobic lipophilic balance) value of 8 to 15 and give good O/W emulsification, whereas ethoxamers with HLB values below 8 contain less than 5 ethyleneoxide groups and tend to be poor emulsifiers and poor detergents.

Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Examples of commercially available nonionic detergents of the foregoing type are C_{11}-C_{15} secondary alkanol condensed with either 9 EO (Tergitol 15-S-9) or 12 EO (Tergitol 15-S-12) marketed by Union Carbide.

Other suitable nonionic detergents include the polyethylene oxide condensates of one mole of alkyl phenol containing from 8 to 18 carbon atoms in a straight- or branched chain alkyl group with 5 to 30 moles of ethylene oxide. Specific examples of alkyl phenol ethoxylates include nonyl condensed with 9.5 moles of EO per mole of nonyl phenol, dinonyl phenol condensed with 12 moles of EO per mole of phenol, dinonyl phenol condensed with 15 moles of EO per mole of phenol and di-isoctylphenol condensed with 15 moles of EO per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630 (nonyl phenol ethoxylate) marketed by GAF Corporation.

~~Condensates of 2 to 30 moles of ethylene oxide with sorbitan mono- and tri-~~ C_{10}-C_{20} alkanoic acid esters having a HLB of 8 to 15 ~~also~~ may be employed as the nonionic detergent ingredient in the described shampoo. These surfactants are well ~~known and are available from Imperial Chemical Industries under the Tween trade~~

Suitable nonionic detergents also include condensates of C_8 - C_{20} alkanol with a heteric mixture of ethylene oxide and propylene oxide having a weight ratio of ethylene oxide to propylene oxide from 2.5:1 to 4:1 and a total alkylene oxide content of 60% to 85% by weight.

Condensates of 2 to 30 moles of ethylene oxide with sorbitan mono- and tri- C_{10} - C_{20} alkanoic acid esters having HLB of 8 to 15 also may be employed as the nonionic detergent ingredient in the described shampoo. These surfactants are well known and are available from Imperial Chemical Industries under the Tween trade

name. Suitable surfactants include polyoxyethylene (4) sorbitan monolaurate, polyoxyethylene (4) sorbitan monostearate, polyoxyethylene (20) sorbitan trioleate and polyoxyethylene (20) sorbitan tristearate.

The anionic surfactant, which is an essential ingredient of present liquid detergent composition, constitutes 4% to 9%, preferably 5 to 8%, by weight thereof and provides good foaming properties.

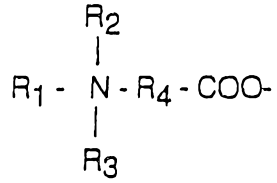
The anionic surfactant which may be used in the nonionic based liquid detergent of the invention are water soluble such as triethanolamine salt and include the sodium, potassium, ammonium and ethanolammonium salts of C_8-C_{18} alkyl sulfates such as lauryl sulfate, myristyl sulfate and the like; linear C_8-C_{16} alkyl benzene sulfonates; C_{10}-C_{20} paraffin sulfonates; alpha olefin sulfonates containing 10-24 carbon atoms; C_8-C_{18} alkyl sulfoacetates; C_8-C_{18} alkyl sulfosuccinate esters; C_8-C_{18} acyl isethionates; and C_8-C_{18} acyl taurates. Preferred anionic surfactants are the water soluble C12-C16 alkyl sulfates, the C_{10}-C_{15} alkylbenzene sulfonates, the C_{12}-C_{17} paraffin sulfonates and the alpha C_{12}-C_{18} olefin sulfonates.

The paraffin sulfonates may be monsulfonates or di-sulfonates and usually are mixtures thereof, obtained by sulfonating paraffins of 10 to 20 carbon atoms. Preferred paraffin sulfonates are those of C_{12-18} carbon atoms chains, and more preferably they are of C_{14-17} chains. Paraffin sulfonates that have the sulfonate group(s) distributed along the paraffin chain are described in U.S. Patents, 2,503,280; 2,507,088; 3,260,744; and 3,372,188; and also in German Patent 735,096. Such compounds may be made to specifications and desirably the content of paraffin sulfonates outside the C_{14-17} range will be minor and will be minimized, as will be any contents of di- or poly-sulfonates.

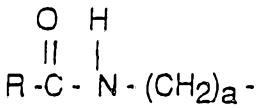
Examples of suitable other sulfonated anionic detergents are the well known higher alkyl mononuclear aromatic sulfonates, such as the higher alkylbenzene sulfonates containing 9 to 18 or preferably 9 or 10 to 15 or 16 carbon atoms in the higher alkyl group in a straight or branched chain, or C_{8-15} alkyl toulene sulfonates. A preferred alkylbenzene sulfonate is a linear alkylbenzene sulfonate having a higher

content of 3-phenyl (or higher) isomers and a correspondingly lower content (well below 50%) of 2-phenyl (or lower) isomers, such as those sulfonates wherein the benzene ring is attached mostly at the 3 or higher (for example 4, 5, 6 or 7) position of the alkyl group and the content of the isomers in which the benzene ring is attached in the 2 or 1 position is correspondingly low. Preferred materials are set forth in U.S. Patent 3,320,174, especially those in which the alkyls are of 10 to 13 carbon atoms.

The water-soluble zwitterionic surfactant, which is also an essential ingredient of present liquid detergent composition, constitutes 1 to 6, preferably 4 to 6, by weight and provides good foaming properties and mildness to the present nonionic based liquid detergent. The zwitterionic surfactant is a water soluble betaine having the general formula:



wherein R_1 is an alkyl group having 10 to 20 carbon atoms, preferably 12 to 16 carbon atoms, or the amido radical:



wherein R is an alkyl group having 9 to 19 carbon atoms and a is the integer 1 to 4; R_2 and R_3 are each alkyl groups having 1 to 3 carbons and preferably 1 carbon; R_4 is an alkylene or hydroxyalkylene group having from 1 to 4 carbon atoms and, optionally, one hydroxyl group. Typical alkyldimethyl betaines include decyl dimethyl betaine or 2-(N-decyl-N, N-dimethyl-ammonia) acetate, coco dimethyl betaine or 2-(N-coco N, N-dimethylammonio) acetate, myristyl dimethyl betaine, palmityl dimethyl betaine, lauryl dimethyl betaine, cetyl dimethyl betaine, stearyl dimethyl betaine, etc. The amidobetaines similarly include cocoamidoethylbetaine, cocoamidopropyl betaine and the like. A preferred betaine is coco (C_8-C_{18}) amidopropyl dimethyl betaine.

All of the aforesaid ingredients in this light duty liquid detergent are water soluble or water dispersible and remain so during storage.

This particular combination of anionic sulfate surfactant, and betaine surfactant, provides a detergent system which coacts with the nonionic surfactant to product a liquid detergent composition with desirable foaming, foam stability and detersive properties. Surprisingly, the resultant homogeneous liquid detergent exhibits the same or better foam performance, both as to initial foam volume and stability of foam in the presence of soils, and cleaning efficacy as an anionic based light duty liquid detergent (LDLD) as shown in the following Examples.

The essential ingredients discussed above are solubilized in an aqueous medium comprising water and optionally, solubilizing ingredients such as alcohols and dihydroxy alcohols such as C_2-C_3 mono and di-hydroxy alkanols, ethanol isopropanol and propylene glycol. Suitable water soluble hydrotropic salts include sodium, potassium, ammonium and mono-, di- and triethanolammonium salts of C_1-C_3 substituted benzene sulfonate salts. While the aqueous medium is primarily water, preferably said solubilizing agents are included in order to control the viscosity of the liquid composition and to control low temperature cloud clear properties. Usually, it is desirable to maintain clarity to a temperature in the range of 5°C to 10°C. Therefore, the proportion of solubilizer generally will be from 1% to 15%, preferably 2% to 12%, most preferably 3% to 8%, by weight of the detergent composition with the proportion of ethanol, when present, being 5% of weight or less in order to provide a composition having a flash point above 46°C. Preferably the solubilizing ingredient will be a mixture of ethanol and either sodium xylene sulfonate or sodium cumene sulfonate or a mixture of said sulfonates or ethanol and urea. Inorganic salts such as alkali metal or alkali earth metal salts, for example sodium sulfate, magnesium sulfate, sodium chloride and sodium citrate can be added at concentrations of 0.5 to 4.0 wt.% to modify the cloud point of the nonionic surfactant and thereby control the haze of the resultant solution. Various other ingredients such as urea at a concentration of 0.5 to 4.0 wt.% or urea at the same concentration in combination with ethanol at a concentration of 0.5 to 4.0 wt. % can be used as solubilizing agents. Other ingredients which have been added to the compositions at

concentrations of 0.1 to 4.0 wt. percent are perfumes, sodium bisulfite, ETDA, isoethanoeic and proteins such as lexine protein. Another extremely effective solubilizing or cosolubilizing agent used at a concentration of 0.1 to 5 wt. percent, more preferably 0.5 to 4.0 weight percent is isethionic acid or an alkali metal salt of isethionic acid having the formula:

$$CH_2OHCH_2SO_3^-X^+$$

wherein X is hydrogen or an alkali metal cation, preferably sodium.

The foregoing solubilizing ingredients also facilitate the manufacture of the inventive compositions because they tend to inhibit gel formation.

In addition to the previously mentioned essential and optional constituents of the light duty liquid detergent, one may also employ normal and conventional adjuvants, provided they do not adversely affect the properties of the detergent. Thus, there may be used various coloring agents, color stabilizers and perfumes; ultraviolet light absorbers such as the Uvinuls, which are products of GAF Corporation; sequestering agents such as ethylene diamine tetraacetates; magnesium sulfate heptahydrate; pearlescing agents and opacifiers; pH modifiers; etc. The proportion of such adjuvant materials, in total will normally be 0.1 to 15% of weight of the detergent composition, and the percentages of most of such individual components will be a maximum of 5% by weight and preferably less than 2% by weight. Sodium formate can be included in the formula as a perservative at a concentration of 0.1 to 4.0%. Sodium bisulfite can be used as a color stabilizer at a concentration of 0.01 to 0.2 wt.% Typical preservatives are dibromodicyano butane, citric acid, benzylic alcohol and poly (Hexamethylene) biguanidium hydrochloride and mixtures thereof.

The instant compositions can contain 0.1 to 4 wt. %, more preferably 0.2 to 3.0 wt. % of an alkyl polysaccharide surfactant. The alkyl polysaccharides surfactants, which are used in conjunction with the aforementioned surfactant have a hydrophobic group containing from 8 to 20 carbon atoms, preferably from 10 to 16 carbon atoms, most preferably from 12 to 14 carbon atoms, and polysaccharide hydrophilic group

containing from 1.5 to 10, preferably from 1.5 to 4, most preferably from 1.6 to 2.7 saccharide units (e.g., galactoside, glucoside, fructoside, glucosyl, fructosyl; and/or galactosyl units). Mixtures of saccharide moieties may be used in the alkyl polysaccharide surfactants. The number x indicates the number of saccharide units in a particular alkyl polysaccharide surfactant. For a particular alkyl polysaccharide molecule x can only assume integral values. In any physical sample of alkyl polysaccharide surfactants there will be in general molecules having different x values. The physical sample can be characterized by the average value of x and this average value can assume non-integral values. In this specification the values of x are to be understood to be average values. The hydrophobic group (R) can be attached at the 2-, 3-, or 4- positions rather than at the 1-position, (thus giving e.g. a glucosyl or galactosyl as opposed to a glucoside or galactoside). However, attachment through the 1- position, i.e., glucosides, galactoside, fructosides, etc., is preferred. In the preferred product the additional saccharide units are predominately attached to the previous saccharide unit's 2-position. Attachment through the 3-, 4-, and 6- positions can also occur. Optionally and less desirably there can be a polyalkoxide chain joining the hydrophobic moiety (R) and the polysaccharide chain. The preferred alkoxide moiety is ethoxide.

Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from 8 to 20, preferably from 10 to 18 carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to 3 hydroxy groups and/or the polyalkoxide chain can contain up to 30, preferably less than 10, alkoxide moieties.

Suitable alkyl polysaccharides are decyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, and octadecyl, di-, tri-, tetra-, penta-, and hexaglucosides, galactosides, lactosides, fructosides, fructosyls, lactosyls, glucosyls and/or galactosyls and mixtures thereof.

The alkyl monosaccharides are relatively less soluble in water than the higher alkyl polysaccharides. When used in admixture with alkyl polysaccharides, the alkyl

monosaccharides are solubilized to some extent. The use of alkyl monosaccharides in admixture with alkyl polysaccharides is a preferred mode of carrying out the invention. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentaglucosides and tallow alkyl tetra-, penta-, and hexaglucosides.

The preferred alkyl polysaccharides are alkyl polyglucosides having the formula

$$R_2O(C_nH_{2n}O)r(Z)_x$$

wherein Z is derived from glucose, R is a hydrophobic group selected from the group consisting of alkyl, alkylphenyl, hydroxyalkylphenyl, and mixtures thereof in which said alkyl groups contain from 10 to 18, preferably from 12 to 14 carbon atoms; n is 2 or 3 preferably 2, r is from 0 to 10, preferable 0; and x is from 1.5 to 8, preferably from 1.5 to 4, most preferably from 1.6 to 2.7. To prepare these compounds a long chain alcohol (R_2OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkyl polyglucosides can be prepared by a two step procedure in which a short chain alcohol (R_1OH) can be reacted with glucose, in the presence of an acid catalyst to form the desired glucoside. Alternatively the alkyl polyglucosides can be prepared by a two step procedure in which a short chain alcohol (C_{1-6}) is reacted with glucose or a polyglucoside (x=2 to 4) to yield a short chain alkyl glucoside (x=1 to 4) which can in turn be reacted with a longer chain alcohol (R_2OH) to displace the short chain alcohol and obtain the desired alkyl polyglucoside. If this two step procedure is used, the short chain alkylglucosde content of the final alkyl polyglucoside material should be less than 50%, preferably less than 10%, more preferably less than 5%, most preferably 0% of the alkyl polyglucoside.

The amount of unreacted alcohol (the free fatty alcohol content) in the desired alkyl polysaccharide surfactant is preferably less than 2%, more preferably less than 0.5% by weight of the total of the alkyl polysaccharide. For some uses it is desirable to have the alkyl monosaccharide content less than 10%.

The used herein, "alkyl polysaccharide surfactant" is intended to represent both the preferred glucose and galactose derived surfactants and the less preferred alkyl polysaccharide surfactants. Throughout this specification, "alkyl polyglucoside" is used to include alkyl polyglycosides because the stereochemistry of the saccharide moiety is changed during the preparation reaction.

An especially preferred APG glycoside surfactant is APG 625 glycoside manufactured by the Henkel Corporation of Ambler, PA. APG25 is a nonionic alkyl polyglycoside characterized by the formula:

$$C_nH_{2n+1}O(C_6H_{10}O_5)_xH$$

wherein n=10 (2%); n=122 (65%); n=14 (21-28%); n=16 (4-8%) and n=18 (0.5%) and x (degree of polymerization) = 1.6. APG 625 has: a pH of 6 to 10 (10% of APG 625 in distilled water); a specific gravity at 25°C of 1.1 g/ml; a density at 25°C of 9.1 lbs/gallon; a calculated HLB of 12.1 and a Brookfield viscosity at 35°C, 21 spindle, 5-10 RPM of 3,000 to 7,000 cps.

The instant compositions can contain a silk derivatives as part of the composition and generally constitute 0.01 to 3.0 % by weight, preferably 0.1 to 3.0% by weight, most preferably 0.2 to 2.5% by weight of the liquid detergent composition.

Included among the silk derivatives are silk fibers and hydrolyzate of silk fibers. The silk fibers may be used in the form of powder in preparing the liquid detergent or as a powder of a product obtained by washing and treating the silk fibers with an acid. Preferably, silk fibers are used as a product obtained by hydrolysis with an acid, alkali or enzyme, as disclosed in Yoshiaki Abe et al., U.S. Patent No. 4,839,168; Taichi Watanube et al., U.S. Patent No. 5,009,813; and Marvin E. Goldberg, U.S. Patent No. 5,069,898, each incorporated herein by reference.

Another silk derivative which may be employed in the composition of the present invention is protein obtained from degumming raw silk, as disclosed, for example, in Udo Hoppe et al., U.S. Patent No. 4,839,165, incorporated herein by reference. The principal protein obtained from the raw silk is sericin which has an empirical formula of $C_{15}H_{25}O_3N_5$ and a molecular weight of 323.5.

Another example of a silk derivative for use in the liquid detergent composition of the present invention is a fine powder of silk fibroin in nonfibrous or particulate form, as disclosed in Kiyoshi Otoi et al., U.S. Patent No. 4,233,212, incorporated herein by reference.

The fine powder is produced by dissolving a degummed silk material in at least one solvent selected from, for example, an aqueous cuprietylene diamine solution, an aqueous ammoniacal solution of cupric hydroxide, an aqueous alkaline solution of cupric hydroxide and glycerol, an aqueous lithium bromide solution, an aqueous solution of the chloride, nitrate or thiocyanate of calcium, magnesium or zinc and an aqueous sodium thiocyanate solution. The resulting fibroin solution is then dialyzed. The dialyzed aqueous silk fibroin solution, having a silk fibroin concentration of from 3 to 20% by weight, is subjected to at least one treatment for coagulating and precipitating the silk fibroin, such as, for example, by the addition of a coagulating salt, by aeration, by coagulation at the isoelectric point, by exposure to ultrasonic waves, by agitation at high shear rate and the like.

The resulting product is a silk fibroin gel which may be incorporated directly into the liquid detergent composition or the same may be dehydrated and dried into a powder and then dissolved in the liquid detergent composition.

The silk material which may be used to form the silk fibroin includes cocoons, raw silk, waste cocoons, raw silk waste, silk fabric waste and the like. The silk material is degummed or freed from sericin by a conventional procedure such as, for example, by washing in warm water containing a surfact-active agent or an enzyme, and then dried. The degummed material is dissolved in the solvent and preheated to a temperature of from 60 to 95°C, preferably 70 to 85°C. Further details of the process of obtaining the silk fibroin are discussed in U.S. Patent No. 4,233,212.

A preferred silk derivative is a mixture of two or more individual amino acids which naturally occur in silk. The principal silk amino acids are glycine, alanine, serine and tyrosine.

A silk amino acid mixture resulting from the hydrolysis of silk of low molecular weight and having a specific gravity of at least 1 is produced by Croda, Inc. and sold under the trade name "CROSILK LIQUID" which typically has a solids content in the range of 27 to 31% by weight. Further details of the silk amino acid mixture can be found in Wendy W. Kim et al., U.S. Patent No. 4,906,460, incorporated herein by reference. A typical amino acid composition of "CROSILK LIQUID" is shown in the following Table .

AMINO ACID	PERCENT BY WEIGHT
Alanine	28.4
Glycine	34.7
Valine	2.0
Leucine	1.2
Proline	1.2
Tyrosine	0.6
Phenylalanine	0.9
Serine	15.4
Threonine	1.9
Arginine	1.5
Aspartic Acid	4.7
Glutamic Acid	4.1
Isoleucine	0.8
Lysine	1.4
Histidine	0.8
Cystine	0.1
Methionine	0.2
TOTAL	99.9

The instant compositions can contain a viscosity modifying solvent at a concentration of 0.1 to 5.0 weight percent, more preferably 0.5 to 4.0 weight percent. The viscosity modifying agent is an alcohol of the formula

$$R_2\text{-}CH(OR_1)\text{-}R_3$$

wherein $R_1 = CH_3, CH_2CH_3$

$R_2 = CH_3, CH_2CH_3$

$R_3 = CH_2OH, CH_2CH_2OH$;

which is preferably 3-methyl-3-methoxy-butanol.

The 3-methyl-3-methoxy butanol is commercially available from Sattva Chemical Company of Stamford, Connecticut and Kuraray Co., Ltd., Osaka, Japan.

The instant composition can contain 0.1 to 4.0% of a protein selected from the group consisting of hydrolyzed animal collagen protein obtained by an enzymatic hydrolysis, lexeine protein, vegetal protein and hydrolyzed wheat protein and mixtures thereof.

The formula can also contain as a viscosity modifier an alkali metal salt such as an alkali metal sulfate or an alkali metal citrate at a concentration of 0.5 to 4.0 wt.%, more preferably 1.0 to 3.0 wt%. Preferred alkali metal salts are sodium sulfate or sodium citrate.

The present nonionic based light duty liquid detergents such as dishwashing liquids are readily made by simple mixing methods from readily available components which, on storage, do not adversely affect the entire composition. However, it is preferred that the nonionic surfactant be mixed with the solubilizing ingredients, e.g., ethanol and, if present, prior to the addition of the water to prevent possible gelation. The nonionic based surfactant system is prepared by sequentially adding with agitation the anionic surfactant and the betaine to the non-ionic surfactant which has been previously mixed with a solubilizing agent such as ethyl alcohol and/or sodium xylene sulfonate to assist in solubilizing said surfactants, and then adding with agitation the formula amount of water to form an aqueous solution of the nonionic based surfactant system. The use of mild heating (up to 100°C.) assists in the solubilization of the surfactants. The viscosities are adjustable by changing the total percentage of active ingredients. No polymeric or clay thickening agent is added. In all such cases the product made will usually be pourable from a relatively narrow mouth bottle (1.5 cm. diameter) or opening, and the viscosity of the detergent formulation will preferably not be so low as to be like water. The viscosity of the detergent desirably will be at least 100 centipoises (cps) at room temperature, but may be up to 1,000 centipoises as measured with a Brookfield Viscometer using a number 2 spindle rotating at 30 rps.

Its viscosity may approximate those of commercially acceptable detergents now on the market. The detergent viscosity and the detergent itself remain stable on storage for lengthy periods of time, without color changes or settling out of any insoluble materials. The pH of this formation is substantially neutral to skin, e.g., 4.5 to 8 and preferably 5.5 to 5.0. The compositions of the instant invention are optical clear that is they exhibit a light transmission of at least 95%, more preferably at least 98%.

These products have unexpectedly desirable properties. For example, the foam quality and detersive property is equal to or better than standard light duty liquid detergents while using a nonionic surfactant as the primary surfactant and minimal amounts of anionic surfactant, thereby achieving a less irritating liquid detergent than the standard light duty liquid detergent.

The following examples are merely illustrative of the invention and are not to be construed as limiting thereof.

The following formulas were prepared at room temperature by simple liquid mixing procedures as previously described:

	A	B	C	D	E	F	G	H
C11 Alcohol 9EO	11.17	11.18	11.18	11.0	11.0	7.5	7.5	7.5
Nonionic Surfactant C11 Alcohol 7EO Nonionic Surfactant								
Cocoamidopropyl Betaine	4.12	4.12	4.12	4	3	5	5	5
Sodium Lauryl Sulfate	4.71	4.71	4.71	5	6	7	7	7
Ammonium Lauryl Sulfate								
EDTA		0.099	0.099	0.099	0.099	0.099	0.099	0.099
HEDTA								
Sodium Bisulfite	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Perfume	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Crothix			0.5					
Sodium Formate				2	2	2	2	2
Sodium Sulfate							0.5	1.0
Sodium Citrate								
Water	Bal	Bal	Bal	Bal	Bal	Bal	Bal	Bal
Brookfield viscosity at pH5 at #2 spindle, 20 rpms (cps)	79	220	615	299	313	1200	935	721
Shell Foam Test								

	I	J	K	L	M	N	O	P
C11 Alcohol 9EO	7.5	9.5	9.5	8.5	8.5	7.5	7.5	7.5
Nonionic Surfactant C11 Alcohol 7EO Nonionic Surfactant								
Cocoamidopropyl Betaine	5	5	5	5	5	5	5	5
Sodium Lauryl Sulfate	7	5	5	6	6	7	7	7
Ammonium Lauryl Sulfate								
EDTA	0.099	0.099	0.099	0.099	0.099	0.099	0.099	0.099
HEDTA								
Sodium Bisulfite	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Perfume	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Crothix			0.5					
Sodium Formate	2	2	2	2	2	2	2	2
Sodium Sulfate	1.5	1	2	1	2	0	1	2
Sodium Citrate								
Water	Bal	Bal	Bal	Bal	Bal	Bal	Bal	Bal
Brookfield Viscosity at pH5 at #2 Spindle, 20 rms (cps)	571	541	494	658	531	1200	760	410
Shell Foam Test								

	Q	R	S	T	U	V	W	X
C11 Alcohol 9EO	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
Nonionic Surfactant C11 Alcohol 7EO Nonionic Surfactant								
Cocoamidopropyl Betaine	5	5	5	5	5	5	5	5
Sodium Lauryl Sulfate	7.0	7.0	7.0	7.0	6	7	7	6
Ammonium Lauryl Sulfate								7.0
EDTA	0.099	0.099	0.099	0.099	0.099	0.099	0.099	0.099
HEDTA								
Sodium Bisulfite	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Perfume	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Crothix			0.5					
Sodium Formate	2	2	2	2	2	2	2	2
Sodium Sulfate	3	0	1	2				3
Sodium Citrate					1	2	3	
Water	Bal	Bal	Bal	Bal	Bal	Bal	Bal	Bal
Brookfield Viscosity at pH5 at #2 Spindle, 20 rms (cps)	370	600	340	220	340	260	220	505
Shell Foam Test								

	Y	Z	AA	Commercial Palmolive Skin Sensitive	Commercial Palmolive LDL
C11 Alcohol 9EO Nonionic Surfactant	7.5	8	7.5		
C11 Alcohol 7EO Nonionic Surfactant					
Cocoamidopropyl Betaine	5	5	5		
Sodium Lauryl Sulfate	7.0				
Ammonium Lauryl Sulfate		7.0	7.25		
EDTA	0.099	0.99			
HEDTA			0.083		
Sodium Bisulfite	0.05	0.05	0.05		
Perfume	0.2	0.2	0.2		
Crothix					
Sodium Formate	2	2	2		
Sodium Sulfate	4	1	2		
Sodium Citrate					
Water	Bal	Bal	Bal		
Brookfield Viscosity at pH5 at #2 Spindle, 20 rms (cps)	335				
Shell Foam Test		88		114	100

	BB	CC	DD	EE	FF	GG	HH	II
Neodol 1-9	8.5	8.5						
Neodol 1-7			8.5	8.5	8.5			
Neodol 91-8						8.5	8.5	8.5
Sodium Lauryl Sulfate	6	6	6	6	6	6	6	6
Betaine (betadet cocoamidopropyl-betaine	5	5	5	5	5	5	5	5
Vencol	0.3		0.3	0.3		0.3	0.3	
C_8-C_{10} alcohol sulfate				1.0				
Formalin		0.1			0.1			0.1
NaCl		1.0						
Na_2SO_4							2.0	
Propylene glycol					2.0			2.0
Water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.
Perfume	0.2							
Sodium bisulfate	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Brookfield Viscosity, RT at #2 Spindle, 30 rms (cps)	370	310	1200	450	490	200	470	450

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A high foaming light duty, liquid detergent comprising approximately, by weight:

(a) 6% to 12% of a water soluble nonionic surfactant selected from the group consisting of primary and secondary C_8-C_{18} alkanol condensates with 5 to 30 moles of ethylene oxide, condensates of C_8-C_{18} alkylphenol with 5 to 30 moles of ethylene oxide, condensates of C_8-C_{20} alkanol with a heteric mixture of ethylene oxide and propylene oxide having a weight ration of ethylene oxide to propylene oxide from 2.5:1 to 4:1 and a total alkylene oxide content of 60% to 85% by weight and condensates of 2 to 30 moles of ethylene oxide with sorbitan mono and tri-C_{10}-C_{20} alkanoic acid esters having an HLB of 8 to 15;

(b) 4% to 9% of a water-soluble anionic detergent which is selected from the group consisting of a C_8-C_{18} alkyl sulfates, C_8-C_{18} alkyl benzene sulfonate and C_{10}-20 paraffin sulfonate;

(c) 1% to 6% of a water-soluble betaine; and

(d) balance being water as an aqueous medium in which said nonionic surfactant, said anionic detergent and said betaine are solubilised in said water;

wherein the weight ratio of the water-soluble nonionic surfactant to the water soluble anionic detergent is from 3:1 to 1:1;

with the proviso that the composition does not contain any amine oxides, fatty acid alkanolamides, alkali metal carbonate, polymeric or clay thickeners, abrasives, clays, silicas or more than 3 wt % of a fatty acid or a metal salt of the fatty acid.

2. A liquid detergent composition according to claim 2 wherein said nonionic surfactant is said condensate of a primary C_8-C_{18} alkanol with 5 to 30 moles of ethylene oxide.

3. A liquid detergent composition according to claim 1 further including a preservative.

4. A liquid detergent composition according to claim 1 further including a colour stabiliser.

5. A liquid detergent composition according to claim 1 further including 0.5 to 4.0 wt % of sodium formate.

6. A liquid detergent composition, according to claim 1, further including 0.5 to 4.0 wt % of an alkali metal salt.

7. A liquid detergent composition according to Claim 1 which includes, in addition, 1% to 15% by weight of at least one additive ingredient selected from the group consisting of alkali metal inorganic salts, alkaline earth metal inorganic salts, urea, proteins, C2-C3 mono- and di-hydroxy alkanols, water soluble salts of C1-C3 substituted benzene sulfonate hydrotropes and mixtures thereof.

8. A liquid detergent composition according to Claim 1 further including ethanol in the amount of 5% by weight or less.

DATED THIS 23 DAY OF JUNE 1994

COLGATE-PALMOLIVE COMPANY

Patent Attorneys for the

Applicant:-

F.B.RICE & CO.

ABSTRACT

A high foaming, nonionic surfactant based, light duty, liquid detergent with desirable cleansing properties and mildness to the human skin comprising three essential surfactants: a water soluble nonionic surfactant; supplemental amount of a water soluble, foaming, sulfate anionic surfactant, a lesser amount of a water soluble, foaming zwitterionic betaine surfactant and the balance being water.