CORRECTED VERSION*

PCT

WORLD INTELLECTUAL
Internatic

INTERNATIONAL APPLICATION PUBLISHED UN

WO 9533033A1

(51) International Patent Classification 6 :
C11D 1/65

A1

(43) International Publication Date: 7 December 1995 (07.12.95)

(21) International Application Number: PCT/US95/06523

(22) International Filing Date: 23 May 1995 (23.05.95)

(30) Priority Data:
08/252,301 1 June 1994 (01.06.94) US

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(81) Designated States: CA, CN, JP, MX, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: LAUNDRY DETERGENT COMPOSITIONS

(57) Abstract

Laundry detergent compositions are provided which are especially effective for removing greasy/oily soils and stains from fabrics during laundering operations. Such compositions essentially contain a surfactant mixture comprising oleoyl sarcosinate and certain cationic surfactants. Processes for laundering and pretreating fabrics using these compositions are also disclosed.

* (Referred to in PCT Gazette No. 06/1996, Section II)

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LAUNDRY DETERGENT COMPOSITIONS

FIELD OF THE INVENTION

This invention relates to laundry detergent compositions which exhibit improved greasy and oily soil and body soil removal capabilities. The compositions are generally free of phosphate; alternatively, they may contain low levels of phosphate materials but not amounts in excess of about 20% by weight. These detergent compositions provide an unexpectedly high level of greasy and oil soil (such as motor oil, triolein, animal fat and lipstick) removal; they also provide excellent removal of particulate soils, especially clay soils, as well as fabric care benefits, such as fabric softening, static control, and dye transfer inhibition.

BACKGROUND OF THE INVENTION

Oleoyl sarcosinate is a known anionic surfactant which has been used as the detersive surfactant in fabric laundering compositions. Oleoyl sarcosinate has been described in the following patents and publications: U.S. 2,542,385; U.S. 3,402,990; U.S. 3,639,568; U.S. 4,772,424; U.S. 5,186,855; European Patent Publication 505,129; British Patent Publication 1,211,545; Japanese Patent Publication 59/232194; Japanese Patent Publication 62/295997; Japanese Patent Publication 02/180811; and Chemical Abstracts Service Abstracts Nos. 61:3244q, 70:58865x, and 83:181020p.

Cationic surfactants have also been used in detergent compositions primarily to provide adjunct fabric care benefits and not for the purpose of enhancing cleaning. Certain cationic surfactants provide a germicidal or sanitization benefit to washed surfaces; see for example, U.S. Pat. No. 2,742,434, Koop, issued Apr. 17, 1956; U.S. Pat. No. 3,539,520, Cantor et al, issued Nov. 10, 1970; and U.S. Pat. No. 3,965,026, Lancz, issued June 22, 1976. Other cationic surfactants, such as ditallowalkyldimethylammonium chloride, are included in detergent compositions to provide a fabric softening benefit, as disclosed in U.S. Pat. No. 3,607,763, Salmem et al, issued Sept. 21, 1971; and U.S. Pat. No. 3,644,203, Lamberti et al, issued Feb. 22, 1972. Such components are also used to control static, as well as to soften laundered fabrics as, for example, in U.S. Pat. No. 3,951,879, Wixon, issued Apr. 20,

1976; and U.S. Pat. No. 3,959,157, Inamorato, issued May 25, 1976. All of these patents are incorporated herein by reference.

The compositions of the present invention have outstanding cleaning capabilities. Such compositions can be very effective in removing some typical greasy and oily soils in comparison with conventional laundry detergents, including commercially-available heavy duty liquid detergents containing a high proportion of nonionic surfactants. These same detergent compositions, with or without phosphate or other builder components, are also effective in removing clay soils at least as well, and in some instances, substantially better than fully-built conventional granular laundry detergent compositions, and, in addition provide a range of fabric care benefits, such as fabric softening, static control and dye transfer inhibition, to the laundered fabrics. Thus, the compositions of the present invention provide the user with a well-rounded cleaning and fabric care package. These are the result of a heretofore unrecognized cleaning potential provided by the combination of selected anionic surfactants, i.e. oleoyl sarcosinates, and certain selected cationic surfactants.

It is an object of this invention to provide laundry detergent compositions which yield outstanding greasy and oily soil and body soil removal.

It is another object of this invention to provide laundry detergent compositions which have excellent particulate soil removal performance and fabric conditioning benefits, in addition to outstanding greasy and oily soil and body soil removal performance, in the presence or absence of builder components.

It is a further object of this invention to provide detergent compositions which may be used in a variety of physical forms, such as liquid, paste, granular, solid, powder, or in conjunction with a carrier such as a substrate.

It is a still further object of this invention to provide a process for laundering fabrics to remove greasy and oily soil and body soil, as well as particulate soil, using certain anionic and cationic surfactant-containing detergent compositions. The compositions also provide excellent color care for dyed fabrics and excellent skin mildness for handwash operations. These and other advantages of the present invention will be seen from the disclosures hereinafter.

SUMMARY OF THE INVENTION

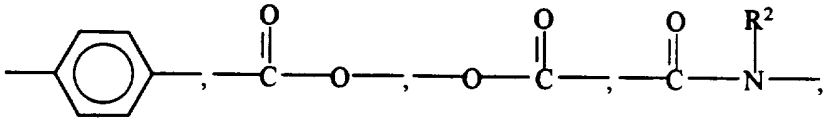
The present invention relates to laundry detergent compositions that comprise from about 5% to 100%, by weight, of a surfactant mixture comprising:

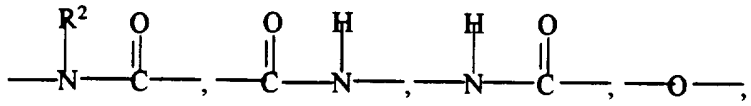
(A) an oleoyl sarcosinate of the formula:

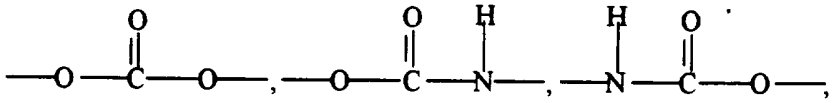
$C_{17}H_{33}C(O)N(CH_3)CH_2COOM$

wherein M is hydrogen or a cationic moiety; and

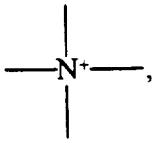
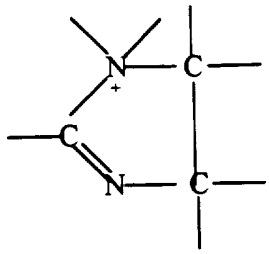
(B) a specific type of cationic surfactant which is free of hydrazinium groups. Such cationic surfactants have the formula $R_m^1R_x^2Y_LZ$ wherein R^1 is an organic group containing a straight or branched alkyl or alkenyl group optionally substituted with up to 3 phenyl or hydroxy groups and optionally interrupted by up to four structures selected from

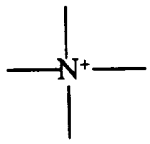






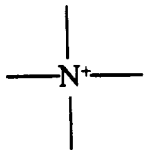
and mixtures thereof, each R^1 containing about 8 to about 22 carbon atoms, and which may additionally contain up to about 12 ethylene oxide groups; m is a number from 1 to 3; each R^2 is an alkyl or hydroxy alkyl group containing from 1 to 4 carbon atoms or a benzyl group, with no more than one R^2 in a molecule being benzyl; x is from 0 to 11, the remainder of any carbon atom positions being filled by hydrogens; Y is selected from

 ,  ,

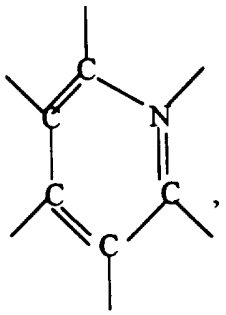
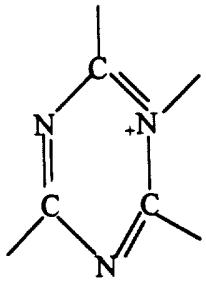
 , wherein p is from 1 to 12,

$(C_2H_4O)_pH$

$(C_2H_4O)_pH$

 , wherein each p is from 1 to 12,

$(C_2H_4O)_pH$

 ,  , and

and mixtures thereof;

L is 1 or 2, the Y groups being separated by a moiety selected from R^1 and R^2 analogs having from one to about twenty-two carbon atoms and 2 free carbon single bonds when L is 2, and Z is an anion in a number sufficient to give electrical neutrality. These cationic surfactants should be at least substantially water dispersible in admixture with the oleoyl sarcosinate surfactant.

These compositions of this invention provide a pH of at least about 6.5 in aqueous laundry solution. The ratio of oleoyl sarcosinate surfactant to cationic surfactant ranges from about 1:1 to 100:1.

The present invention also relates to a process for cleaning fabrics soiled with greasy and/or oily soils. Such a process comprises contacting such soiled fabrics

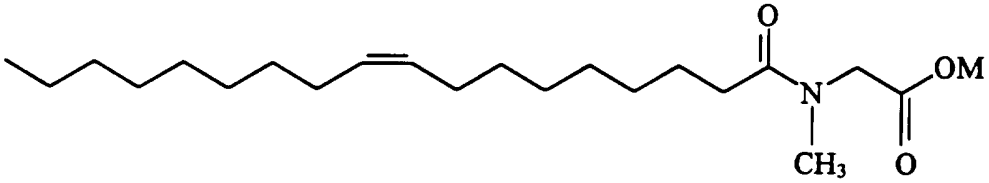
with an aqueous solution containing water and from about 0.1% to 1% of the oleoyl sarcosinate/cationic surfactant combinations hereinbefore described. Fabric pretreatment processes are also provided.

DETAILED DESCRIPTION OF THE INVENTION

The components of the detergent compositions herein, their preparation, composition formulation and composition use are described in detail as follows. All concentrations and ratios are expressed on a weight basis unless otherwise indicated.

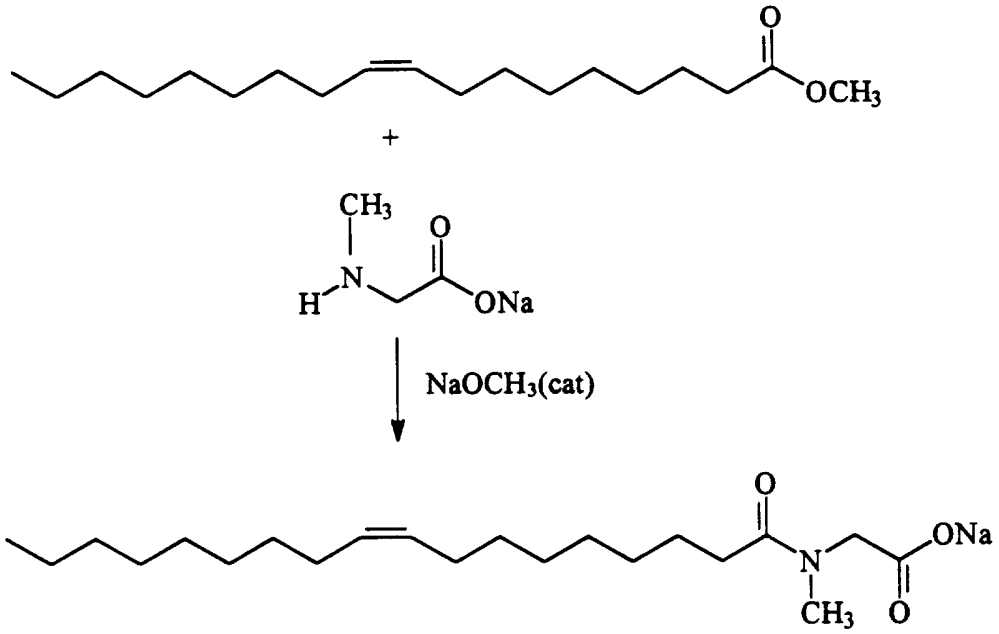
(A) The Oleoyl Sarcosinate Component

One essential component of the surfactant mixture employed in the detergent compositions herein is the anionic surfactant oleoyl sarcosinate in its acid and/or salt form. Preferably the oleoyl sarcosinate will comprise from about 0.1% to about 80%, more preferably from about 1% to about 40%, and most preferably about 2% to about 30% by weight of the compositions. Oleoyl sarcosinate has the general formula: $C_{17}H_{33}C(O)N(CH_3)CH_2COOM$ wherein M is hydrogen or a cationic moiety. The configuration of oleoyl sarcosinates can be represented as follows



Preferred M substituents are hydrogen and alkali metal cations, especially sodium and potassium. Oleoyl sarcosinate is commercially available, for example as Hamposyl O marketed by W. R. Grace & Co.

In addition to the commercially-available oleoyl sarcosinate, oleoyl sarcosinate useful herein can also be prepared from the ester (preferably the methyl ester) or oleic acid and a sarcosine salt (preferably the sodium salt) under anhydrous reaction conditions in the presence of a base catalyst with a basicity equal to or greater than alkoxide catalyst (preferably sodium methoxide). For example, the reaction may illustrated by the scheme:



This salt may be optionally neutralized to form the oleoyl sarcosinate in its acid form.

The preferred method for preparing oleoyl sarcosinate is conducted at a temperature from about 80°C to about 200°C, especially from about 120°C to about 200°C. It is preferred to conduct the reaction without solvent although alcohol solvents which have a boiling point of at least 100°C and are stable to the reaction conditions (i.e., glycerol is not acceptable) can be used. The reaction may proceed in about 85% yield with a molar ratio of methyl ester reactant to sarcosine salt reactant to basic catalyst of about 1:1:0.05-0.2.

Methyl ester mixtures derived from high oleic content natural oils (preferably having at least about 60%, more preferably at least about 75%, and most preferably at least about 90% oleic content) are especially preferred as starting materials. Examples include high-oleic sunflower and rapeseed/canola oil. In addition, a high-oleic methyl ester fraction derived from either palm kernel oil or tallow is acceptable. It is to be understood that such oils typically will contain some levels of impurities, including some fatty acid impurities that may be converted to sarcosinate compounds by this synthesis method. For example, commodity canola/rapeseed oil may comprise a majority of oleic acid, and a mixture of fatty acid impurities such as palmitic, stearic, linoleic, linolenic and/or eicosenoic acid, some or all of which are converted to the sarcosinate by this reaction method. If desired for formulation purposes, some or all of such impurity materials may be excluded from the starting oil before preparing the oleoyl sarcosinate to be used in the present invention.

Finally, sarcosine remaining in the reaction mixture can be converted to an amide by addition of maleic or acetic anhydride to the mixture, thereby minimizing the sarcosine content and any potential for formation of undesired nitrogen-containing impurities.

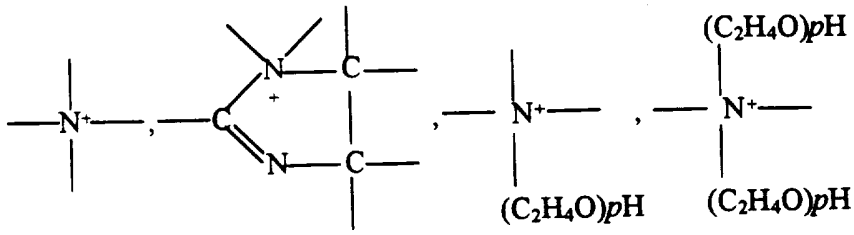
The synthesis of oleoyl sarcosinate may be carried out as follows to prepare the sodium oleoyl sarcosinate.

Synthesis of Oleoyl Amide of Sarcosine Sodium Salt - A 2 L, 3-neck round bottom flask is fitted with thermometer, Dean-Stark trap with condenser, mechanical stirring, and a gas inlet adapter through which nitrogen is passed over the reaction mixture. The reaction vessel is charged with sarcosine (43.3 g, 0.476 mol), sodium methoxide 25% in methanol (97.7 g, 0.452 mol), and methanol (400 mL). The reaction mixture is refluxed 15 min. to neutralize the sarcosine and then methyl ester derived from Cargill regular high-oleyl sunflower oil (148.25 g, 0.5 mol) is added. After the methanol is removed with the Dean-Stark trap, reaction mixture is heated to 170°C for 1 hr. to drive off any water. The reaction is initiated by the addition of sodium methoxide 25% in methanol (15.4 g, 0.0714 mol). The reaction mixture is kept at 170°C for 2.5 hr. during which methanol is collected in the Dean-Stark trap. The reaction is allowed to cool slightly, and then methanol (200 g) is added. Maleic anhydride (9.43 g, 0.095 mol) is added to the methanol solution, and the reaction is stirred at 60°C for 0.5 hr. Then most of the methanol is removed by rotary evaporation, and acetone (2 L) is added to precipitate the product. The product is collected by suction filtration and allowed to air dry to give an off-white solid. Analysis of the reaction mixture by GC indicates the majority of the product is oleoyl sarcosinate, with minor amounts of the following impurities: sarcosine, oleic acid, and the sarcosinates derived from palmitic acid, stearic acid, and linoleic acid.

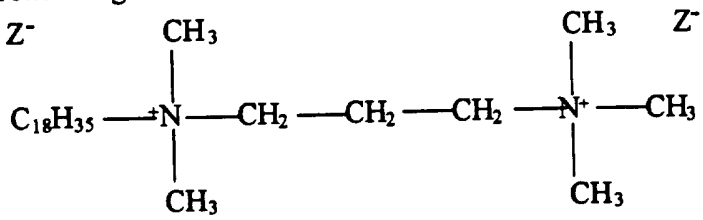
(B) The Cationic Surfactant Component

The second essential component of the surfactant mixture employed herein is a certain type of cationic surfactant material. Such cationics are those of the general formula $R_m{}^1R_x{}^2Y_LZ$ wherein the elements of this formula are as described hereinbefore in the Summary of the Invention section.

In preferred cationic materials, Z is a water-soluble anion such as halide, methyl sulfate, sulfate, or nitrate anion with particularly preferred anions being chloride, bromide, iodide, sulfate, or methyl sulfate, in a number to give electrical neutrality of the cationic component. Also in preferred cationic materials, L is equal to 1, p is from 1 to 12, preferably from 1 to 10, and Y is

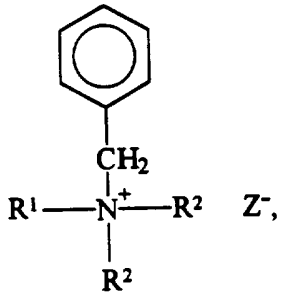


or mixtures thereof. However, L may be equal to two, thereby yielding cationic components containing two cationic charge centers. An example of a di-cationic component is given below:



In preferred cationic materials, described above, where m is equal to 1, it is preferred that x is equal to 3, and R^2 is a methyl group. Preferred compositions of this mono-long chain type include those in which R^1 is a C_{10} to C_{18} alkyl group. Particularly preferred components of this class include C_{16} (palmitylalkyl) trimethylammonium halide, tallowalkyl trimethylammonium halide and coconutalkyl trimethylammonium halide. In preferred systems, tallowalkyl trimethylammonium or coconutalkyl trimethylammonium materials are combined with oleoyl sarcosinate in sarcosinate/cationic ratios of from 1:1 to 10:1, more preferably 5:1 to 9:1.

Another preferred surfactant mixture utilizes mono- long chain cationic surfactants of the formula



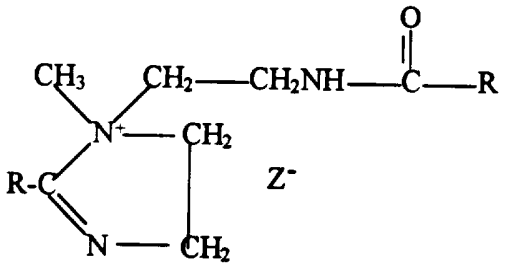
wherein R^1, R^2 and Z are as defined above, in combination with sarcosinate in sarcosinate:cationic ratios of from 5.1:1 to 15:1.

Useful di- long chain cationics include those of the above formula wherein m is 2. When m is equal to 2, it is preferred that x is equal to 2, and that R^2 is a methyl group. In this instance it is also preferred that R^1 is a C_{10} to C_{20} alkyl group. Particularly preferred cationic materials of the class include dicoconutalkyl (C_{12}-

C_{14}) dimethylammonium halide, distearylalkyl (C_{18}) dimethylammonium halide and ditallowalkyl (C_{16}-C_{18}) dimethylammonium halide materials.

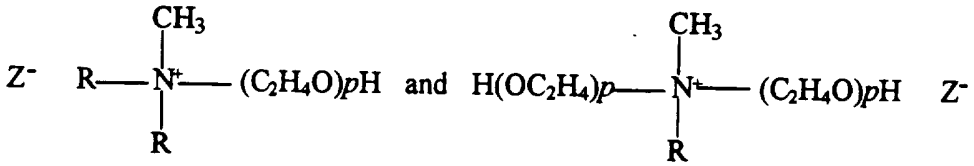
Where tri-long chain materials are used (m=3), it is preferred that x is equal to 1 and that R^2 is a methyl group. In these compositions it is preferred that R^1 is a C_8 to C_{11} alkyl group. Particularly preferred tri-long chain cationic materials include trioctylalkyl (C_8) methyl ammonium halide and tridecyalkyl (C_{10}) methyl ammonium halide.

Another preferred type of cationic surfactant useful in the surfactant mixtures employed in the present invention is of the imidazolinium variety. A particularly preferred surfactant of this type is one having the structural formula



wherein R is C_{10} to C_{20} alkyl, particularly C_{14} to C_{20} alkyl. These imidazolinium surfactants may be used alone as the cationic component in the compositions of the present invention, or may be used in mixtures, together with other cationic surfactants, such as those described above. In these mixtures, it is preferred that the ratio of the imidazolinium surfactant to the other cationic surfactant is from about 4:1 to about 1:4. Particularly preferred mixtures of this type include the imidazolinium surfactant, shown above, together with palmitylalkyl trimethylammonium chloride or coconutalkyl trimethylammonium chloride or a mixture of coconutalkyl trimethylammonium chloride and palmitylalkyl trimethylammonium chloride.

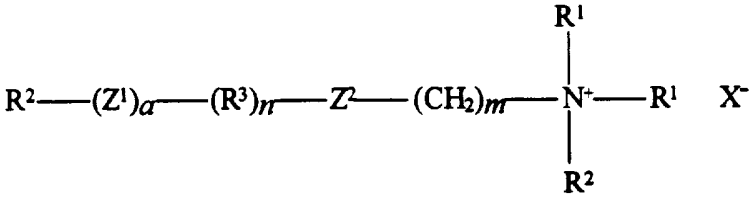
Another type of preferred cationic surfactant for use in the compositions of the present invention are the alkoxylated alkyl quaternaries. Examples of such compounds are given below:



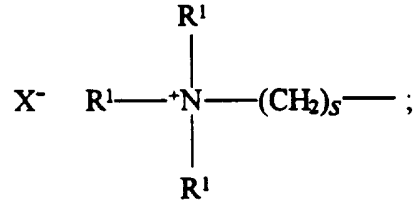
wherein each p is from 1 to 12, preferably from 1 to 10 (with the total ethylene oxide groups in a molecule not exceeding about 13), and each R is a C_{10} to C_{20} alkyl group. It is preferred that these compounds contain no more than a total of about 10, preferably no more than about 7, ethylene oxide groups in order to obtain the best removal of greasy and oily soils.

The compositions of the present invention are preferably substantially free of cationic compounds containing about 13 or more ethylene oxide groups. These compounds tend to be relatively non-biodegradable, do not enhance the cleaning or fabric conditioning benefits provided by the compositions and may, in some circumstances, decrease the overall laundering performance provided by them. It is to be noted that polyethoxylated cationic surfactants having relatively low levels of ethoxylation, such as those described above, exhibit better biodegradability characteristics and may be advantageously included in the compositions of the present invention.

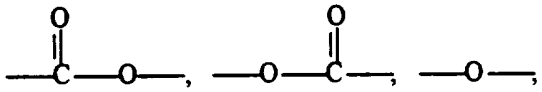
A particularly preferred type of cationic component, which is described in Letton; U.S. Patent 4,260,529; Issued April 7, 1981 (incorporated herein by reference) has the formula:

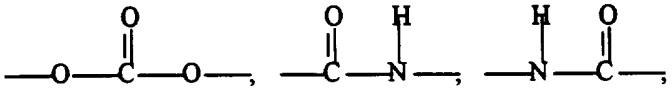


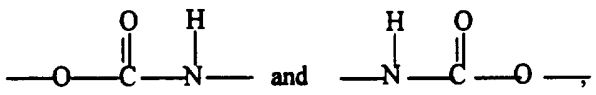
wherein R^1 is C_1 to C_4 alkyl or hydroxyalkyl; R^2 is C_5 to C_{30} straight or branched chain alkyl, alkenyl, alkyl phenyl, or



wherein s is from 0 to 5; R^3 is C_1 to C_{20} alkylene or alkenylene; a is 0 to 1, and n is 1 when a is 1; m is from 1 to 5; Z^1 and Z^2 are each selected from the group consisting of





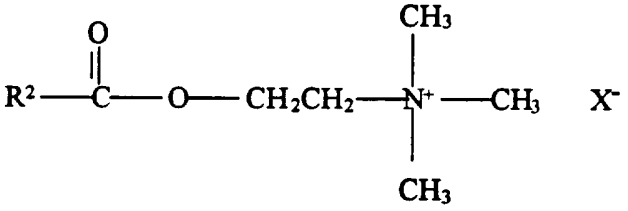


and wherein at least one of said groups is an ester, reverse ester, amide or reverse amide; and X is an anion which makes the compound at least water-dispersible,

preferably selected from the group consisting of halide, methyl sulfate, sulfate, and nitrate, more preferably chloride, bromide, iodide, methyl sulfate and sulfate.

In addition to the advantages of the other cationic surfactants disclosed herein, this particular cationic component is environmentally desirable, since it is biodegradable, yielding environmentally acceptable compounds, both in terms of its long alkyl chain and its nitrogen-containing segment. These preferred cationic components, when used in the compositions of the present invention, are employed in surfactant mixtures which have sarcosinate to cationic surfactant ratios of from 5.1:1 to about 100:1, particularly from 5.1:1 to about 50:1 most preferably from about 6:1 to 40:1, especially from about 6:1 to about 20:1.

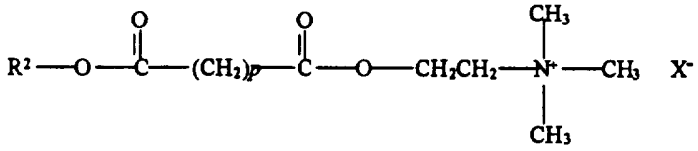
Particularly preferred cationic surfactants of this type are the choline ester derivatives having the following formula:

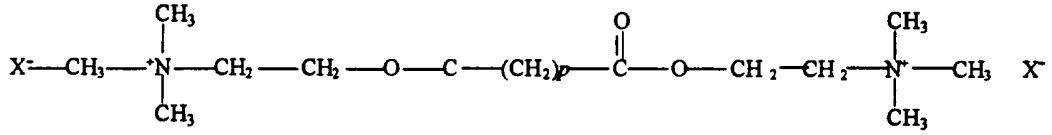


as well as those compounds in which the ester linkage in the above formula is replaced with a reverse ester, amide or reverse amide linkage.

Particularly preferred examples of this type of choline ester cationic surfactant include stearoyl choline ester quaternary ammonium halides ($R^2=C_{17}$ alkyl), palmitoyl choline ester quaternary ammonium halides ($R^2=C_{15}$ alkyl), myristoyl choline ester quaternary ammonium halides ($R^2=C_{11}$ alkyl), and tallowyl choline ester quaternary ammonium halides ($R^2=C_{15}$-C_{17} alkyl).

Additional preferred cationic components of the choline ester variety are given by the structural formulas below, wherein p may be from 0 to 20.

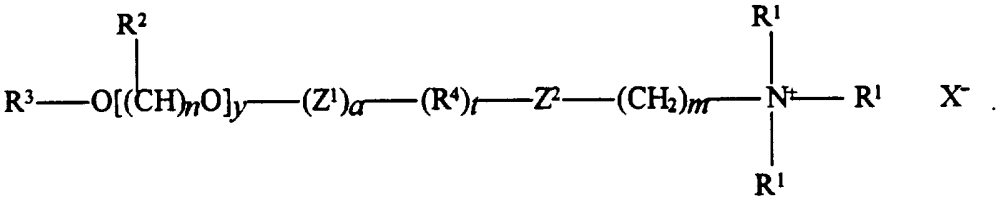




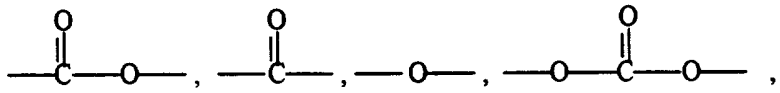
The preferred choline-derivative cationic substances, discussed above, may be prepared by the direct esterification of a fatty acid of the desired chain length with dimethylaminoethanol, in the presence of an acid catalyst. The reaction product is then quaternized with a methyl halide, forming the desired cationic material. The

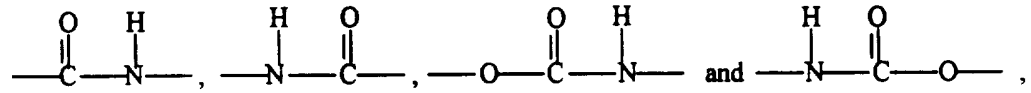
choline-derived cationic materials may also be prepared by the direct esterification of a long chain fatty acid of the desired chain length together with 2-haloethanol, in the presence of an acid catalyst material. The reaction product is then used to quaternize trimethylamine, forming the desired cationic component.

Another type of particularly preferred cationic material, described in the hereinbefore referenced U.S. 4,260,529, has the formula:

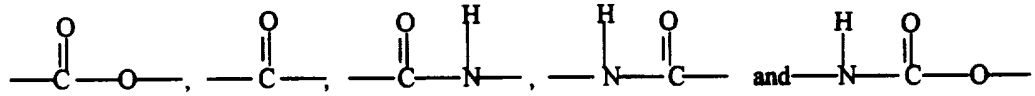


In the above formula, each R^1 is a C_1 to C_4 alkyl or hydroxyalkyl group, preferably a methyl group. Each R^2 is either hydrogen or C_1 to C_3 alkyl, preferably hydrogen. R^3 is a C_4 to C_{30} straight or branched chain alkyl, alkenyl, or alkylbenzyl group, preferably a C_8 to C_{18} alkyl group, most preferably a C_{12} alkyl group. R^4 is a C_1 to C_{10} alkylene or alkenylene group; n is from 2 to 4, preferably 2; y is from 1 to 20, preferably from about 1 to 10, most preferably about 7; a may be 0 or 1, and t may be 0 or 1, but t is 1 when a is 1; and m is from 1 to 5, preferably 2. Z^2 is selected from the group consisting





Z^1 is selected form the group consisting of:

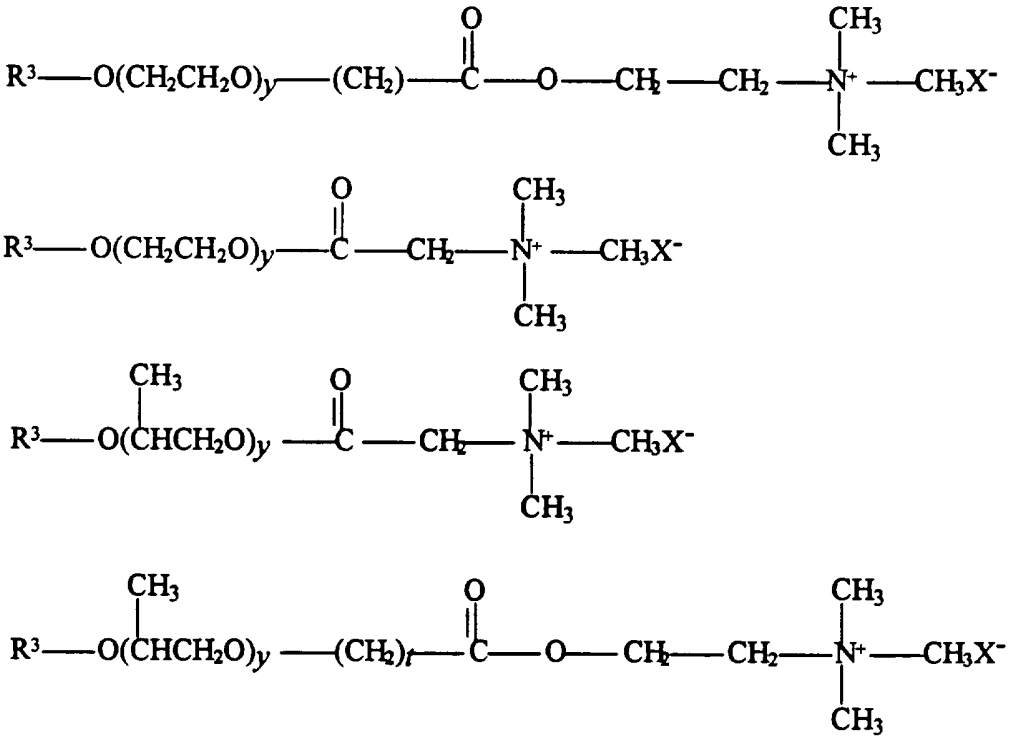


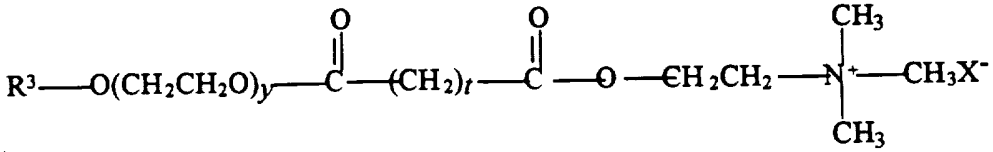
with at least one of Z^1 and Z^2 groups being selected form the group consisting of ester, reverse ester, amide or reverse amide. X is an anion which makes the compound at least water dispersible, and is selected from the group consisting of halides, methyl sulfate, sulfate, and nitrate, particularly chloride, bromide, iodide, methyl sulfate and sulfate. Mixtures of the above structures can also be used.

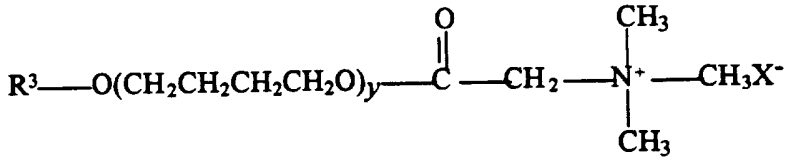
This particular type of cationic surfactant may be used in sarcosinate/cationic surfactant mixtures in the compositions of the present invention in sarcosinate to cationic ratios of from 5.1:1 to about 100:1, preferably from 5.1:1 to about 50:1, most preferably from about 6:1 to about 40:1, especially from about 6:1 to about 20:1. These surfactants, when used in the compositions of the present invention,

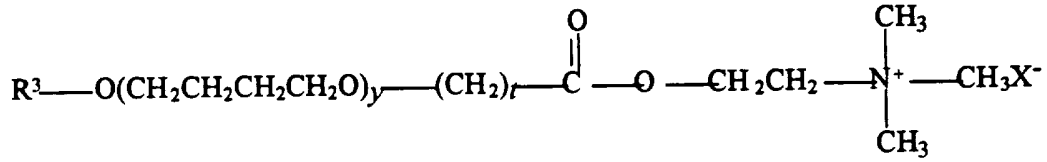
yield excellent particulate soil, body soil, and greasy and oil soil removal. In addition, the detergent compositions control static and soften fabrics laundered therewith, and inhibit the transfer of dyes in the wash solution. Further, these cationic surfactants are environmentally desirable, since both their long chain alkyl segments and their nitrogen segments are biodegradable.

Preferred embodiments of this type of cationic component are esters in which R^1 is a methyl group and Z^2 is an ester or reverse ester group. Particular examples of these compounds are given below, in which t is 0 or 1 and y is from 1 to 20.

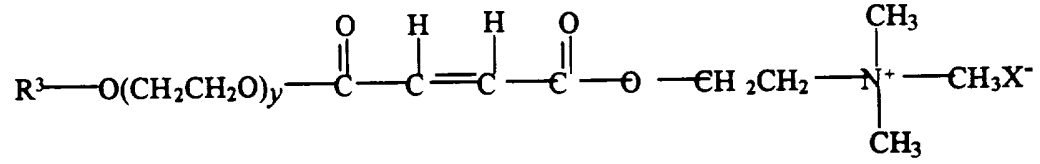








and



The preferred derivatives, described above, may be prepared by the reaction of a long chain alkyl polyalkoxy (preferably polyethoxy) carboxylate, having an alkyl chain of desired length, with oxalyl chloride, to form the corresponding acid chloride. The acid chloride is then reacted with dimethylaminoethanol to form the appropriate amine ester, which is then quaternized with a methyl halide to form the desired ester compound. Another way of preparing these compounds is by the direct esterification of the appropriate long chain ethoxylated carboxylic acid together with 2-haloethanol or dimethyl aminoethanol, in the presence of heat and an acid catalyst. The reaction product formed is then quaternized with methylhalide or used to quaternize trimethylamine to form the desired ester compound.

(C) Surfactant Mixture Concentration and Formulation

The compositions of the present invention comprise, by weight, from about 5% to 100%, preferably from about 10% to about 95%, and most preferably from about 20% to about 90% of a mixture of the particularly defined sarcosinate and cationic surfactants described hereinbefore in the ratios stated. It is preferred that the detergent compositions contain at least about 1% of the cationic component; otherwise, sufficient cationic surfactant may not be present in the wash solution to provide the desired cleaning and conditioning results. Further, preferred compositions do not contain more than about 10% of the cationic component, due to cost and commercial availability considerations.

Furthermore, the detergent compositions herein, containing the hereinbefore described sarcosinate/cationic surfactant mixtures, along with other optional detergent composition components described hereinafter, are preferably prepared in accordance with formulation criteria analogous to those such as the "cloud point" and Reduced Monomer Concentration (C_R) characteristics of the cationic surfactant, as described in Murphy; U.S. 4,259,217; Issued March 31, 1981. This '217 patent is incorporated herein by reference in its entirety.

(D) Optional Detergent Composition Components

In addition to the oleoyl sarcosinate and cationic surfactants essentially utilized, the detergent compositions herein may also comprise a wide variety of optional ingredients. Such optional ingredients include optional additional detersive surfactants, builders and other conventional detergent composition adjuvants.

a) Optional Detersive Surfactants

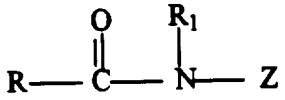
The detergent compositions herein may optionally comprise from about 1% to 80% by weight of an additional non-sarcosinate, non-cationic detersive surfactant. Preferably such compositions will comprise from about 5% to 50% by weight of this optional surfactant. Optional detersive surfactants utilized can be of the anionic, nonionic, zwitterionic, or ampholytic type or can comprise compatible mixtures of these surfactant types. Optional detersive surfactants useful herein are described in U.S. Patent 3,664,961, Norris, issued May 23, 1972, U.S. Patent 3,919,678, Laughlin et al., issued December 30, 1975, U.S. Patent 4,222,905, Cockrell, issued September 16, 1980, and in U.S. Patent 4,239,659, Murphy, issued December 16, 1980. All of these patents are incorporated herein by reference.

Of these optional surfactants, anionics and nonionics are preferred and non-sarcosinate anionics are most preferred. Such preferred anionic surfactants can themselves be of several different types. For example, water-soluble salts of the higher fatty acids, i.e., "soaps", are useful anionic surfactants in the compositions herein. This includes alkali metal soaps such as the sodium, potassium salts and the ammonium, alkylammonium and alkanolamine salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap. Soaps can also perform a builder function in the detergent compositions herein. Use of fatty acid soaps in the compositions herein will generally result in a diminution of sudsing. This effect should be taken into account by the formulator.

Additional non-sarcosinate anionic surfactants which suitable for use herein include the water-soluble salts, preferably the alkali metal, ammonium, alkylammonium and alkanolamine salts, or organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants are a) the sodium, potassium and ethanolamine alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8-C_{18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil; b) the sodium, potassium and ethanolamine alkyl polyethoxylate sulfates, particularly those in which the alkyl group contains from 10 to 22, preferably from 12 to 18 carbon atoms, and wherein the polyethoxylate chain contains from 1 to 15, preferably 1 to 6 ethoxylate moieties; and c) the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patents 2,220,099 and 2,477,383. Especially valuable are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 13, abbreviated as C_{11-13} LAS.

Preferred optional nonionic surfactants are those of the formula $R^1(OC_2H_4)_nOH$, wherein R^1 is a C_{10}-C_{16} alkyl group or a C_8-C_{12} alkyl phenyl group, and n is from 3 to about 80. Particularly preferred are condensation products of C_{12}-C_{15} alcohols with from about 3 to about 20 moles of ethylene oxide per mole of alcohol, e.g., C_{12}-C_{13} alcohol condensed with about 6.5 moles of ethylene oxide per mole of alcohol.

Additional suitable nonionic surfactants include polyhydroxy fatty acid amides of the formula



wherein R is a C_{9-17} alkyl or alkenyl, R_1 is a preferably a methyl or 3-methoxypropyl group and Z is glycityl derived from a reduced sugar or alkoxylated derivative thereof. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucityl oleamide and other C_{12}-C_{18} N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C_{10}-C_{18} N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C_{12}-C_{18} glucamides can be used for low sudsing. Processes for making polyhydroxy fatty acid amides are known and can be found in

Wilson, U.S. Patent 2,965,576 and Schwartz, U.S. Patent 2,703,798, the disclosures of which are incorporated herein by reference.

b) Detergent Builder

The detergent compositions herein may also optionally comprise from about 0.1% to 80% by weight of a detergent builder. Preferably such compositions in liquid form will comprise from about 1% to 10% by weight of the builder component. Preferably such compositions in granular form will comprise from about 1% to 50% by weight of the builder component. Detergent builders are well known in the art and can comprise, for example, phosphate salts as well as various organic and inorganic nonphosphorus builders.

Water-soluble, nonphosphorus organic builders useful herein include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxy sulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium, and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid. Other suitable polycarboxylates for use herein are the polyacetal carboxylates described in U.S. Patent 4,144,226, issued March 13, 1979 to Crutchfield et al., and U.S. Patent 4,246,495, issued March 27, 1979 to Crutchfield et al., both of which are incorporated herein by reference. Particularly preferred polycarboxylate builders are the oxydisuccinates and the ether carboxylate builder compositions comprising a combination of tartrate monosuccinate and tartrate disuccinate described in U.S. Patent 4,663,071, Bush et al., issued May 5, 1987, the disclosure of which is incorporated herein by reference.

Examples of suitable nonphosphorus, inorganic builders include the silicates, aluminosilicates, borates and carbonates. Particularly preferred are sodium and potassium carbonate, bicarbonate, sesquicarbonate, tetraborate decahydrate, and silicates having a weight ratio of SiO_2 to alkali metal oxide of from about 0.5 to about 4.0, preferably from about 1.0 to about 2.4. Also preferred are aluminosilicates including zeolites. such materials and their use as detergent builders are more fully discussed in Corkill et al., U.S. Patent No. 4,605,509, the disclosure of which is incorporated herein by reference. Also, crystalline layered silicates such as those discussed in Corkill et al., U.S. Patent No. 4,605,509, incorporated herein by reference, are suitable for use in the detergent composition of the invention.

c). Conventional Detergent Composition Ingredients

The detergent composition of the present invention can also include any number of additional optional ingredients. These include conventional detergent

composition components such as suds boosters or suds suppressers, anti-tarnish and anti-corrosion agents, soil suspending agents, soil release agents, germicides, pH adjusting agents, non-builder alkalinity sources, chelating agents, smectite clays, hardness ions such as Ca^{++} and/or Mg^{++} cations, enzymes, enzyme-stabilizing agents and perfumes. (See U.S. Patent 3,936,537, issued February 3, 1976 to Baskerville, Jr. et al., the disclosure of which is incorporated herein by reference.) Dye transfer inhibiting agents and add optical brighteners may also be included.

Chelating agents are described in U.S. Patent 4,663,071, Bush et al., from Column 17, line 54, through Column 18, line 68, incorporated herein by reference. Suds modifiers are also optional ingredients and are described in U.S. Patents 3,933,672, issued January 20, 1976, to Bartoletta et al., and 4,136,045, issued January 23,1979, to Gault et al., both incorporated herein by reference. Suitable smectite clays for use herein are described in U.S. Patent 4,762,645, Tucker et al., issued August 9, 1988, column 6, line 3 through Column 7, line 24, incorporated herein by reference. A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from about 1% to about 30%, more typically from about 5% to about 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from about 0.1% to about 60%, more typically from about 0.5% to about 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

While not essential to the detergent compositions of this invention, it is preferable to include an enzyme component. Suitable enzyme components are available from a wide variety of commercial sources. For example, suitable enzymes are available from NOVO Industries under product names T-Granulate™ and Savinase ™, and Gist-Brocades under product names Maxacal™ and Maxatase™. Included within the group of enzymes are proteases, amylases, lipases, cellulases and mixtures thereof. The enzyme concentration preferably should be from about 0% to about 5%, more preferably from about 0.001% to about 2.5%, and most preferably from about 0.01% to about 2%. Typically, proteases are used at an Activity Unit (Anson Unit) level of from about 0.001 to about 0.05, most preferably from about 0.002 to about 0.02, while amylases are used at an amylase unit level of from about 5

to about 5000, most preferably from about 50 to about 500 per gram of detergent composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniforms. Another suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985). Most preferred is what is called herein "Protease C", which is a variant of an alkaline serine protease from Bacillus, particularly Bacillus lentus, in which arginine replaced lysine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4; U.S. Patent No. 5,185,250; and U.S. Patent No. 5,204,015. Also preferred are protease which are described in copending application U.S. Serial No. 08/136,797, entitled Protease-containing Cleaning Compositions and copending Application U.S. Serial No. 08/136,626, entitled Bleaching Compositions Comprising Protease Enzymes, which are incorporated herein by reference. Genetically modified variants, particularly of Protease C, are also included herein.

(E) Detergent Composition Formulation

The detergent compositions according to the present invention can be in liquid, gel or granular forms. Such compositions can be prepared by combining the essential and optional components in the requisite concentrations in any suitable order and by an conventional means.

Granular compositions, for example, are generally made by combining base granule ingredients (e.g. surfactants, builders, water, etc.) as a slurry, and spray drying the resulting slurry to a low level of residual moisture (5-12%). The remaining dry ingredients can be admixed in granular powder form with the spray dried granules in a rotary mixing drum and the liquid ingredients (e.g. enzymes, binders and perfumes) can be sprayed onto the resulting granules to form the finished detergent composition. Granular compositions according to the present invention can also be in "compact form", i.e. greater than about 600 g/l. In such case, the granular detergent compositions according to the present invention will contain a lower amount of "inorganic filler salt", compared to conventional granular detergents; typical filler salts are alkali earth metal salts of sulfates and chlorides, typically sodium sulfate; "compact" detergents typically comprise not more than 10% filler salt.

Liquid detergent compositions can be prepared by admixing the essential and optional ingredients thereof in any desired order to provide compositions containing components in the requisite concentrations. Liquid compositions according to the present invention can also be in "compact form." In such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents.

The compositions of the present invention are formulated so as to have a pH of at least about 6.5, preferably greater than about 7 in the laundry solution at conventional usage concentrations in order to optimize cleaning performance on greasy and oily soils; acidic wash solution pH's tend to decrease performance on such soils. Preferably, the compositions herein are more alkaline in nature when placed in the laundry solution and have a pH of greater than about 7.5. Some of the cationic/sarcosinate systems of the present invention will attain optimum removal of greasy/oily soils at these higher pH's. In such systems, overall performance may be improved by varying the wash solution pH during the laundering process.

The compositions should generally be free of oily hydrocarbon materials, such as many dry cleaning solvents, mineral oil, paraffin oil and kerosene, because these materials (which are themselves oily in nature) load the washing liquor with excessive oily material, thereby diminishing the cleaning effectiveness of the compositions of this invention.

The cationic component should also be free of hydrazinium groups due to their relatively high toxicity level which makes them unsuitable for use in the compositions of this invention.

Preferred compositions contain sarcosinate to cationic surfactant ratios of from 5.1:1 to about 50:1, preferably from about 6:1 to about 40:1, particularly from about 6:1 to about 20:1. Greasy and oil soil removal is greatly enhanced at ratios between about 8:1 to about 20:1, the improvement in performance generally being most noticeable as the amount of sarcosinate is increased so that the ratio of sarcosinate to cationic surfactant becomes greater than 5.1:1 and approaches 8:1.

(F) Fabric Laundering and Pretreatment Process

The present invention also provides a process for laundering fabrics soiled with greasy/oily stains or soil. Such a process employs contacting these fabrics with an aqueous washing solution formed from an effective amount of the detergent compositions hereinbefore described. Contacting of fabrics with washing solution will generally occur under conditions of agitation.

Agitation is preferably provided in a washing machine for good cleaning. Washing is preferably followed by drying the wet fabric in a conventional clothes dryer. An effective amount of the liquid or granular detergent composition in the aqueous wash solution in the washing machine is preferably from about 500 to about 10000 ppm, more preferably from about 1000 to 3000 ppm.

The detergent compositions herein may also be used to pretreat fabrics containing greasy/oily soils or stains prior to washing such fabrics using conventional aqueous washing solutions. Such pretreatment involves the application of highly concentrated forms of the detergent compositions herein directly onto the greasy or oily stains or soils found on the fabric to be cleaned. For compositions herein in liquid or gel form, this will generally involve the direct application of the composition as is to the stain/soil on the fabric. For detergent compositions herein in granular form, pretreatment involves the application of an aqueous paste formed from such granular products. Aqueous pastes of this type will generally contain from about 1% to 50% water, preferably from about 5% to 20% water.

Pretreatment of greasy/oily stains or soils will generally occur for a period of from about 30 seconds to 24 hours prior to washing the pretreated soiled/stained substrate in conventional manner. More preferably, pretreatment times will range from about 1 to 180 minutes.

EXAMPLES

The following examples illustrate the compositions of the present invention but are not necessarily meant to limit or otherwise define the scope of the invention.

EXAMPLE I

Several liquid detergent compositions are prepared. The formulation for these compositions are set forth in Table I.

TABLE I

Liquid Detergent Compositions

Component	Wt. % A	B	C	D
Oleoyl sarcosinate	10.0	9.0	3.0	10.0
[1]Palmitylalkyl trimethylammonium chloride	5.0	---	2.3	---
[2]Coconutalkyl trimethylammonium chloride	---	4.0	---	3.5
C_{12}-C_{15} Alkyl ethoxylated sulfate	13.0	14.0	14.0	15.0
C_{12}-C_{14} N-methyl glucamide	6.0	6.0	6.0	6.0
C_{12}-C_{14} Fatty alcohol ethoxylate	3.0	3.0	3.0	3.0
C_{12}-C_{16} Fatty acid	9.0	6.8	14.0	14.0
Citric acid anhydrous	6.0	4.5	3.5	3.5
Diethylene triamine penta acetic acid (DTPP)	1.0	1.0	2.0	2.0
Monoethanolamine	13.2	12.7	12.8	11.0
Propanediol	12.7	14.5	13.1	10.0
Ethanol	1.8	1.8	4.7	5.4
Enzymes (protease, lipase, cellulase)	2.4	2.4	2.0	2.0
Terephthalate-based polymer	0.5	0.5	0.5	0.5
Boric acid	2.4	2.4	2.8	2.8
2-butyl-octanol	2.0	2.0	2.0	2.0
[3]DC 3421 R	0.3	0.4	0.3	0.4
[4]FF 400 R				
Tinopal UNPA-GX Brightener	0.075	0.21	---	---
Tinopal 5BM-GX Brightener	---	---	0.21	0.075
Water & minors	----------up to 100%----------			

[1]Commercially available as ADOGEN 444.

[2]Commercially available as ADOGEN 461.

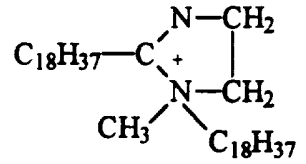
[3]DC 3421 is a silicone oil commercially available from Dow Corning.

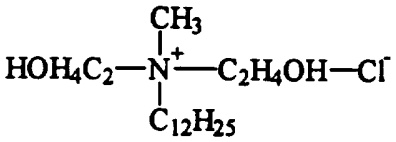
[4]Is a silicone glycol emulsifier available from Dow Corning.

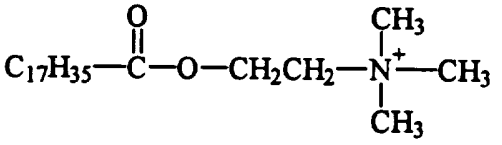
The compositions described in Table I are suitable for laundering fabrics soiled with grease or oil using aqueous washing solutions formed from such compositions. The compositions of Table I are also especially effective for pretreating fabrics with greasy or oily stains. To effect such pretreatment, greasy/oily stains and soils on the

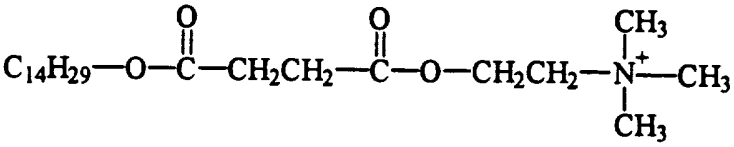
fabrics are contacted with the full strength Table I liquid compositions for 30 minutes prior to washing the fabrics in a conventional fabric laundering process.

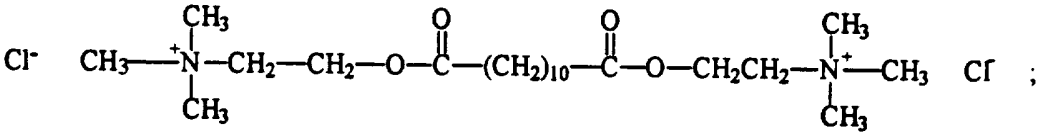
Compositions having substantially similar greasy/oily soil removal performance properties are realized when in the above compositions the cationic surfactants are replaced with an equivalent amount of decylalkyl trimethylammonium chloride, decylalkyl trimethylammonium hydroxide, C_{14} alkyl trimethylammonium chloride, distearylalkyl dimethylammonium chloride, tridecylalkyl methylammonium chloride, a mixture of methyl (1) tallowalkyl amido ethyl (2) tallowalkyl imidazolinium methyl sulfate (VARISOFT 475) together with coconutalkyl trimethylammonium chloride (ADOGEN 461) in a ratio of VARISOFT to ADOGEN of about 1:1, 3:3, 3:1, 2:3, or 1:3, or a mixture of palmitylalkyl trimethylammonium chloride with coconutalkyl trimethylammonium chloride in a ratio of palmityl to coconut compound of about 3:1, 2:1, 1:1, 1:2, or 1:3, or any surfactant corresponding to any of the following formulae:

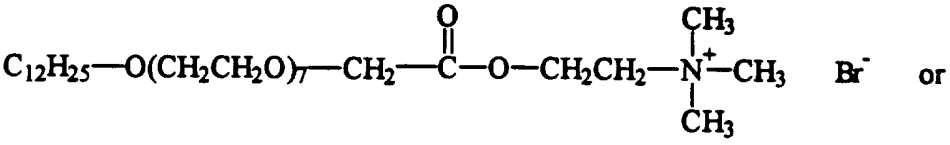


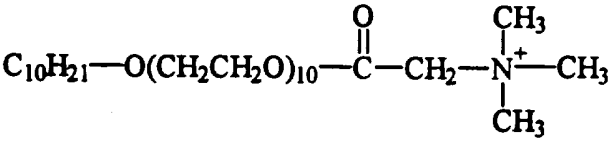












EXAMPLE II

Several compact granular detergent compositions are prepared. The formulations for these compositions are set forth in Table II.

TABLE II

Granular Detergent Compositions

	Wt. %		
Component	A	B	C
Oleoyl sarcosinate	5.8	6.1	10.2
[1]Palmitylalkyl trimethylammonium	1.0	—	1.0

chloride			
[2]Coconutalkyl trimethylammonium chloride	---	1.2	---
C_{11}-C_{14} Linear alkyl benzene sulfonate	6.17	---	---

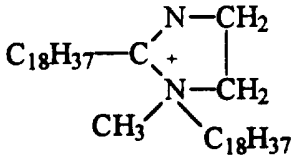
C_{12}-C_{15} Alkyl alkoxylated sulfate	---	4.0	---
C_{12}-C_{14} N-methyl glucamide	---	---	1.0
C_{45} alkyl sulfate	3.00	3.00	3.00
C_{45} alcohol 7 times ethoxylated	4.00	4.00	4.00
Tallow alcohol 11 times ethoxylated	1.80	1.80	1.80
Dispersant	0.07	0.07	0.07
Silicone fluid	0.80	0.80	0.80
Trisodium citrate	14.00	14.00	14.00
Citric acid	3.00	3.00	3.00
Zeolite	32.50	32.50	32.50
Maleic acid acrylic acid copolymer	5.00	5.00	5.00
Cellulase (active protein)	0.03	0.03	0.03
Alkalase/BAN	0.60	0.60	0.60
Lipase	0.36	0.36	0.36
Sodium silicate	2.00	2.00	2.00
Sodium sulfate	3.50	3.50	3.50
Brightener	0.20	0.20	0.20
Water & minors	-------Balance to 100%-------		

[1]Commercially available as ADOGEN 444.

[2]Commercially available as ADOGEN 461.

The compositions described in Table II are suitable for laundering fabrics soiled with grease or oil using aqueous washing solutions formed from such compositions.

Compositions having substantially similar greasy/oily soil removal performance properties are realized when in the above compositions the cationic surfactants are replaced with an equivalent amount of decylalkyl trimethylammonium chloride, decylalkyl trimethylammonium hydroxide, C_{14} alkyl trimethylammonium chloride, distearylalkyl dimethylammonium chloride, tridecylalkyl methylammonium chloride, a mixture of methyl (1) tallowalkyl amido ethyl (2) tallowalkyl imidazolinium methyl sulfate (VARISOFT 475) together with coconutalkyl trimethylammonium chloride (ADOGEN 461) in a ratio of VARISOFT to ADOGEN of about 1:1, 3:3, 3:1, 2:3, or 1:3, or a mixture of palmitylalkyl trimethylammonium chloride with coconutalkyl trimethylammonium chloride in a ratio of palmityl to coconut compound of about 3:1, 2:1, 1:1, 1:2, or 1:3, or any surfactant corresponding to any of the following formulae:



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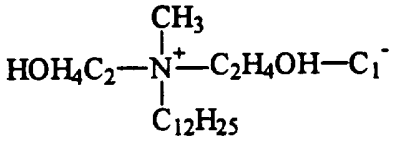

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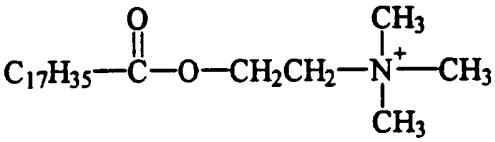

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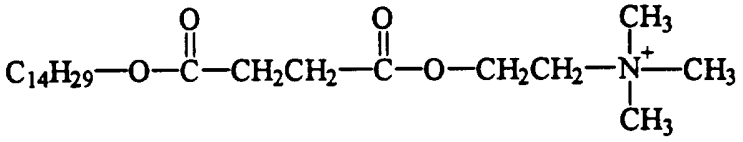

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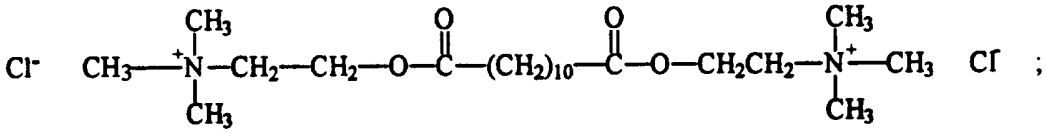

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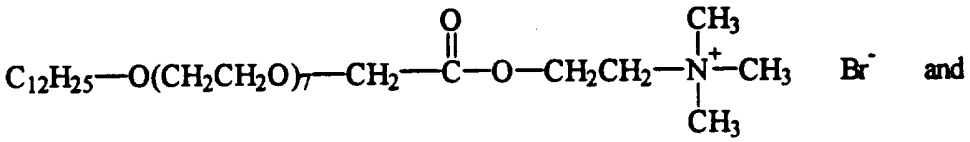
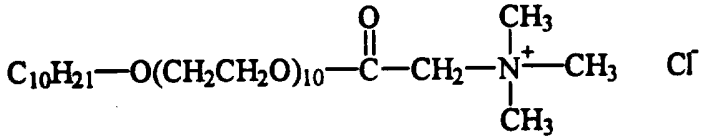


and



WHAT IS CLAIMED IS:

1. A detergent composition especially useful for removing greasy/oil stains from fabrics during fabric laundry operations, which composition comprises from 5% to 100% of a surfactant mixture comprising:

(a) an oleoyl sarcosinate surfactant of the formula:

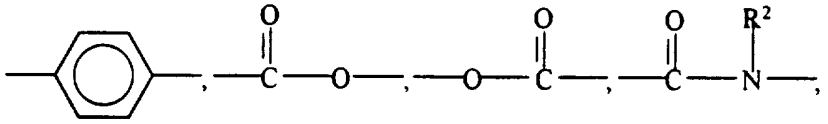
$$C_{17}H_{33}C(O)N(CH_3)CH_2COOM$$

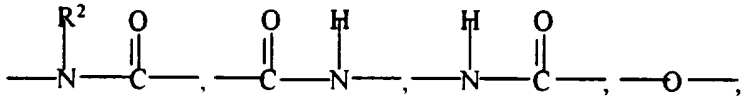
wherein M is H or a cationic moiety; and

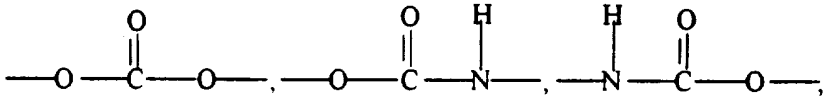
(b) a cationic surfactant which is free of hydrazinium groups and which has the formula

$$R_m{}^1R_x{}^2Y_LZ$$

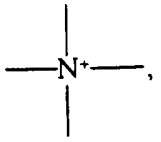
wherein each R^1 is an organic group containing a straight or branched alkyl or alkenyl group optionally substituted with up to 3 phenyl or hydroxy groups and optionally interrupted by up to 4 structures from

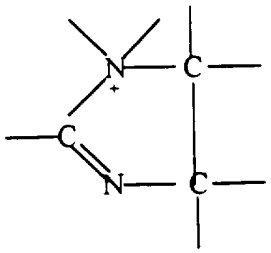


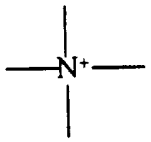




and mixtures thereof, each R^1 containing from 8 to 22 carbon atoms, and which may additionally contain up to 12 ethylene oxide groups; m is a number from 1 to 3; each R^2 is an alkyl or hydroxy alkyl group containing from 1 to 4 carbon atoms or a benzyl group, with no more than one R^2 in a molecule being benzyl; x is from 0 to 11, the remainder of any carbon atom positions being filled by hydrogens; Y is selected from

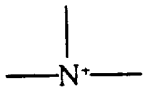
 ,

 ,

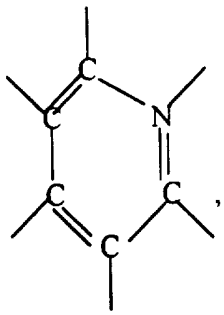
 , wherein p is from 1 to 12,

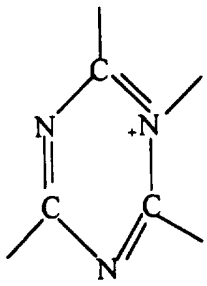
$(C_2H_4O)pH$

$(C_2H_4O)pH$

 , wherein each p is from 1 to 12,

$(C_2H_4O)pH$

 ,



and

and mixtures thereof;

L is 1 or 2, the Y groups being separated by a moiety selected from R^1 and R^2 analogs having from one to twenty-two carbon atoms and 2 free carbon single bonds when L is 2, and Z is an anion in a number sufficient to give electrical neutrality,

wherein the ratio of oleoyl sarcosinate surfactant to cationic surfactant ranges from 1:1 to 100:1; and

wherein said composition provides an aqueous washing solution pH of at least 6.5.

2. A composition according to Claim 1 wherein

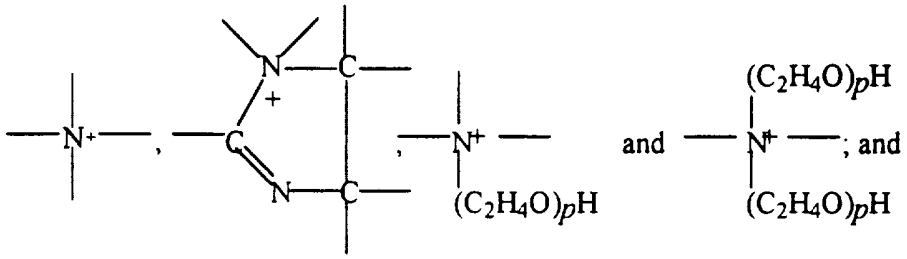
(a) in the formula for the oleoyl sarcosinate, M is selected from sodium and potassium; and

(b) in the formula for the cationic surfactant, L is equal to 1.

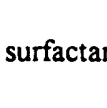
3. A composition according to either Claims 1or 2 wherein

(a) the sarcosinate/cationic surfactant mixture comprises from 10% to 95% of the composition; and

(b) in the formula for the cationic surfactant, p is from 1 to 10 and Y is selected from



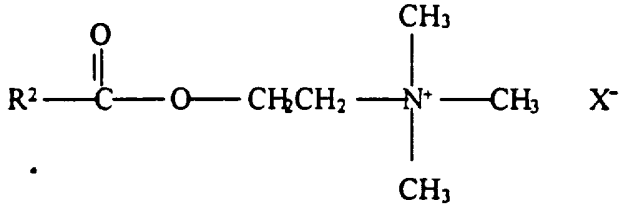
(c) the ratio of sarcosinate to cationic surfactant ranges from 5.1:1 to 50:1.

4. A composition according to any of Claims 1-3 wherein in the formula for the cationic surfactant Y is  .

5. A composition according to any of Claims 1-4 wherein in the formula for the cationic surfactant, m is 1; x is 3; R^1 is a C_{10} to C_{18} alkyl group and each R^2 is a methyl group.

6. A composition according to any of Claims 1-4 wherein in the formula for the cationic surfactant, m is 2; x is 2; each R^1 is a C_{10} to C_{20} alkyl group and each R^2 is a methyl group.

7. A composition according to any of Claims 1-3 wherein the cationic surfactant is a choline ester derivative of the formula:



wherein R^2 is C_5 to C_{30} straight or branched chain alkyl, alkenyl or alkylphenyl and x is an anion selected from halide, methylsulfate, sulfate and nitrate.

8. A composition according to Claim 7 wherein $R_2—\overset{O}{\overset{\|}{C}}—O—$ is selected from stearoyl, palmitoyl, myristoyl and tallowyl.

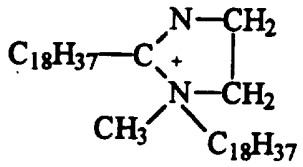
9. A detergent composition especially useful for removing greasy/oily stains from fabrics during fabric laundry operations, which composition comprises from 20% to 90% of a surfactant mixture comprising:

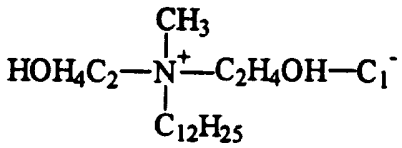
(a) an oleoyl sarcosinate surfactant of the formula:

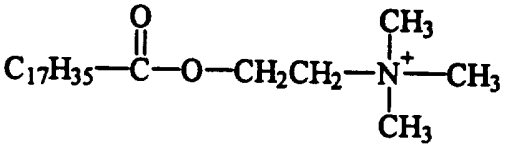
$$C_{17}H_{33}C(O)N(CH_3)CH_2COOM$$

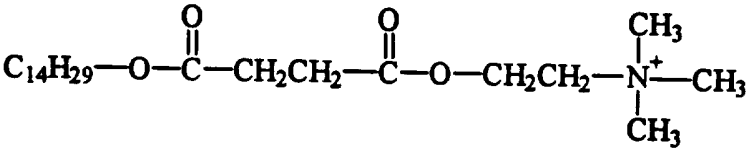
wherein M is H or a cationic moiety; and

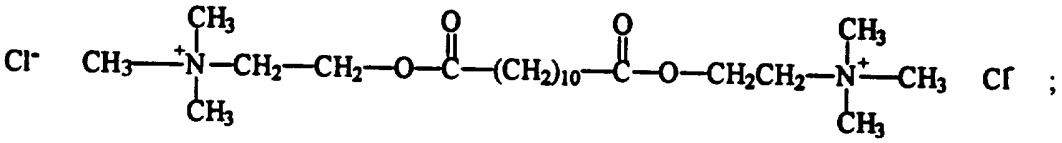
(b) a cationic surfactant selected from coconutalkyl trimethylammonium chloride, palmitylalkyl trimethylammonium chloride, decylalkyl trimethylammonium chloride, decylalkyl trimethylammonium hydroxide, C_{14} alkyl trimethylammonium chloride, distearylalkyl dimethylammonium chloride, tridecylalkyl methylammonium chloride, mixtures of methyl (1) tallowalkyl amido ethyl (2) tallowalkyl imidazolinium methyl sulfate and coconutalkyl trimethylammonium chloride in a ratio of methyl sulfate to chloride of 1:1, 3:3, 3:1, 2:3, or 1:3, mixtures of palmitylalkyl trimethylammonium chloride with coconutalkyl trimethylammonium chloride in a ratio of palmityl to coconut compound of 3:1; 2:1, 1:1, 1:2, or 1:3, and any cationic surfactant corresponding to any of the following formulae:

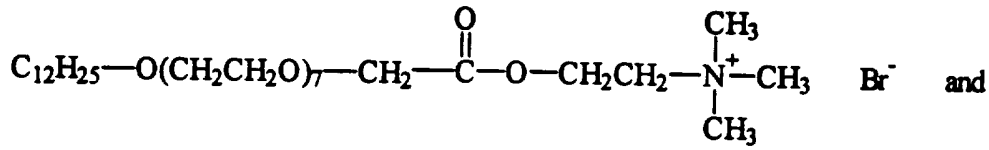




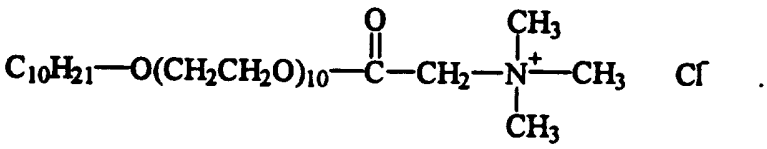








and



wherein the ratio of oleoyl sarcosinate surfactant to cationic surfactant range from about 5.1:1 to 50:1, and

wherein said composition provide an aqueous washing solution pH of at least about 7.5.

10. A detergent composition according to Claim 9 which in addition to the sarcosinate/cationic surfactant mixture also comprises:

(a) from about 5% to 50% by weight of an additional detersive surfactant selected from

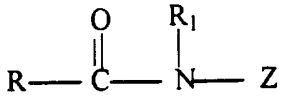
i) sodium and potassium alkylpolyethoxylate sulfates wherein the alkyl group contains from 10 to 22 carbon atoms and the polyethoxylate chain contains from 1 to 15 ethylene oxide moieties;

ii) sodium and potassium C9 to C15 alkyl benzene sulfonates;

iii) sodium and potassium C8 to C18 alkyl sulfates;

iv) nonionic surfactants of the formula $R^1(OC_2H_4)_nOH$ wherein R^1 is a C_{10} - C_{16} alkyl group or a C_8 - C_{12} alkylphenyl group and n is from 3 to 80;

v) polyhydroxy fatty acid amides of the formula



wherein R is a C_{9-17} alkyl or alkenyl, R_1 is a preferably a methyl or 3-methoxypropyl group and Z is glycityl derived from a reduced sugar or alkoxylated derivative thereof; and

vi) combinations of these surfactants; and

(b) from 1% to 50% by weight of a detergent builder selected from sodium carbonate, sodium silicate, crystalline layered silicates, aluminosilicates, oxydisuccinates and citrates.

11. A detergent composition according to any of Claims 1-10 which also comprises from 0.001% to 5% by weight of an enzyme component selected from proteases, lipases, amylases, cellulases and combinations of said enzymes.

12. A composition according to any of Claims 1-11 which additionally contains up to 80% of the composition of one or more detergent composition adjuvants selected from suds boosters, suds supressors, anti-tarnish and anti-corrosion agents, soil suspending agents, soil release agents, germicides, pH adjustment agents, non-builder alkalinity sources, chelating agents, smectite clays, hardness ions, enzyme-stabilizing agents, hydrotropes, carrier liquids, perfumes, optical brighteners and dye transfer inhibition agents.

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/US 95/06523

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D1/65

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)
IPC 6 C11D

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 practical, search terms used)

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,4 772 424 (GREEB H. R.) 20 September 1988 cited in the application see column 2, line 41 - column 4, line 22; claims ---	1-6,9, 10,12
A	EP,A,0 314 141 (KAO CORP.) 3 May 1989 see page 5, line 15 - line 37; claims 1,2; example 6 --- -/--	1-4,9, 10,12

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"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)

"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

"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

"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

"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.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
4 October 1995	13.10.95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Serbetsoglou, A

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/US 95/06523

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8806 Derwent Publications Ltd., London, GB; Class A97, AN 88-038463 & JP,A,62 295 997 (KANEBO KK) , 23 December 1987 cited in the application see abstract	1,9
A	GB,A,459 039 (I.G. FARBENINDUSTRIE AG.) 28 December 1936 see the whole document	1,9
A	US,A,4 181 634 (KENNEDY R. R. ET AL.) 1 January 1980 see column 5, line 56 - column 7, line 40; claims	1,9
A	WO,A,92 14810 (S.C. JOHNSON & SON INC.) 3 September 1992 see page 11, line 19 - page 12, line 5 see page 16, line 4 - page 19, line 9 see claims 1-9	1-4,9,10

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INTERNATIONAL SEARCH REPORT

Inter. nal Application No
PCT/US 95/06523

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A-4772424	20-09-88	CA-A-	1293692	31-12-91
		EP-A-	0229690	22-07-87
EP-A-0314141	03-05-89	JP-A-	1185397	24-07-89
		JP-C-	1813221	27-12-93
		JP-B-	5024196	07-04-93
		JP-A-	1117821	10-05-89
		JP-C-	1848591	07-06-94
		AT-T-	122380	15-05-95
		DE-D-	3853762	14-06-95
		US-A-	4931216	05-06-90
GB-A-459039		NONE		
US-A-4181634	01-01-80	US-A-	4110263	29-08-78
		AT-B-	376685	27-12-84
		AU-B-	518837	22-10-81
		AU-B-	3673378	06-12-79
		AU-B-	528547	05-05-83
		AU-B-	4693379	08-11-79
		BE-A-	876055	05-11-79
		CA-A-	1091157	09-12-80
		CA-A-	1110640	13-10-81
		CH-A-	650001	28-06-85
		CH-A-	640134	30-12-83
		FR-A,B	2424925	30-11-79
		GB-A-	1594290	30-07-81
		GB-A,B	2020289	14-11-79
		JP-C-	1493762	20-04-89
		JP-A-	55007262	19-01-80
		JP-B-	63040798	12-08-88
		JP-C-	1389955	23-07-87
		JP-A-	54007407	20-01-79
		JP-B-	61059283	16-12-86
		LU-A-	79829	07-12-78
		NL-A-	7806535	19-12-78
		NL-A-	7903526	07-11-79
		BE-A-	868215	18-12-78
WO-A-9214810	03-09-92	AU-B-	655621	05-01-95

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 95/06523

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A-9214810		AU-B-	9144691	15-09-92
		EP-A-	0640122	01-03-95
		JP-T-	6505036	09-06-94
		US-A-	5411585	02-05-95