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(54) Title: MANUAL DISHWASHING COMPOSITION COMPRISING LIPASE ENZYMES

(57) Abstract

There is provided a composition containing a surfactant system and lipolytic enzyme suitable for use in a manual dishwashing process. Preferably said composition is high sudsing and in the form of a liquid or a gel. Preferably said composition contains no builder salts and no bleaching components.

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MANUAL DISHWASHING COMPOSITION COMPRISING LIPASE ENZYMES

The formulator of a manual dishwashing detergent composition faces the challenge of deriving a formulation which meets a number of distinct consumer relevant performance demands.

Firstly, such a composition should be effective at removing soils from dirty "dishes" when used in a manual dishwashing process. The term "dishes" is used herein in a generic sense, and encompases essentially any items which may be found in a dishwashing load, including chinaware, glassware, plasticware, hollowware and cutlery, including silverware.

The soils encountered in dishwashing will largely but not exclusively be food based. Particularly difficult soils to remove would include greasy soils, burnt on food soils, dried on food soils, highly coloured soils derived from eg : highly coloured vegetables such as beetroot and tomato, as well as non-food soils such as lipstick on the rims of glasses or nicotine stains on saucers which have been used as ashtrays.

Once the soils has been removed from the dishes the dishwashing detergent should act such as to suspend these soils in the wash solution and thus prevent their redeposition onto the dishes, or onto the surface of the sink.

Whilst good soil removal and antiredeposition are performance demands shared with compositions formulated for machine dishwashing purposes, the manual dishwashing formulator is faced with meeting other performance demands.

For example, the manual dishwashing composition should be high sudsing and the sudsing should persist throughout the washing process. The sudsing is used as an indicator by the person doing the washing up that the wash solution still contains active detergent ingredients. When the sudsing subsides the sink will generally be emptied and a fresh wash solution prepared. The persistence of suds throughout the washing process is measured in the industry by various suds mileage indices.

The manual dishwashing composition should also be mild to the skin, and particularly to the hands. That is, it should not cause skin dryness, chapping or rougness when in contact with the skin. Such skin dryness, chapping or roughness largely results from the removal of natural oils from the skin. Thus, the manual dishwashing composition should desirably be effective at removing grease from plates but not natural oils from the skin.

Reflecting the different nature of the performance demands for a manual dishwashing composition, such compositions are formulated in a distinct way from, for example, machine dishwashing, laundry, and hard-surface cleaner compositions.

Manual dishwashing compositions are usually unbuilt, and may contain added levels of Ca and Mg to aid cleaning performance. Laundry and automatic dishwashing compositions typically contain high levels of builder.

Manual dishwashing compositions typically contain no bleaching components, which are by contrast common components of laundry, machine dishwashing and hard-surface cleaner compositions.

Manual dishwashing detergent typically contain high levels of high-sudsing surfactant and often suds booster. Machine laundry and dishwashing compositions are desirably low foaming and typically contain lower levels of surfactant.

Manual dishwashing compositions are formulated to perform well at near neutral pH. Machine dishwashing and laundry compositions are typically alkaline with a pH of usually 9-11, hard-surface cleaner compositions are often acidic with a pH of less than 6.

The key active component of a manual dishwashing composition is most usually a surfactant system, which will typically comprise from 5 to 80% by weight of the composition. The surfactant system has a primary soil removal purpose, and also acts so as to suspend the soils in solution and prevent redeposition of these soils. In particular, the surfactant system should be effective at removing and suspending greasy soils.

There is a common perception that washing-up liquid is essentially just a surfactant solution with certain other minor components. This perception seems exemplified by a recent Economist Intelligence Unit market report on dishwashing products to be found in EIU, Retail Business No 409, March 1992 where level of surfactant in a product is employed essentially as an indicator of "quality" of the product.

Enzymes are common components of laundry and machine dishwashing compositions. Amylolytic and proteolytic enzymes are common components of such compositions. Enzymes are not commonly recognized to be of use in manual dishwashing compositions.

Lipolytic enzymes, or lipases, act to hydrolyse fats or oils, which comprise esters of glycerol and fatty acids, into these glycerol and fatty acid components. There is teaching in the art of the use of lipolytic enzymes in laundry and machine dishwashing compositions, most particularly as a coenzyme in combination with, for example amylolytic and proteolytic enzymes.

The Applicants have now recognized the value of the inclusion of lipolytic enzymes in compositions specifically formulated for use in manual dishwashing. The utility of lipolytic enzymes in such compositons has not previously been recognized in the art. Indeed, the extensive art relating to the use of such enzymes in machine dishwashing compositions, but neglecting to provide clear teaching of their utility in manual dishwashing, would seem to imply a prejudice against the use of these enzymes in manual dishwashing compositions.

At the heart of this implied prejudice may lie the well-established reliance in the manual dishwashing art on surfactants to aid grease removal. With high concentrations of surfactant to remove the grease, it might be believed that the inclusion of a grease hydrolysing enzyme would not be useful. A further reason for the implied prejudice might rest in the belief that the fatty acid products obtained when oils or fats are broken down may act as suds suppressors, thereby impending the desired high sudsing performance.

The Applicants have also found that lipolytic enzyme is a particularly useful component of a manual dishwashing composition containing certain surfactant systems which act such as to stabilize the enzyme when formulated in liquid compositions.

Summary of the invention

According to one aspect of the present invention there is provided a composition containing a surfactant system and lipolytic enzyme suitable for use in a manual dishwashing process.

Preferably said composition is high sudsing.

Preferably said composition is in the form of a liquid or a gel.

Preferably said composition contains no builder salts.

Preferably said composition contains no bleaching components.

Preferably said compositon contains from 5% to 80% by weight of said surfactant system, wherein the surfactant system comprises surfactant selected from nonionic, anionic, cationic, zwitterionic, ampholytic and amphoteric surfactants.

Preferably a 1% by weight solution of said composition has a pH of from 6 to 9.

Said composition can be formulated to contain no other enzyme components.

Detailed description of the invention

The first essential component of the compositions in accordance with the invention is lipolytic enzyme (lipase) which is preferably present at levels of active lipolytic enzyme of from 0.001% to 2% by weight, more preferably 0.01% to 1% by weight, most preferably from 0.05% to 0.5% by weight of the compositions.

The lipase is preferably bacterial in origin being obtained, for example, from a lipase producing strain of Humicola sp.or Thermomyces sp. or Pseudomonas pseudoalcaligenes or Pseudomas fluorescens.

Lipase from chemically or genetically modified mutants of these strains are also included herein. Mixtures of lipase from various strains are included herein, though not preferred.

A preferred lipase is derived from Pseudomonas pseudoalcaligenes, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from Humicola lanuginosa and expressing the gene in Aspergillus oryza, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Huge-Jensen et al, issued March 7, 1989.

Lipases herein are preferably compatible with surfactants. They are preferably stable in the present compositions and improve cleaning when they are included in the present compositions.

Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase produced by Pseudomonas flluorescens. This lipases described in Japanese Patent Application 53-20487, laid open February 24, 1987. It is available under the trade name Lipase P Amano. A method for testing immunological cross-reaction with Amano P antibody is described in U.S. Patent 4,707,291, Thom et al, issued November 17, 1987.

A lipase unit (LU) is defined as the amount of lipase which produces 1 umol of titratable butyric acid per minute in a pH stat, where pH is 7.0, temperature is 30°C, and substrate is an emulsion of ributyrin and gum arabic in the presence of Ca++ and NaCl in phosphate buffer.

Surfactant system

The compositions of the invention contain a surfactant system at a level of from 5 % to 80 %, preferably from 10 % to 60 %, most preferably from 15 % to 50 % by weight of the composition.

The surfactant system is preferably formulated to be compatible with the lipolytic enzyme. In liquid or gel compositions the surfactant system is most preferably formulated such that it promotes, or at least does not degrade, the stability of the lipolytic enzyme in these compositions.

The surfactant system comprises surfactant selected from nonionic, anionic, cationic, zwitterionic, ampholytic and amphoteric surfactants, and any mixtures thereof.

Preferably the surfactant system comprises from 5% to 90% by weight, more preferably from 30% to 70% by weight of the surfactant system of anionic surfactant, and from 5% to 60% by weight, more preferably from 15% to 50% by weight of the surfactant system of nonionic surfactant.

Anionic surfactant

The anionic surfactant may be essentially any anionic surfactant, including anionic sulfate, sulfonate or carboxylate surfactant.

Anionic sulfate surfactant

The anionic sulfate surfactant may be any organic sulfate surfactant. It is preferably selected from the group consisting of C_{10}-C_{16} alkyl sulfate which has been ethoxylated with from about 0.5 to about 20 moles of ethylene oxide per molecule, C_9-C_{17} acyl-N-(C_1-C_4 alkyl) glucamine sulfated, -N-(C_2-C_4 hydroxyalkyl) glucamine sulfate, and mixtures thereof. More preferably, the anionic sulfate surfactant is a C_{10}-C_{16} alkyl sulfate which has been ethoxylated with from about 0.5 to about 20, preferably from about 0.5 to about 12, moles of ethylene oxide per molecule.

Alkyl ethoxy sulfate surfactants comprises a primary alkyl ethoxy sulfate derived from the condensation product of a C_{10}-C_{16} alcohol with an average of from about 0.5 to about 20, preferably from about 0.5 to about 12, ethylene oxide groups. The C_{10}-C_{16} alcohol itself is commercially available. C_{12}-C_{14} alkyl sulfate which has been ethoxylated with from about 3 to about 10 moles of ethylene oxide per molecule is preferred.

Conventional base-catalyzed ethoxylation processes to produce an average degree of ethoxylation of 12 result in a distribution of individual ethoxylates ranging from 1 to 15 ethoxy groups per mole of alcohol, so that the desired average can be obtained in a variety of ways. Blends can be made of material having different degrees of ethoxylation and/or different ethoxylate distributions arising from the specific ethoxylation techniques employed and subsequent processing steps such as distillation.

Anionic sulfate surfactants include the C_9-C_{17} acyl-N-(C_1-C_4 alkyl) and -N-(C_1-C_2 hydroxyalkyl) glucamine sulfates, preferably those in which the C_9-C_{17} acyl group is derived from coconut or palm kernel oil. These materials can be prepared by the method disclosed in U.S. Patent 2,717,894, Schwartz, issued September 13, 1955.

The counterion for the anionic sulfate surfactant component is preferably selected from calcium, sodium, potassium, magnesium, ammonium, or alkanol-ammonium, and mixtures thereof, with calcium and magnesium being preferred for cleaning and sudsing, respectively.

Anionic sulfonate surfactant

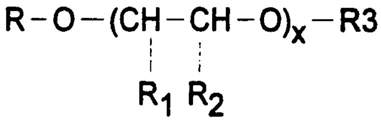
Anionic sulfonate surfactants suitable for use herein include essentially any sulfonate surfactants including, for example, the salts (eg : alkali metal salts) of C_9-C_{20} linear alkylbenzene sulfonates, C_8-C_{22} primary or secondary alkane sulfonates, C_8-C_{24} olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, paraffin sulfonates, and any mixtures thereof.

Anionic alkyl ethoxy carboxylate surfactant

Alkyl ethoxy carboxylates suitable for use herein include those with the fomula $RO(CH_2CH_20)_x CH_2C00^-M^+$ wherein R is a C_{12} to C_{16} alkyl group, x ranges from O to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than about 20 %, preferably less than about 15 %, most preferably less than about 10 %, and the amount of material where x is greater than 7, is less than about 25 %, preferably less than about 15 %, most preferably less than about 10 %, the average x is from about 2 to 4 when the average R is C_{13} or less, and the average x is from about 3 to 6 when the average R is greater than C_{13}, and M is a cation, preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanol-ammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred alkyl ethoxy carboxylates are those where R is a C_{12} to C_{14} alkyl group.

Anionic alkyl polyethoxy polycarboxylate surfactant

Alkyl polyethoxy polcarboxylate surfactants suitable for use herein include those having the formula :



$$R-O-(\underset{R_1}{CH}-\underset{R_2}{CH}-O)_x-R3$$

wherein R is a C_6 to C_{18} alkyl group, x is from 1 to 25, R_1 and R_2 are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, wherein at least one R_1 or R_2 is a succinic acid radical or hydroxysuccinic acid radical, and R_3 is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

Anionic secondary soap surfactant

Secondary soap surfactants (aka "alkyl carboxyl surfactants") useful herein are those which contain a carboxyl unit connected to a secondary carbon. It is to be understood herein that the secondary carbon can be in a ring structure, e.g. as in p-octyl benzoic acid, or as in alkyl-substituted cyclohexyl carboxylates. The secondary soap surfactants should contain no ether linkages, no ester linkages and no hydroxyl groups. There should be no nitrogen atoms in the head-group (amphiphilic portion). The secondary soap surfactants usually contain 11-13 total carbon atoms, although slightly more (e.g., about 14-16) can be tolerated if the soap contains a ring structure, as noted above, e.g. p-octyl benzoic acid.

The following general structures further illustrate some of the secondary soap surfactants (or their precursor acids) useful herein.

A. A highly preferred class of secondary soaps useful herein comprises the secondary carboxyl materials of the formula R^3 $CH(R^4)COOM$, wherein R^3 is $CH_3(CH_2)_x$ and R^4 is $CH_3(CH_2)y$, wherein y can be O or an integer from 1 to 4, x is an integer from 4 to 10 and the sum of (x + y) is 6-10, preferably 7-9, most preferably 8.

B. Another class of secondary soaps useful herein comprises those carboxyl compounds wherein the carboxyl substituent is on a ring hydrocarbyl unit, i.e., secondary soaps of the formula R^5-R^6-COOM, wherein R^5 is C_7-C_{10}, preferably C_8-C_9, alkyl or alkenyl and R^6 is a ring structure, such as benzene, cyclopentane and cyclohexane. (Note : R^5 can be in the ortho, meta or para position relative to the carboxyl on the ring.)

C. Still another class of secondary soaps comprises secondary carboxyl compounds of the formula $CH_3(CHR)_k$-$(CH_2)_m$-$(CHR)_n$-$CH(COOM)(CHR)_o$-$(CH_2)_p$-$(CHR)_q$-CH_3, wherein each R is C_1-C_4 alkyl, wherein k, n, o, q are integers in the range of 0-8, provided that the total number of carbon atoms (including the carboxylate) is in the range of 10 to 18.

In each of the above formulas A, B and C, the species M can be any suitable, especially water-solubilizing, counterion, e.g., H, alkali metal, alkaline earth metal, ammonium, alkanolammonium, di- and tri- alkanolammonium, and C_1-C_5 alkyl substituted ammonium. Sodium is convenient, as is diethanolammonium.

Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-pentyl-1-heptanoic acid.

Other anionic surfactants

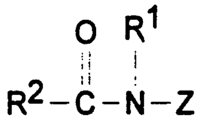
Other anionic surfactants useful for detersive purposes can also be included in the compositions hereof. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C_{12}-C_{18} monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C_6-C_{14} diesters), N-acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_kCH_2COO\text{-}M^+$ wherein R is a C_8-C_{22} alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation, and fatty acids esterified with isethionic acid and neutralized with sodium hydroxide. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23.

Nonionic surfactant

Suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, at column 13, line 14 through column 16, line 6, incorporated herein by reference. Exemplary, non-limiting classes of useful nonionic surfactants are listed below.

Nonionic polyhydroxy fatty acid amide surfactant

Polyhydroxy fatty acid amides suitable for use herein are those having the structural formula :



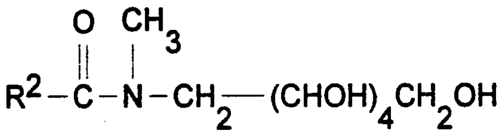
$$R^2-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle R^1}{|}}{N}-Z$$

wherein : R1 is H, C_1-C_4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl, or a mixture thereof, preferable C1-C4 alkyl, more preferably C_1 or C_2 alkyl, most preferably C_1 alkyl (i.e., methyl); and R_2 is a C_5-C_{31} hydrocarbyl, preferably straight-chain C_7-C_{19} alkyl or alkenyl, more preferably straight-chain C_9-C_{17} alkyl or alkenyl, most preferably straight-chain C_{11}-C_{17} alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of $-CH_2-(CHOH)_n-CH2-OH_2$, $-CH(CH_2OH)-(CHOH)_n-$, $-CH_2OH$, $-CH_2-(CHOH)_2(CHOR')(CHOH)-CH_2OH$, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxylate derivative thereof. Most preferred are glycityls wherein n is 4, particularly $-CH_2-(CHOH)_4-CH_2OH$.

In Formula (I), R^1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl.
R2-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactityl, 1-deoxygalactityl, 1-deoxymannityl, 1-deoxymaltotriotityl, etc.

The most preferred polyhydroxy fatty acid amide has the general formula :



$$R^2-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle CH_3}{|}}{N}-CH_2-(CHOH)_4CH_2OH$$

wherein R^2 is a straight chain C_{11}-C_{17} alkyl or alkenyl group.

Nonionic condensates of alkyl phenols

The polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use herein. In general, the polyethylene oxide condensates are preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 5 to about 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type include Igepal^{TM} CO-630, marketed by the GAF Corporation; and Triton^{TM} X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company.

Nonionic ethoxylated alcohol surfactant

The alkyl ethoxylate condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use herein. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from 8 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 10 to 20 carbon atoms with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. Most preferred are the condensation products of alcohols having an alkyl group containing from 10 to 14 carbon atoms with from about 6 to about 10 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol^{TM} 15-S-9 (the condensation product of C_{11}-C_{15} linear alcohol with 9 moles ethylene oxide), Tergitol^{TM} 24-L-6 NMW (the condensation product of C_{12}-C_{14} primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol^{TM} 45-9 (the condensation product of C_{14}-C_{15} linear alcohol with 9 moles of ethylene oxide), Neodol^{TM} 23-6.5 (the condensation product of C_{12}-C_{13} linear alcohol with 6.54 moles of ethylene oxide), Neodol^{TM} 45-7 (the condensation product of C_{14}-C_{15} linear alcohol with 7 moles of ethylene oxide), Neodol^{TM} 45-4 (the condensation product of C_{14}-C_{15} linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro^{TM} EOBN (the condensation product of C_{13}-C_{15} alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company.

Nonionic EO/PO condensates with propylene glycol

The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are suitable for use herein. The hydrophobic portion of these compounds preferably has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties of this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by BASF.

Nonionic EO condensation products with propylene oxide/ethylene diamine adducts

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

Nonionic alkylpolysaccharide surfactant

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

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

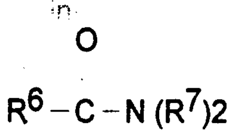
The preferred alkylpolyglycosides have the formula

$$R^2O(C_nH_{2n}O)t(glycosyl)_x$$

wherein R2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from 10 to 18, preferably from 12 to 14, carbon atoms; n is 2 or 3, x is from 0 to 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7, t is from 0 to 10. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-,3-, 4- and/or 6-position, preferably predominantly the 2-position.

Nonionic fatty acid amide surfactant

Fatty acid amide surfactants suitable for use herein are those having the formula:



$$R^6-\overset{O}{C}-N(R^7)2$$

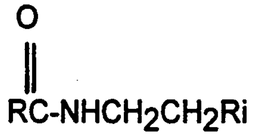
wherein R^6 is an alkyl group containing from 7 to 21, preferably from 9 to 17 carbon atoms and each R^7 is selected from the group consisting of hydrogen, C_1-C_4 alkyl, C_1-C_4 hydroxyalkyl, and -$(C_2H_4O)_xH$, where x is in the range of from 1 to 3.

Ampholytic surfactant

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

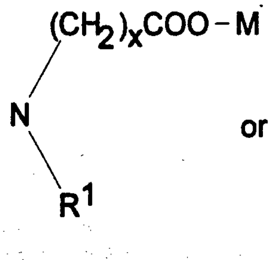
Amphoteric surfactant

Suitable amphoteric surfactants for use herein include the alkyl amphocarboxylic acids of the formula

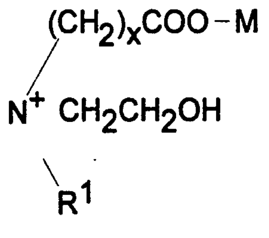


$$R\overset{\overset{O}{\|}}{C}\text{-}NHCH_2CH_2Ri$$

wherein R is a C_8-C_{18} alkyl group, and R_i is of the general formula



or



wherein R^1 is a $(CH_2)_xCOOM$ or CH_2CH_2OH, and x is 1 or 2 and M is preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanolammonium, most preferably from sodium, potassium, ammonium and mixtures thereof with magnesium ions. The preferred R alkyl chain length is a C_{10} to C_{14} alkyl group. A preferred amphocarboxylic acid is produced from fatty imidazolines wherein the dicarboxylic acid functionality of the amphodicarboxylic acid is diacetic acid and/or dipropionic acid. A suitable example of an alkyl aphodicarboxylic acid for use herein in the amphoteric surfactant Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic surfactant

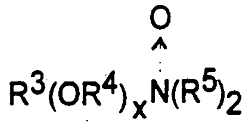
Zwitterionic surfactants can also be incorporated into the detergent compositions herein. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium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

Ampholytic, amphoteric and zwitterionic surfactants are generally used in combination with one or more anionic and/or nonionic surfactants.

Suds-enhancing agents

The compositions of the present invention preferebly further comprise from 1% to 20%, preferably from 2% to 20% by weight of a suds enhancing agent selected from the group consisting of amine oxides, betaines, sultaines, complex betaines, and certain nonionics.

Amine oxides useful in the present invention include those compounds having the formula :



$$R^3(OR^4)_x\overset{\overset{O}{\uparrow}}{N}(R^5)_2$$

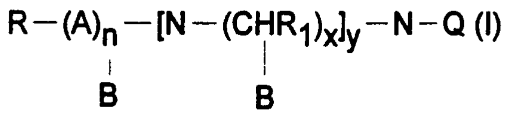
wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms, preferably 8 to 16 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, preferably 2 carbon atoms, or mixtures thereof; x is from 0 to 3, preferably 0; and each R^5 is an alkyl or hydyroxyalkyl group containing from 1 to 3, preferably from 1 to 2 carbon atoms, or a polyethylene oxide group containing from 1 to 3, preferable 1, ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10}-C_{18} alkyl dimethyl amine oxides and C_8-C_{12} alkoxy ethyl dihydroxyethyl amine oxides. Examples of such materials include dimethyloctylamine oxide, diethyldecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dipropyltetradecylamine oxide, methylethylhexadecylamine oxide, dodecylamidopropyl dimethylamine oxide and dimethyl-2-hydroxyoctadecylamine oxide. Preferred are C_{10}-C_{18} alkyl dimethylamine oxide, and C_{10-18} acylamido alkyl dimethylamine oxide.

The betaines useful in the present invention are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C_6-C_{18} hydrocarbyl group, preferably a C_{10}-C_{16} alkyl group or C_{10-16} acylamido alkyl group, each R^1 is typically C_1-C_3 alkyl, preferably methyl,m and R^2 is a C_1-C_5 hydrocarbyl group, preferably a C_1-C_3 alkylene group, more preferably a C_1-C_2 alkylene group. Examples of suitable betaines include coconut acylamidopropyldimethyl betaine; hexadecyl dimethyl betaine; C_{12-14} acylamidopropylbetaine; C_{8-14} acylamidohexyldiethyl betaine; 4[C_{14-16} acylmethylamidodiethylammonio]-1-carboxybutane; C_{16-18} acylamidodimethylbetaine; C_{12-16} acylamidopentanediethyl-betaine; [C_{12-16} acylmethylamidodimethylbetaine. Preferred betaines are C_{12-18} dimethyl-ammonio hexanoate and the C_{10-18} acylamidopropane (or ethane) dimethyl (or diethyl) betaines.

The sultaines useful in the present invention are those compounds having the formula $(R(R^1)_2N^+R^2SO_3^-$ wherein R is a C_6-C_{18} hydrocarbyl group, preferably a C_{10}-C_{16} alkyl group, more preferably a C_{12}-C_{13} alkyl group, each R^1 is typically C_1-C_3 alkyl, preferably methyl, and R^2 is a C_1-C_6 hydrocarbyl group, preferably a C_1-C_3 alkylene or, preferably, hydroxyalkylene group. Examples of suitable sultaines include C_{12}-C_{14} dimethylammonio-2-hydroxypropyl sulfonate, C_{12-14} amido propyl ammonio-2-hydroxypropyl sultaine, C_{12-14} dihydroxyethylammonio propane sulfonate, and C_{16-18} dimethylammonio hexane sulfonate, with C_{12-14} amido propyl ammonio-2-hydroxypropyl sultaine being preferred.

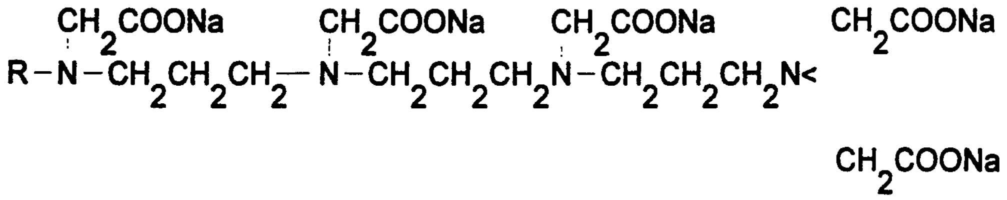
The complex betaines for use herein have the formula



$$R-(A)_n-[\underset{B}{N}-(CHR_1)_x]_y-\underset{B}{N}-Q \quad (I)$$

wherein R is a hydrocarbon group having from 7 to 22 carbon atoms, A is the group (C(O)), n is 0 or 1, R_1 is hydrogen or a lower alkyl group, x is 2 or 3, y is an integer of 0 to 4, Q is the group $-R_2COOM$ wherein R_2 is an alkylene group having from 1 to 6 carbon atoms and M is hydrogen or an ion from the groups alkali metals, alkaline earth metals, ammonium and substituted ammonium and B is hydrogen or a group Q as defined.

An example in this category is tallowamphopolycarboxy glycinate, of the formula :



$$R-\overset{CH_2COONa}{N}-CH_2CH_2CH_2-\overset{CH_2COONa}{N}-CH_2CH_2CH_2\overset{CH_2COONa}{N}-CH_2CH_2CH_2N\!<\!\begin{matrix}CH_2COONa\\CH_2COONa\end{matrix}$$

Preferred amides are C_8-C_{20} alkyl mono- or di-C_2-C_3 alkanolamides, especially monoethanolamides, diethanolamides, and isopropanolamides.

Preferred suds enhancing agents are C_{10-18} acyl amide alkyl dimethyl amine oxides, betaines, sultaines, condensation products of aliphatic alcohols with ethylene oxides, and alkylpolysaccharides, and mixtures thereof.

Hydrotropes

A hydrotrope is typically added to the compositions of the present invention, and may be present at levels of from 0.5% to 10%, preferably from 1% to 5%, by weight.

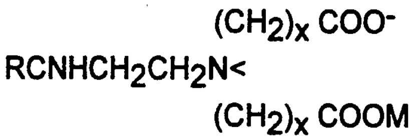
Useful hydrotropes include sodium, potassium, and ammonium xylene sulfonates, sodium, potassium, and ammonium toluene sulfonate, sodium potassium and ammonium cumene sulfonate, and mixtures thereof.

Other compounds useful as hydrotropes herein include polycarboxylates. Some polycarboxylates have calcium chelating properties as well as hydrotropic properties.

Particularly useful hydrotropes are alkylpolyethoxy polycarboxylate surfactants of the type as previously described herein.

An example of a commercially available alkylpolyethoxy polycarboxylate which can be employed herein is POLY-TERGENT C, Olin Corporation, Cheshire, CT.

Another compound useful as a hydrotrope is alkyl amphodicarboxylic acid of the generic formula :



$$RCNHCH_2CH_2N< \begin{array}{l} (CH_2)_x\,COO^- \\ (CH_2)_x\,COOM \end{array}$$

wherein R is a C_8 to C_{18} alkyl group, x is from 1 to 2, M is preferably chosen from alkali metal, alkaline earth metal, ammonium, mono-, di-, and tri-ethanolammonium, most preferably from sodium, potassium, ammonium, and mixtures thereof with magnesium ions. The preferred alkyl chain length (R) is a C_{10} to C_{14} alkyl group and the dicarboxylic acid functionally is diacetic acid and/or dipropionic acid.

A suitable example of an alkyl amphodicarboxylic acid is the amphoteric surfactant Miranol R 2CM Conc.manufactured by Miranol, Inc., Dayton, NJ.

Lime Soap Dispersants

The compositions of the present invention are particularly useful when formulated to contain a lime soap dispersant compound which acts to disperse any insoluble lime soap salts which may be formed between the fatty acids produced by the lipolytic hydrolysis of fats/oils and calcium ions in the wash soluble, thereby preventing the deposition of these salts as spots or films on the articles in the wash, or as an unseemly ring around the rim of the sink. Certain lime soap dispersant compounds may also provide improved product stability particularly where the product is formulated as a liquid product containing calcium ions.

A lime soap dispersant compound herein is defined as a compound, which has a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap dispersant compound is typically present at a level of from 0.1% to 40% by weight, more preferably 1% to 20% by weight, most preferably from 2% to 10% by weight of the compositions.

A lime soap dispersant is a material that prevents the precipitation of alkali metal, ammonium or amine salts of fatty acids by calcium or magnesium ions. A numerical measure of the effectiveness of a lime soap dispersant is given by the lime soap dispersing power (LSDP) which is determined using the lime soap dispersion test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to , for example, in the following review articles; W.N. Linfield, Surfactant Science Series, Volume 7, p3; W.N. Linfield, Tenside Surf. Det. , Volume 27, pages159-161, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, Volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm
$CaCO_3$ (Ca:Mg=3:2) equivalent hardness.

In the Borghetty/Bergman lime soap dispersion test 5ml of a 0.5% by weight solution of sodium oleate is added to a test tube, followed by 10ml of a hard water solution containing 600ppm Ca^{2+} and 400ppm Mg^{2+} (1000ppm as

$CaCO_3$ equivalent, 70° Clark Hardness) which will cause formation of a lime soap deposit (or curd). An arbitrary amount (less than 15ml) of dispersing agent as a 0.25% by weight solution is then added to the test tube. The total volume of solution in the test tube is then made up to 30ml and the test tube is stoppered, inverted 20 times and then allowed to stand for 30 seconds. The contents of the test tube are then visually inspected to check if the lime soap deposits are still intact or whether they have been dispersed into the solution. The test procedure is repeated using different amounts of dispersing agent solution until the minimum amount of dispersing agent solution which will cause dispersion of the lime soap deposits is obtained.

The lime soap dispersing power is then obtained as:

LSDP = (weight of lime soap dispersing agent) x 100
(weight of sodium oleate)

Thus in accord with the test method described above a material with a lower LSDP is a more effective lime soap dispersant than one with a higher LSDP.

Calcium

From 0.05% to 3%, more preferably from 0.15% to 2% of calcium ions may be included in the detergent compositions herein. It has been found for compositions containing polyhydroxy fatty acid amide that the presence of calcium greatly improves the cleaning of greasy soils. This is especially true when the compositions are used in softened water, which contains few divalent ions.

The calcium ions can, for example, be added as a chloride, hydroxide, oxide, formate or acetate, or nitrate salt.
If the anionic surfactants are in the acid form, the calcium can be added as a calcium oxide or calcium hydroxide slurry in water to neutralise the acid.

The calcium ions may be present in the compositions as salts. The amount of calcium ions present in compositions of the invention may be dependent upon the amount of total anionic surfactant present herein. The molar ratio of calcium ions to total anionic surfactant is preferably from 1:0.1 to 1:25, more preferably from 1:2 to 1:10, for compositions of the invention.

Calcium stabilizing agent

Malic or maleic acid or certain lime soap dispersant compounds may be added to a composition formulated to contain calcium to provide good product stability, and in particular to prevent the precipitation of insoluble calcium salts. Malic or maleic acid may, where calcium is present, preferably be added at levels of from 0.05% to 10% of the composition and a molar ratio with calcium of from 0.01:1 to 1:10.

Magnesium

From 0.01% to 3%, most preferably from 0.15% to 0.9%, by weight, of magnesium ions are preferably added to the liquid detergent compositions of the invention for improved product stability, as well as improved sudsing.

If the anionic surfactants are in the acid form, then the magnesium can be added by neutralization of the acid with a magnesium oxide or magnesium hydroxide slurry in water. Calcium can be treated similarly. This technique minimises the addition of chloride ions, which reduces corrosive properties. The neutralized surfactant salts and the hydrotrope are then added to the final mixing tank and any optional ingredients are added before adjusting the pH.

Composition pH

Liquid detergent compositions in accord with the invention will preferably be formulated such that during use in aqueous cleaning operations, the wash water will have a pH of between about 5.0 and about 8.0. The liquid compositions themselves preferably have a pH in a 10% solution water at 20°C of between about 5.5 and about 8.5, most preferably between about 6.8 and about 7.8.

Techniques for controlling pH at recommended usage levels include the use of buffers, alkali, acids, etc., and are well known to those skilled in the art. Dilute hydrochloric acid is preferred for downward pH adjustment, and sodium hydroxide for upward pH adjustment.

Enzyme Stabilizing System

The preferred compositions herein may additionally comprise from 0.001% to 10%, preferably from 0.005% to 8%, most preferably from 0.1% to 6%, by weight of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing system which is compatible with the enzyme of the present invention. Such stabilizing systems can comprise calcium ion, boric acid, propylene glycol, short chain carboxylic acid, boronic acid, polyhydroxyl compounds and mixtures thereof such as are described in U.S. Patents 4,318,818, Letton et al; 4,462,922, Boskamp, issued July 31, 1984; 4,532,064, Boskamp, issued July 30, 1985; and 4,537,707, Severson Jr., issued August 27, 1985, all of which are incorporated herein by reference.

Additionally, from 0 to 10%, preferably from 0.01% to 6% by weight, of chlorine bleach scavengers can be added to compositions of the present invention to prevent chlorine bleach species present in many water supplies from attacking and inactivating the enzymes, especially under alkaline conditions. While chlorine levels in water may be small, typically in the range from 0.5 ppm to 1.75 ppm, the available chlorine in the total volume of water that comes in contact with the enzyme during dishwashing is usually large; accordingly, enzyme stability in-use can be problematic.

Suitable chlorine scavenger anions are salts containing ammonium cations. These can be selected from the group consisting of reducing materials like sulfite, bisulfite, thiosulfite, thiosulfate, iodide, etc., antioxidants like carbamate, ascorbate, etc., organic amines such as ethylenediaminetetracetic acid (EDTA) or alkali metal salt thereof and monoethanolamine (MEA), and mixtures thereof. Other conventional scavenging anions like sulfate, bisulfate, carbonate, bicarbonate, percarbonate, nitrate, chloride, borate, sodium perborate tetrahydrate, sodium perborate monohydrate, percarbonate, phosphate, condensed phosphate, acetate, benzoate, citrate, formate, lactate, malate, tartrate, salicylate, etc. and mixtures thereof can also be used. The preferred ammonium salts or other salts of the specific chlorine scavenger anions can either replace the suds controlling agent or be added in addition to the suds controlling agent.

Although ammonium salts can be mixed with the detergent composition, they are prone to adsorb water and/or give off ammonia gas. Accordingly, it is better if they are protected in a particle like that described in U.S. Patent 4,652,392, Baginski et al, which is incorporated herein by reference.

Liquid or gel compositions

In a preferred embodiment, the detergent compositions of the present invention are liquid detergent compositions. These preferred liquid detergent compositions comprise from 94% to 35% by weight, preferably from 90% to 40% by weight, most preferably from 80% to 50% by weight of a liquid carrier, e.g., water, preferably a mixture of water and a C1-C4 monohydric alcohol (e.g., ethanol, propanol, isopropanol, butanol, and mixtures thereof), with ethanol being the preferred monohydric alcohol or a mixture of water and C_1-C_4 dihydric alcohol (e.g.: propylene glycol).

Gels

The detergent compositions of the present invention may also be in the form of a gel. Such compositions are typically formulated in polyakenyl polyether and having a molecular weight of from about 750,000 to about 4,000,000.

Highly preferred examples of these polycarboxylate polymer thickeners are the Carbopol 600 series resins available from B.F. Goodrich. Especially preferred are Carbopol 616 and 617. It is believed that these resins are more highly cross-linked than the 900 series resins and have molecular weights between about 1,000,000 and 4,000,000. Mixtures of polycarboxylate polymers as herein described may also be used in the present invention. Particularly preferred is a mixture of Carbopol 616 and 617 series resins.

The polycarboxylate polymer thickener is utilized preferably with essentially no clay thickening agent. In fact, it has been found that if the polycarboxylate polymers of the present invention are utilized with clay in the composition of the present invention, a less desirable product, in terms of phase instability, results. In other words, the polycarboxylate polymer is preferably used instead of clay as a thickening/stabilizing agent in the present compositions.

If the polycarboxylate polymer is used as a thickening agent in the compositions of the present invention, it is typically present at a level of from about 0.1% to about 10%, preferably from about 0.2% to about 2% by weight.

The thickening agents are preferably used to provide a yield value of from about 50 to about 350 and most preferably from about 75 to about 250. The yield value is an indication of the shear stress at which the gel strength is exceeded and flow is initiated. It is measured herein with a Brookfield RVT model viscometer with a T-bar B spindle at 25°utilizing a Helipath.

Other desirable ingredients typically used in the compositions herein include dyes, perfumes and opacifiers.

Opacifiers such as Lytron (Morton Thiokol, Inc.), a modified polystyrene latex, or ethylene glycol distearate can be added, preferably as a last step. Lytron can be added directly as a dispersion with mixing. Ethylene glycol distearate can be added in a molten state with rapid mixing to form pearlescent crystals. Opacifiers useful herein, particularly for light duty liquids, are typically present at levels from about 0.2% to about 10%, preferably from about 0.5% to about 6% by weight.

Manual diswashing process

According to the manual dishwashing process aspect of this invention, soiled dishes are contacted with an effective amount, typically from about 0.5 ml. to about 20 ml. (per 25 dishes being treated), preferably from about 3 ml. to about 10 ml., of the composition of the present invention. The actual amount of liquid detergent composition used will be based on the judgement of user, and will depend upon factors such as the particular product formulation of the composition, the concentration of the composition, the number of soiled dishes to be cleaned and the degree of soiling of the dishes.

The process by which the soiled dishes are contacted with the effective amount of the composition of the invention may be essentially any of the processes for manual dishwashing commonly known and encompasses the dilute solution in sink process, commonly used in Northern Europe and the US ; the solution in bowl process, commonly used in Latin America and Japan, and the direct application process, commonly used in Southern Europe and developing countries.

Dilute solution in sink process

In the typical dilute solution in sink process from about 3 ml. to 15 ml., preferably from 5 ml. to 10 ml. of a liquid detergent composition is combined with from 1,000 ml. to 10,000 ml., more typically from 3,000 ml. to 5,000 ml. of water in a sink having a volumetric capacity in the range of from 5,000 ml. to 20,000 ml., more typically from 10,000 ml. to 15,000 ml. The detergent composition has a surfactant concentration of from about 10 % to about 60 % by weight, preferably from about 45 % to about 50 % by weight. The soiled dishes are immersed in the sink containing the detergent composition and water, where they are cleaned by contacting the soiled surface of the dish with a cloth, sponge or similar article. The cloth, sponge or similar article may be immersed in the detergent composition and water mixture prior to being contacted with the dish surface and is typically contacted with the dish surface for a period of time ranging from about 1 to about 10 seconds, although the actual time will vary with each application and user. The contacting of the cloth, sponge or similar article to the dish surface is preferably accompanied by a concurrent scrubbing of the dish surface.

Solution in bowl process

In a typical solution in bowl process from 1 ml. to 50 ml., prefrably from 2 ml. to 10 ml. of a detergent composition is combined with from 50 ml. to 2,000 ml., more typically from 100 ml. to 1,000 ml. of water in a bowl having a volumetric capacity in the range of from 500 ml. to 5,000 ml., more typically from 500 ml. to 2,000 ml. The detergent composition has a surfactant concentration of from about 10 % to about 60 % by weight, preferably from about 15 % to about 50 % by weight. The soiled dishes are cleaned by contacting the soiled surface of the dish with a cloth, sponge or similar article. The cloth, sponge or similar article may be immersed in the detergent composition and water mixture prior to being contacted with the dish surface and is typically contacted with the dish surface for a period of time ranging from about 1 to about 10 seconds, although the actual time will vary with each application and user. The contacting of the cloth, sponge or similar article to the dish surface is preferably accompanied by a concurrent scrubbing of the dish surface.

Direct Application Process

The direct application process will typically comprise as a first step immersing the soiled dishes into a water bath without any liquid dishwashing detergent. A device for absorbing liquid dishwashing detergent, such as a sponge, is then placed directly into a separate quantity of undiluted liquid or gel detergent composition for a period of time typically ranging from about 1 to about 5 seconds. The absorbing device, and consequently the undiluted detergent composition, is then contacted individually to the surface of each of the soiled dishes to remove said soiling. The absorbing device is typically contacted with each dish surface for a period of time range from 1 to 10 seconds, although the actual time of application will be dependent upon factors such as the degree of soiling of the dish. The contacting of the absorbing device to the dish surface is preferably accompanied by concurrent scrubbing.

EXAMPLES

The following compositions in accord with the invention were prepared.

	% by weight				
	I	II	III	IV	V
C12/13 alkyl ethoxy (ave. 0.8) sulphate	10.0	10.0	9.0	5.0	10.0
C12/13 alkyl ethoxy (ave. 3) sulphate	7.0	7.0	8.0	15.0	7.0
C12/14 alkyl amine oxide	2.0	1.0	-	1.0	2.0
C12/14 alkyl di methyl betaine	-	1.0	1.5	2.0	-
C12/14 Ampholak(TM)	-	-	1.5	-	-
C12 alkyl N-methyl glucamide	12.0	12.0	9.0	11.0	12.0
C10 Alkyl Ethoxylate (ave. 8)	5.0	5.0	5.0	4.6	5.0
Mg^{++} ion	-	0.6	-	0.3	0.6
Ca^{++}ion	-	-	0.3	0.15	0.1
Maleic acid	-	-	0.2	0.3	-
Miranol (TM)	-	-	2.0	-	-
Polytergent (TM)	-	-	-	2.0	-
Lipolase (TM)	0.05	0.1	0.2	0.3	0.4

The compositions were prepared by mixing all of the surfactants with the exception of the glucamide. The magnesium and calcium salts were then pre-dissolved into solution together with the maleic acid and added to the surfactant mixture with the remaining components. Finally the pH was trimmed to 7.3 using hydrochloric acid and the viscosity checked.

What is claimed is:

1. A composition containing a surfactant system and lipolytic enzyme suitable for use in a manual dishwashing process.

2. A composition according to Claim 1 wherein said composition is high sudsing.

3. A composition according to either of Claims 1 or 2 wherein said composition is the form of a liquid or gel.

4. A composition according to any of Claims 1-3 wherein said composition contains no builder salts.

5. A composition according to any of Claims 1-4 wherein said composition contains no bleaching components.

6. A compostion according to any of Claims 1-5 containing from 5% to 80% by weight of said surfactant system, wherein the surfactant system comprises surfactant selected from nonionic, anionic, cationic, zwitterionic, ampholytic and amphoteric surfactants.

7. A composition according to any of Claims 1-6 wherein the pH of 1% by weight solution of said composition is from 6 to 9.

8. A compostion according to any of Claims 1-7 containing from 0.05% to 3% by by weight of calcium ions.

9. A composition according to any of Claims 1-8 containing from 0.01% to 3% by weight of magnesium ions.

10. A compostion according to any of Claims 2-9 containing from 0.1% to 20% by weight of a suds enhancing agent.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/08415

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C11D 3/386,
US CL : 252/174.12, Dig. 12, 173, Dig.14,
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/174.12, Dig. 12, 173, Dig.14,

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: lipase# or lipolytic, surfactant#, Liquid or gel, sudsing or suds, dishwash?

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,089,163 (Aronson et al.) 18 FEBRUARY 1992, col. 3, line 49- col. 4, line 25, col.5, line 3-5, and Examples II and V	1-3
X --- Y	US, A, 4,950,417 (Bycroft et al.) 21 August 1990 col. line 64, col. 2, lines 5-8 and Example 1	1-3 ----- 1-3
X	US, A, 4,707,291 (Thom et al) 17 November 1987 col. 3, lines 1-30, and Example 1	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search 07 NOVEMBER 1994	Date of mailing of the international search report 23 NOV 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer PAUL LIEBERMAN Telephone No. (703) 308-0687

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/08415

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 4-10
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.