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(54) Title: HANDWASH LAUNDRY DETERGENT COMPOSITIONS

(57) Abstract
The present invention relates to a handwash laundry detergent composition comprising a surfactant system comprising anionic, cationic and nonionic surfactants in specific ratios. Said system provides improved overall cleaning and skin mildness benefits.
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HANDWASH LAUNDRY DETERGENT COMPOSITIONS

Field of the Invention

The present invention is directed to a handwash laundry detergent composition. The laundry detergent composition comprises a surfactant system comprising anionic, nonionic and cationic surfactants which provide improved cleaning and high sudsing and skin mildness benefits.

Background of the Invention

Detergent compositions in the form of synthetic detergent granules, liquids and bars are used in many areas throughout the world for the purpose of laundering soiled clothes. In areas where mechanical washing machines are not prevalent, laundering soiled clothes and fabrics generally entails a handwashing method of laundering.

Detergent compositions formulated for the handwash laundering of fabrics are required to provide a number of consumer relevant performance benefits particularly with respect to cleaning, skin mildness and sudsing which are required to be applicable over a wide range of wash conditions and habits.
In order to address the consumer performance demands with respect to cleaning, current handwash laundry detergent compositions frequently comprise high levels of surfactants. Generally, formulators of detergent compositions used for hand laundering operations incorporate high levels of anionic surfactants, especially linear alkylbenzene sulphonate and alkyl sulphate surfactants. The linear alkylbenzene sulphonate surfactants have been frequently utilised due to their ability to provide excellent cleaning of grease and oil stains. Alkyl sulphate surfactants are desirable because they provide excellent particulate soil removal performance. Furthermore both of these surfactants are effective in both hot and cold wash water conditions.

However, many anionic surfactants, particularly when present at high concentrations, are harsh towards the skin. Handwash laundering methods involve the exposure of the hands and arms of the user to the aqueous laundering solutions in which the detergent composition is contained. Repeated exposure to laundering solutions during handwashing operations can lead to skin irritation which can eventually lead to skin lesions or other skin damage. Many attempts have been made by formulators of handwash laundry detergents to alleviate the detrimental effects of hand laundering operations on the arms and hands of users of such detergent products. It is therefore desirable to provide a laundry detergent composition suitable for handwash operations which exhibits mildness towards the skin of users while maintaining or improving cleaning performance.

Additionally, in certain geographies the wash solution is often repeatedly used for a number of laundering operations. This results in a decrease in the amount of detergent actives present and an increase in the amount of soils present in the wash liquor. Thus, in addition, to good soil and stain removal, it is also essential that the detergent composition provides the wash liquor with excellent soil suspension properties. This is particularly important for the effective laundering of highly soiled fabrics.

Furthermore, the performance of a handwash detergent formulation is generally equated by consumers with its ability to form and retain a
high sudsing level. Thus, it is desirable that laundry detergents which are utilised in handwashing operations have a high degree of sudsing or lathering.

Therefore, it is an aim of the present invention to provide a handwash laundry detergent composition that exhibits improved cleaning performance over a broad range of temperatures and skin mildness benefits to the hands and arms of users. In addition it is a further aim of the present invention to provide a detergent composition which maintains excellent sudsing or lathering features.

It has now been found that these objectives can be achieved by the combination of anionic, cationic and nonionic surfactants in specific ratios.


US Application 08/078494 discloses a detergent composition comprising polyhydroxy fatty acid amide and anionic surfactants at certain ratios. U.S. Patent Nos. 2,982,737; 3,312,627; and 5,254,281 disclose laundry detergent or toilet bars including various surfactants.

**Summary of the Invention**

The present invention is a handwash laundry detergent composition comprising from 15% to 35% of a surfactant system comprising anionic, nonionic and cationic surfactants, characterised in that said nonionic surfactant comprises a polyhydroxy fatty acid amide and the ratio of said anionic surfactant to said cationic surfactant is from 3:1 to 15:1 and the ratio of said cationic surfactant to said nonionic surfactant is from 2:1 to 1:10.

The present invention also relates to a method of laundering soiled fabrics, whereby said fabrics are manually contacted with an effective
amount of a laundering detergent composition according to the present invention, in an aqueous solution.

All percentages, amounts and ratios are given as weight of the composition unless otherwise specified.

**Detailed Description of the Invention**

The present invention is a handwash laundry detergent composition comprising from 15% to 35%, preferably from 18% to 30%, more preferably from 18% to 25% of a surfactant system. Said system comprises anionic, nonionic and cationic surfactants.

According to the present invention the ratio of said anionic surfactant to said cationic surfactant is from 3:1 to 15:1, preferably from 5:1 to 15:1, most preferably from 7:1 to 15:1. The ratio of said cationic surfactant to said nonionic surfactant is from 2:1 to 1:10, preferably from 2:1 to 1:7, more preferably from 2:1 to 1:5. Said system has been found to deliver improved cleaning performance and skin mildness for handwash detergent compositions.

**Anionic Surfactant**

According to the present invention the detergent composition comprises as an essential feature an anionic surfactant. The anionic surfactant may be essentially any anionic surfactant, including anionic sulphate, sulphonate or carboxylate surfactant.

According to the present invention the detergent composition may comprise from 8% to 25%, preferably from 10% to 20%, more preferably from 12% to 20% of said anionic surfactant.
Anionic sulphate surfactant

The anionic sulphate surfactant may be any organic sulphate surfactant. It is preferably selected from the group consisting of C_{10}-C_{16} alkyl sulphate 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 sulphate, C_{9}-C_{17}-N-(C_{2}-C_{4} hydroxyalkyl) glucamine sulphate, and mixtures thereof, wherein the C_{9}-C_{17} acyl group is derived from coconut or palm kernel oil, as described in US patent 2 717 894. More preferably, the anionic sulphate surfactant is a C_{10}-C_{16} alkyl sulphate 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 sulphate surfactants comprises a primary alkyl ethoxy sulphate 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 sulphate which has been ethoxylated with from about 3 to about 10 moles of ethylene oxide per molecule is preferred.

Conventional base-catalysed 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.

The counterion for the anionic sulphate 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 sulphonate surfactant

Anionic sulphonate surfactants suitable for use herein include, for example, the salts (e.g. alkali metal salts) of C9-C20 linear alkylbenzene sulphonates, C8-C22 primary or secondary alkane sulphonates, C8-C24 olefin sulphonates, sulphonated polycarboxylic acids, alkyl glycerol sulphonates, fatty acyl glycerol sulphonates, fatty oleyl glycerol sulphonates, paraffin sulphonates, and any mixtures thereof.

Anionic alkyl ethoxy carboxylate surfactant

Alkyl ethoxy carboxylates suitable for use herein include those with the formula RO(CH2CH2O)x CH2C00-M+ wherein R is a C12 to C16 alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20%, preferably less than 15%, most preferably less than 10%, and the amount of material where x is greater than 7, is less than 25%, preferably less than 15%, most preferably less than 10%, the average x is from 2 to 4 when the average R is C13 or less, and the average x is from 3 to 6 when the average R is greater than C13, 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 C12 to C14 alkyl group.

Anionic alkyl polyethoxy polycarboxylate surfactant

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

\[
\text{R} \cdot \text{O} \cdot (\text{CH} - \text{CH} - \text{O}) \cdot \text{x} \cdot \text{R3}
\]

\[
\text{R1} \quad \text{R2}
\]

wherein R is a C6 to C18 alkyl group, x is from 1 to 25, R1 and R2 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 11-15 total carbon atoms, although slightly more (e.g., up to 16) can be tolerated, 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 $R_3^3 CH(R_4^4)COOM$, wherein $R_3$ is $CH_3(CH_2)x$ and $R_4$ is $CH_3(CH_2)y$, wherein $y$ can be 0 or an integer from 1 to 4, $x$ is an integer from 4 to 10 and the sum of $(x + y)$ is 6-14, preferably 7-13, most preferably 12.

B. Another class of secondary soaps useful herein comprises those carboxyl compounds wherein the carboxyl substituent is on a ring hydrocarbonyl unit, i.e., secondary soaps of the formula $R_5^5-R_6^6-COOM$, 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)_{0-(CH2)}_{p-(CHR)}_{q-CH3}, wherein each R is C_{1-C4} 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-C5} alkyl substituted ammonium. Sodium is convenient, as is diethanolammonium.

Preferred secondary soap surfactants for use herein are watersoluble 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, 2-pentyl-1-heptanoic acid and isopentadecanoic acid.

Other anionic surfactants useful for detressive 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 sulphates, alkyl phenol ethylene oxide ether sulphates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates, N-acyl sarcosinates, branched primary alkyl sulphates, alkyl polyethoxy carboxylates such as those of the formula RO(CH\_2CH\_2O)_kCH\_2COO-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 neutralised 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

According to the present invention the detergent composition comprises as an essential feature from 1% to 10%, preferably from 2% to 8%, more preferably from 3% to 7.5% of nonionic surfactant, comprising a polyhydroxy fatty acid amide.

Nonionic polyhydroxy fatty acid amide surfactant

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

\[
\begin{array}{c}
O \\
R^{1} \\
R^{2}-C-N-Z
\end{array}
\]

wherein \( R^{1} \) is H or a C1-C4 hydrocarbaryl, 2-hydroxy ethyl, 2-hydroxy propyl and \( R^{2} \) is a C5-C31 hydrocarbaryl and \( Z \) is a polyhydroxyhydrocarbaryl having a linear hydrocarbaryl chain with at least 3 hydroxy groups directly connected to the chain or an alkoxylated derivative thereof. Preferably \( R^{1} \) is a methyl, \( R^{2} \) is a straight chain C11-C15 alkyl or alkenyl such as coconut alkyl or mixtures thereof and \( Z \) is derived from a reducing sugar such as glucose, fructose, maltose, lactose in a reductive amination reaction.

Other polyhydroxy fatty acid amides suitable for use herein are gemini polyhydroxy fatty acid amides having the formula:

\[
\begin{array}{c}
Z & Z \\
N-X-N \\
O-C & C=O \\
R & R^{'}
\end{array}
\]

wherein: \( X \) is a bridging group having from about 2 to about 200 atoms; \( Z \) and \( Z' \) are the same or different alcohol-containing moieties having two or more hydroxyl groups (e.g., glycerol, and units derived from reducing sugars such as glucose, maltose and the like), or either one (but not both) of
Z or Z' is hydrogen; and R and R' are the same or different hydrocarbyl moieties having from about 1 to about 21 carbon atoms and can be saturated, branched or unsaturated (e.g., oleoyl) and mixtures thereof.

Preferred X groups are selected from substituted or unsubstituted, branched or linear alkyl, ether alkyl, amino alkyl, or amido alkyl moieties having from about 2 to about 15 carbon atoms. Preferred alkyl moieties are unsubstituted, linear alkyl moieties having the formula -(CH₂)ₙ-, wherein n is an integer from 2 to about 15, preferably from 2 to about 10, and most preferably from 2 to about 6; and also unsubstituted, branched alkyl moieties having from 3 to about 15 carbon atoms, preferably from 3 to about 10 carbon atoms, and most preferably from 3 to about 6 carbon atoms. Most preferred are ethylene and propylene (branched or linear) alkyl moieties. Also preferred are unsubstituted, branched or linear ether alkyl moieties having the formula -R²-(O-R²)ₘ-, wherein each R² is independently selected from C₂-C₈ branched or linear alkyl and/or aryl moieties (preferably ethyl, propyl or combinations thereof) and m is an integer from 1 to about 5. X may also be unsubstituted, branched or linear amino and/or amido alkyl moieties having the formula -R²-(N(R³)-R²)ₘ-, wherein each R² is independently selected from C₂-C₈ branched or linear alkyl and/or aryl moieties (preferably ethyl, propyl or combinations thereof), m is an integer from 1 to about 5, and R³ is selected from hydrogen, C₁-C₅ alkyl, and -C(O)R⁴-, wherein R⁴ is C₁-C₂₁ alkyl, including -C(O)R. The X moiety may be derived from commercially available amine compounds such as, for example, JefferminesR (supplied by Texaco) such as JED600, JEDR148, JEDR192, JED230, JED2000, J-D230 and J-D400.

Preferred X moieties therefore include: -(CH₂)₂-, -(CH₂)₃-, -(CH₂)₅-, -(CH₂)₆-, -CH₂CH(CH₃)(CH₂)₃-, -(CH₂)₂-O-(CH₂)₂-, -(CH₂)₃-O-(CH₂)₃-, -(CH₂)₂-O-(CH₂)₃-, -(CH₂)₂-O-(CH₂)₂-O-(CH₂)₂-, -(CH₂)₃-O-(CH₂)₂-O-(CH₂)₃-, -(CH₂)₂-O-(CH₂)₂-O-(CH₂)₂-, -(CH₂)₂- NH-(CH₂)₂-, -(CH₂)₃-NH-(CH₂)₃-, -(CH₂)₂-NH-(CH₂)₃-, -(CH₂)₂-N(CH(O)R)-(CH₂)₂-, -(CH₂)₃-N(CH(O)R)-(CH₂)₂-, -(CH₂)₂-N(CH(O)R)-(CH₂)₃-, -(CH₂)₂-NH(CH₆H₄)NH-(CH₂)₂-, -(CH₂)₃-NH(CH₆H₄)NH-(CH₂)₃-, -(CH₂)₂-NHCH₂(CH₆H₄)CH₂NH-(CH₂)₂-, -(CH₂)₃-NHCH₂(CH₆H₄)CH₂NH-(CH₂)₃-, etc.
Preferred Z and Z' groups are independently selected from polyhydroxyhydrocarbyl moieties having a linear hydrocarbyl chain with at least 2 hydroxyls (in the case of glycerol) or at least 3 hydroxyls (in the case of other sugars) directly connected to the chain, or an alkoxylated derivative (preferably ethoxylated or propoxylated) thereof. Z and Z' preferably will be derived from a reducing sugar, more preferably Z and/or Z' is a glycicyl moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. 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 and Z'. It should be understood that it is by no means intended to exclude other suitable raw materials. Z and/or Z' preferably will be selected from the group consisting of -CH2-(CHOH)-p-CH2OH, -CH(CH2OH)-(CHOH)p-1-CH2OH, -CH2-(CHOH)2(CHOR1)(CHOH)-CH2OH, where p is an integer from 1 to 5, inclusive, and R1 is H or a cyclic mono- or polysaccharide, and alkoxylated derivatives thereof. Most preferred are glycyls wherein p is 4, particularly -CH2-(CHOH)4-CH2OH.

Preferred R and R' groups are independently selected from C3-C21 hydrocarbyl moieties, preferably straight or branched chain C3-C13 alkyl or alkenyl, more preferably straight chain C5-C11 alkyl or alkenyl, most preferably straight chain C5-C9 alkyl or alkenyl, or mixtures thereof. R-CO-N< and/or R'-CO-N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

Examples of such compounds therefore include, but are not limited to:

- \( \text{CH}_3(\text{CH}_2)_6\text{C(O)N[CH}_2(\text{CHOH})_4\text{CH}_2\text{OH]}-(\text{CH}_2)_2-[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC(O)(CH}_2)_6\text{CH}_3; \)
- \( \text{CH}_3(\text{CH}_2)_8\text{C(O)N[CH}_2(\text{CHOH})_4\text{CH}_2\text{OH]}-(\text{CH}_2)_2-[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC(O)(CH}_2)_8\text{CH}_3; \)
- \( \text{CH}_3(\text{CH}_2)_{10}\text{C(O)N[CH}_2(\text{CHOH})_4\text{CH}_2\text{OH]}-(\text{CH}_2)_2-[\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}]\text{NC(O)(CH}_2)_{10}\text{CH}_3; \)
- \( \text{CH}_3(\text{CH}_2)_8\text{C(O)N[CH}_2(\text{CHOH})_4\text{CH}_2\text{OH]}-(\text{CH}_2)_2-O-(\text{CH}_2)_2-O-(\text{CH}_2)_2- \)
[CH₂(CHOH)₄CH₂OH]NC(O)(CH₂)₈CH₃;
CH₃(CH₂)₈C(O)N[CH₂(CHOH)₄CH₂OH]-CH₂CH(CH₃)(CH₂)₃-
[CH₂(CHOH)₄CH₂OH]NC(O)(CH₂)₈CH₃;
CH₃(CH₂)₈C(O)N[CH₂(CHOH)₄CH₂OH]-(CH₂)₃-O-(CH₂)₂-O-(CH₂)₃-
[CH₂(CHOH)₄CH₂OH]NC(O)(CH₂)₈CH₃;
CH₃(CH₂)₃CH(CH₂CH₃)C(O)N[CH₂(CHOH)₄CH₂OH]-(CH₂)₂-
[CH₂(CHOH)₄CH₂OH]NC(O)(CH₂CH₃)(CH₂)₃CH₃;
CH₃(CH₂)₆C(O)N[CH₂(CHOH)₄CH₂OH]-(CH₂)₃-O-(CH₂)₂-O-(CH₂)₃-
[CH₂(CHOH)₄CH₂OH]NC(O)(CH₂)₆CH₃;
CH₃(CH₂)₄C(O)N[CH₂(CHOH)₄CH₂OH]-(CH₂)₃-O-(CH₂)₂-O-(CH₂)₃-
[CH₂(CHOH)₄CH₂OH]NC(O)(CH₂)₈CH₃;
C₆H₅C(O)N[CH₂(CHOH)₄CH₂OH]-(CH₂)₃-O-(CH₂)₂-O-(CH₂)₃-
[CH₂(CHOH)₄CH₂OH]NC(O)C₆H₅;
CH₃(CH₂)₄C(O)N[CH₂(CHOH)₄CH₂OH]-(CH₂)₂-
[CH₂(CHOH)₄CH₂OH]NC(O)(CH₂)₈CH₃.

These compounds can be readily synthesised from the following disugar diamines:
HN[CH₂(CHOH)₄CH₂OH]-(CH₂)₂-
[CH₂(CHOH)₄CH₂OH]NH;
HN[CH₂(CHOH)₄CH₂OH]-
CH₂CH(CH₃)(CH₂)₃-[CH₂(CHOH)₄CH₂OH]NH;
HN[CH₂(CHOH)₄CH₂OH]-(CH₂)₂-O-(CH₂)₂-O-(CH₂)₂-
[CH₂(CHOH)₄CH₂OH]NH;
HN[CH₂(CHOH)₄CH₂OH]-(CH₂)₃-O-(CH₂)₂-O-(CH₂)₃-[CH₂(CHOH)₄CH₂OH]NH;
HN[CH₂(CHOH)₄CH₂OH]-(CH₂)₃-[CH₂(CHOH)₄CH₂OH]NH.

and

According to the present invention the nonionic surfactant may comprise, in addition to the polyhydroxy fatty acid amide, other nonionic surfactants, particularly alkoxyalted nonionic surfactants.

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.
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 6 to 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from 8 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 8 to 14 carbon atoms with from about 3 to about 9 moles of ethylene oxide per mole of alcohol. Examples of commercially available nonionic surfactants of this type include Tergitol™ 15-S-9 (the condensation product of C_{11}-C_{15} linear alcohol with 9 moles ethylene oxide), Tergitol™ 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™ 45-9 (the condensation product of C_{14}-C_{15} linear alcohol with 9 moles of ethylene oxide), Neodol™ 23-6.5 (the condensation product of C_{12}-C_{13} linear alcohol with 6.54 moles of ethylene oxide), Neodol™ 45-7 (the condensation product of C_{14}-C_{15} linear alcohol with 7 moles of ethylene oxide), Neodol™ 45-4 (the condensation product of C_{14}-C_{15} linear alcohol with 4 moles of ethylene oxide), Neodol™ 23-3 (the condensation product of C_{12}-C_{13} linear alcohol with 3 moles of ethylene oxide) Dobanol™ C_{12}-C_{15} E5, (the condensation product of C_{12}-C_{15} linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, KyroTM EOBN (the condensation product of C_{13}-C_{15} alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, Dobanol 91 and Dobanol 25 marketed by the Shell Chemical Company and Lial 111 marketed by Enichem.

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. 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. 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 containing 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. The preferred alkylpolyglycosides have the formula

\[ R^2O(C_nH_{2n}O)_{t}(\text{glycosyl})_x \]

wherein R2 is selected from the group consisting of alkyl, alklyphenyl, 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 and t is from 0 to 10. The glycosyl is preferably derived from glucose.

**Cationic surfactant**

According to the present invention another essential ingredient of the compositions of the present invention is a cationic surfactant. The detergent compositions of the present invention comprise from 0.1% to 10%, preferably from 0.5% to 5%, most preferably from 0.5% to 3% of a cationic surfactant.

Cationic surfactants suitable for use herein are according to the formula

\[ R_m^{1} R_x^{2} Y_{LZ} \]

wherein each \( R^1 \) is an organic group containing a straight or branched alkyl or alkenyl group optionally substituted with up to three phenyl or hydroxy groups and optionally interrupted by up to four structures selected from the following group:

\[ \text{and mixtures thereof and which contains from about 8 to 22 carbon atoms. The } R^1 \text{ groups may additionally contain up to 12 ethoxy groups.} \]

\[ m \text{ is a number from 1 to 3. No more than one } R^1 \text{ group in a molecule can have 16 or more carbon atoms when } m \text{ is 2 or no more than 12 carbon atoms when } m \text{ is 3. Each } R^2 \text{ group is an alkyl or a hydroxy alkyl group containing from 1 to 4 carbon atoms or a benzyl group with no more than one } R^2 \text{ group in a molecule being benzyl, and } x \text{ is a number from 0 to 11, preferably from 0 to 6. The remainder of any carbon atom positions on the } Y \text{ group are filled by hydrogens. } Y \text{ is selected from the group consisting of:} \]
and mixtures thereof. L is 1 or 2, with the Y groups being separated by a moiety selected from R¹ and R² analogues (preferably alkylene or alkenylene) having from 1 to 22 carbon atoms and two free carbon single
bonds when L is 2. Z is a water soluble anion such as a halide, sulphate, methyl sulphate, hydroxide or nitrate anion, particularly preferred being chloride, bromide, iodide, sulphate or methyl sulphate anions in a number to give electrical neutrality of the cationic component.

Examples of such cationic surfactants include the ammonium surfactants such as alkylidimethylammonium halogenides and surfactants having the formula:

$$[R^2(OR^3)_y][R^4(OR^3)_y]_2R^5N^+X^-$$

wherein $R^2$ is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each $R^3$ is selected from the group consisting of $\text{CH}_2\text{CH}_2^-$, $\text{-CH}_2\text{CH}(\text{CH}_3^-)$, $\text{-CH}_2\text{CH(}\text{CH}_2\text{OH})^-$, $\text{-CH}_2\text{CH}_2\text{CH}_2^-$, and mixtures thereof; each $R^4$ is selected from the group consisting of $\text{C}_1$-$\text{C}_4$ alkyl, $\text{C}_1$-$\text{C}_4$ hydroxyalkyl, benzyl ring structures formed by joining the two $R^4$ groups, $\text{-CH}_2\text{CHOH}$- $\text{CHOH}$COR$^6$ $\text{CHOH}$CH$_2$OH wherein $R^6$ is any hexose or hexose polymer having a molecular weight less than about 1000 and hydrogen when y is not 0; $R^5$ is the same as $R^4$ or is an alkyl chain wherein the total number of carbon atoms of $R^2$ plus $R^5$ is not more than about 18; each y is from about 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Preferred cationic surfactants are the water soluble quaternary ammonium compounds useful in the present composition have the formula:

$$R_1R_2R_3R_4N^+X^-$$

wherein $R_1$ is a $\text{C}_8$-$\text{C}_{16}$ alkyl, each of $R_2$, $R_3$ and $R_4$ is independently $\text{C}_1$-$\text{C}_4$ alkyl, $\text{C}_1$-$\text{C}_4$ hydroxy alkyl, benzyl and $(\text{C}_2\text{H}_4\text{O})_x\text{H}$ where x has a value of from 1 to 5 and X is an anion. Not more than one of the $R_2$, $R_3$ or $R_4$ should be benzyl.

The preferred alkyl chain length for $R_1$ is from $\text{C}_{12}$-$\text{C}_{15}$, particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived from synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for the $R_2R_3$ and
R₄ are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds for use herein are:
- coconut trimethyl ammonium chloride or bromide; coconut methyl dihydroxyethyl ammonium chloride or bromide; decyl trimethyl ammonium chloride; decyl dimethyl hydroxyethyl ammonium chloride or bromide; C₁₂-C₁₅ dimethyl hydroxyethyl ammonium chloride or bromide; coconut dimethyl hydroxyethyl ammonium chloride or bromide; myristyl trimethyl ammonium methyl sulphate; lauryl dimethyl benzyl ammonium chloride or bromide; lauryl dimethyl (ethoxy)₄ ammonium chloride or bromide and choline esters. Other cationic surfactants useful herein are also described in U.S. patent 4 228 044.

In addition to the anionic, nonionic and cationic surfactants the surfactant system of the detergent composition of the present invention may further comprise from 0.1% to 10%, preferably from 0.5% to 3% of amphoteric or zwitterionic surfactants and mixtures thereof.

**Amphoteric surfactant**

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

\[
\begin{align*}
&\text{O} \\
&\text{||} \\
&\text{RC-NHCH₂CH₂R₁}
\end{align*}
\]

wherein R is a C₈-C₁₈ alkyl group, and R₁ is of the general formula

\[
\begin{align*}
&(\text{CH₂})ₓ\text{COO-} \\
&(\text{CH₂})ₓ\text{COO-} \\
&\text{N} \quad \text{or} \quad \text{N}^{(\text{+})}\text{-CH₂CH₂OH} \\
&\text{R₁} \quad \text{R₁}
\end{align*}
\]
wherein $R^1$ is a $(\text{CH}_2)_x\text{COOM}$ or $\text{CH}_2\text{CH}_2\text{OH}$, 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 diacetate acid and/or dipropionic acid. A suitable example of an alkyl amphodicarboxylic acid for use herein in the amphoteric surfactant Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

**Zwitterionic surfactant**

In a preferred embodiment of the present invention the detergent compositions additionally comprise zwitterionic surfactants, such as betaines and sultaines.

**Betaine surfactants**

Suitable betaines are those compounds having the formula $R(R^1)_2N^+R^2\text{COO}^-$ 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, 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 acylamidopropylbetaine; 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 complex betaines for use herein have the formula

\[
R - (A)_n - [N - (CHR_1)_x]y - N - Q \ (I)
\]

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.

**Sultaines**

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.

**Amine oxide surfactant**

The compositions of the present invention may further comprise as an optional ingredient an amine oxide. Amine oxides useful in the present invention include those compounds having the formula:

\[
O
\]

\[
R^3(OR^4)_xN(R^5)_2
\]
wherein R³ is selected from an alkyl, hydroxyalkyl, acylamido propoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms, preferably 8 to 16 carbon atoms; R⁴ 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 R⁵ is an alkyl or hydroxyalkyl 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 R⁵ 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 C₁₀-C₁₈ alkyl dimethyl amine oxides and C₈-C₁₂ alkoxy ethyl dihydroxyethyl amine oxides. Examples of such materials include dimethylolctamine oxide, diethyldecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, dimethyldodecylamine oxide, dipropyltetradecylamine oxide, methylethylhexadecylamine oxide, dodecylamidopropyl dimethylamine oxide and dimethyl-2-hydroxyoctadecylamine oxide. Preferred are C₁₀-C₁₈ alkyl dimethylamine oxide, and C₁₀-₁₈ acylamido alkyl dimethylamine oxide.

The compositions according to the present invention may comprise as optional ingredients detergent adjuncts selected from bleaching agents, bleach activators, enzymes, polymeric anti-redeposition agents, polymeric dispersants, polymeric soil release agents, chelants, builders, dye transfer inhibitors and mixtures thereof.

Enzymes

Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of refugee dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their
choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 5 mg by weight, more typically about 0.01 mg to about 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from about 0.001% to about 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniformis. 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).

Amylases include, for example, α-amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL and BAN, Novo Industries.

The cellulase usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307,
Barbesgaard et al., issued March 6, 1984, which discloses fungal cellulase produced from Humicola insolens and Humicola strain DSM1800 or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusk (Dolabella Auricula Solander). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME (Novo) is especially useful.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. The LIPOLASE enzyme derived from Humicola lanuginosa and commercially available from Novo (see also EPO 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent

**Enzyme Stabilizers**

The enzymes employed herein are stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species: see Severson, U.S. 4,537,706. Typical detergents, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme
slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from about 0.05% to about 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from about 0.25% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.75% to about 3%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

**Bleaching Compounds - Bleaching Agents and Bleach Activators**

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. 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.
The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents. Preferred oxygen bleaches are perhydrates such as percarbonate and perborate, e.g., sodium perborate in mono- or tetra-hydrate form.

Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, issued November 20, 1984, U.S. Patent Application 740,446, Burns et al, filed June 3, 1985, European Patent Application 0,133,354, Banks et al, published February 20, 1985, and U.S. Patent 4,412,934, Chung et al, issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. Patent 4,634,551, issued January 6, 1987 to Burns et al.

Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

A preferred percarbonate bleach comprises dry particles having an average particle size in the range from about 500 micrometers to about 1,000 micrometers, not more than about 10% by weight of said particles being smaller than about 200 micrometers and not more than about 10% by weight of said particles being larger than about 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or watersoluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.
Mixtures of bleaching agents can also be used. Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854, issued April 10, 1990 to Mao et al, and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

Highly preferred amido-derived bleach activators are those of the formulae:

\[ R^1N(R^5)C(O)R^2C(O)L \quad \text{or} \quad R^1C(O)N(R^5)R^2C(O)L \]

wherein \( R^1 \) is an alkyl group containing from about 6 to about 12 carbon atoms, \( R^2 \) is an alkylene containing from 1 to about 6 carbon atoms, \( R^5 \) is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and \( L \) is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamido-caproyl)oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

Another class of bleach activators comprises the benzoazxin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723, issued October 30, 1990, incorporated herein by reference. A highly preferred activator of the benzoazxin-type is:
Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:

\[
\begin{align*}
&\begin{array}{c}
\text{O} \\
R^6 - C - \text{N} \\
\text{CH}_2 - \text{CH}_2 - \text{CH}_2 \\
\end{array} \\
&\begin{array}{c}
\text{O} \\
\text{CH}_2 - \text{CH}_2 \\
\end{array}
\]

wherein \( R^6 \) is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to about 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminum phthalocyanines. See U.S. Patent 4,033,718, issued July 5, 1977 to Holcombe et al. If used, detergent compositions will typically contain from about 0.025% to about 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.
If desired, the bleaching compounds can be catalysed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,14,606; and European Pat. App. Pub. Nos. 549,271 A1, 549,272 A1, 544,440 A2, and 544,490 A1; Preferred examples of these catalysts include MnIV₂(u-O)₃(1,4,7-trimethyl-1,4,7-triazacyclononane)₂(PF₆)₂, MnIII₂(u-O)₁(u-OAc)₂(1,4,7-trimethyl-1,4,7-triazacyclononane)₂(ClO₄)₂, MnIV₄(u-O)₆(1,4,7-triazacyclononane)₄(ClO₄)₄, MnIII₄MnIV₄(u-O)₁(u-OAc)₂(1,4,7-trimethyl-1,4,7-triazacyclononane)₂(ClO₄)₃, MnIV(1,4,7-trimethyl-1,4,7-triazacyclononane)(OCH₃)₃(PF₆), and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; 5,227,084.

Builders

Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least about 1% builder. Liquid formulations typically comprise from about 5% to about 50%, more typically about 5% to about 30%, by weight, of detergent builder. Granular formulations typically comprise from about 10% to about 80%, more typically from about 15% to about 50% by weight, of the detergent builder.

Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid,
silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the alkali metal silicates, particularly those having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-$\text{Na}_2\text{Si}_2\text{O}_5$ morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaM}_x\text{Si}_y\text{O}_{2x+y} \cdot \text{yH}_2\text{O}$ wherein $M$ is sodium or hydrogen, $x$ is a number from 1.9 to 4, preferably 2, and $y$ is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-$\text{Na}_2\text{Si}_2\text{O}_5$ (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilising agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a
significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

$$M_2(zAlO_2)_y \cdot xH_2O$$

wherein $z$ and $y$ are integers of at least 6, the molar ratio of $z$ to $y$ is in the range from 1.0 to about 0.5, and $x$ is an integer from about 15 to about 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot xH_2O$$

wherein $x$ is from about 20 to about 30, especially about 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralised salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18,
1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethylhexa-2,5-dicarboxylic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethylhexa-2,5-dicarboxylic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C5-C20 alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

**Polymeric Soil Release Agent**

Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil release agents are characterised by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophilic components consisting essentially of (i) polyoxyethylene segments with a
degree of polymerisation of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophilic segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophilic component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fibre surfaces upon deposit of the soil release agent on such surface, said hydrophilic segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C₃ oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate: C₃ oxyalkylene terephthalate units is about 2:1 or lower, (ii) C₄₋C₆ alkylene or oxy C₄₋C₆ alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2, or (iv) C₁₋C₄ alkyl ether or C₄ hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C₁₋C₄ alkyl ether or C₄ hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C₁₋C₄ alkyl ether and/or C₄ hydroxyalkyl ether units to deposit upon conventional polyester synthetic fibre surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fibre surface, to increase fibre surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C₄₋C₆ alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as MO₃S(CH₂)ₙOCH₂CH₂O⁻, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.
Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C₁-C₄ alkyl and C₄ hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

Soil release agents characterised by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.
Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel and E.P. Gosselin. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselin et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselin, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselin.

Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least
one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 500 ppm, of the catalyst species in the laundry liquor.
Chelating Agents

The detergent compositions herein may also optionally contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylene diaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionate, triethylenetetraminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetraakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.


If utilized, these chelating agents will generally comprise from about 0.1% to about 10% by weight of the detergent compositions herein. More
preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

Clay Soil Removal/Anti-redeposition Agents

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from about 0.01% to about 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain about 0.01% to about 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published June 27, 1984. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published June 27, 1984; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published July 4, 1984; and the amine oxides disclosed in U.S. Patent 4,548,744, Connor, issued October 22, 1985. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Dispersing Agents

Polymeric dispersing agents can advantageously be utilized at levels from about 0.1% to about 7%, by weight, in the compositions herein, especially in the presence of zeolite and/or layered silicate builders. Suitable polymeric dispersing agents include polymeric polycarboxylates and polyethylene glycols, although others known in the art can also be used. It is believed, though it is not intended to be limited by theory, that
polymeric dispersing agents enhance overall detergent builder performance, when used in combination with other builders (including lower molecular weight polycarboxylates) by crystal growth inhibition, particulate soil release peptization, and anti-redeposition.

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. Such materials include the water-soluble salts of copolymers of acrylic acid and maleic acid. The average molecular weight of such copolymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 5,000 to 75,000, most preferably from about 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from about 30:1 to about 1:1, more preferably from about 10:1 to 2:1. Water-soluble salts of such acrylic acid/maleic acid copolymers can
include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published December 15, 1982, as well as in EP 193,360, published September 3, 1986, which also describes such polymers comprising hydroxypropylacrylate. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

Another polymeric material which can be included is polyethylene glycol (PEG). PEG can exhibit dispersing agent performance as well as act as a clay soil removal-antiredeposition agent. Typical molecular weight ranges for these purposes range from about 500 to about 100,000, preferably from about 1,000 to about 50,000, more preferably from about 1,500 to about 10,000.

Polyaspartate and polyglutamate dispersing agents may also be used, especially in conjunction with zeolite builders. Dispersing agents such as polyaspartate preferably have a molecular weight (avg.) of about 10,000.

**Dye Transfer Inhibiting Agents**

The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: R-A_X-P; wherein P is a polymerizable unit to which an N-O group can be attached.
or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: - NC(O)\text{-}, -C(O)O\text{-}, -S\text{-}, -O\text{-}, -N=\text{-}; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:

\[
\begin{align*}
\overset{\text{O}}{(R_1)x} & = N \overset{\text{O}}{(R_2)y} \quad \overset{\text{O}}{(R_1)x} \\
\quad \overset{\text{=N}}{(R_3)z} & \quad \overset{\text{=N}}{\quad (R_1)x} \\
\end{align*}
\]

wherein R1, R2, R3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa < 10, preferably pKa < 7, more preferred pKa < 6.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".
The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

The detergent compositions herein may also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.01% to 1% by weight of such optical brighteners.
The hydrophilic optical brighteners useful in the present invention are those having the structural formula:

\[
\begin{aligned}
\text{R}_1 & \quad \text{N-H-} \quad \text{N-H} \\
\text{N} & \quad \text{C-C} \\
\text{R}_2 & \quad \text{SO}_3\text{M} \\
\text{R}_1 & \quad \text{N-H-} \quad \text{N-H} \\
\end{aligned}
\]

wherein \( \text{R}_1 \) is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; \( \text{R}_2 \) is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and \( \text{M} \) is a salt-forming cation such as sodium or potassium.

When in the above formula, \( \text{R}_1 \) is anilino, \( \text{R}_2 \) is N-2-bis-hydroxyethyl and \( \text{M} \) is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, \( \text{R}_1 \) is anilino, \( \text{R}_2 \) is N-2-hydroxyethyl-N-2-methylamino and \( \text{M} \) is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal SBM-GX by Ciba-Geigy Corporation.

When in the above formula, \( \text{R}_1 \) is anilino, \( \text{R}_2 \) is morphilino and \( \text{M} \) is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

The specific optical brightener species selected for use in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye
transfer inhibiting agents herein before described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners (e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Other Ingredients

The detergent compositions of the present invention may be in any form and include granules, particulates, liquids, gels and bars. A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, such as carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations and solid fillers for bar compositions. Suds boosters such as the C_{10}-C_{16} alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C_{10}-C_{14} monoethanol and diethanol amides illustrate a typical class of such suds boosters. If desired, soluble magnesium salts such as MgCl$_2$, MgSO$_4$, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.
Various deterve ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterve ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterve ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterve function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C_{13-15} ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorsceners, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents, including liquid laundry detergent compositions.

Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to about 6 carbon atoms and from 2 to about 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of from 8.5 to 11, preferably between 9 and 11, most preferably pH 9 to 10. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.
Methods of washing

According to the present invention the detergent compositions may be used for any handwash laundry process. The term handwash as used herein includes any process whereby the laundering process is not fully automated and thus includes use in high sudsing washing machines such as 'twin tub' types. Preferably the detergent compositions are used in laundry process which involve manual agitation.

Handwash laundry process

According to the handwash process aspect of this invention, soiled fabrics are contacted with an effective amount, of the composition of the present invention. The actual amount of 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 garments to be cleaned, the degree of soiling of the garments, the amount of sudsing and the process used by the consumer.

The process by which the garments are contacted with the effective amount of the composition of the invention may be essentially any of the processes for handwashing commonly known and encompasses the dilute solution in bowl process, and the direct application process.

Solution in bowl process

In the typical dilute solution in bowl process the detergent composition is combined with from 1,000 ml. to 15,000 ml., more typically from 3,000 ml. to 10,000 ml. of water in a bowl or sink. The water may be at ambient temperature or may be heated. The soiled garments are immersed in the bowl containing the detergent composition and water, where they are cleaned by manual agitation of the water and garment for a given time period varying from 1 to 5 minutes to 20 to 30 minutes, although the actual time will vary with each application and user. Alternatively, the garments may be left in the wash solution for a period of time ranging from 30 minutes to 12 hours to aid the removal of
the soils prior to manual agitation. The wash solution is then replaced by water in which the garment is rinsed to remove the detergent composition. This may be repeated a number of times.

**Direct Application Process**

The direct application process will typically comprise as a first step combining an amount of the detergent composition with sufficient water to form a paste. The soiled garments are then scrubbed with the paste for a period of time until the consumer is satisfied that the soils have been removed from the garment. The garment is then rinsed in water to remove the detergent composition.

According to the present invention the effect of the detergent composition with respect to mildness to the hands of the consumer can be evaluated by controlled tests evaluated by a dermatologist.

**Examples**

The following granular detergent compositions of the present invention were prepared by mixing all the listed ingredients in the amounts specified.

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WHAT IS CLAIMED IS:

1. A handwash laundry detergent composition comprising from 15% to 35% of a surfactant system comprising anionic, nonionic and cationic surfactants, characterised in that said nonionic surfactant comprises a polyhydroxy fatty acid amide and the ratio of said anionic surfactant to said cationic surfactant is from 3:1 to 15:1 and the ratio of said cationic surfactant to said nonionic surfactant is from 2:1 to 1:10.

2. A handwash laundry detergent composition according to claim 1, wherein said nonionic surfactant further comprises an alkoxyethylated nonionic surfactant.

3. A handwash laundry detergent composition according to either of the preceding claims, wherein said cationic surfactant is according to the formula $R_1R_2R_3R_4N^+X^-$, wherein $R_1$ is a C8-C16 alkyl, $R_2$, $R_3$, and $R_4$ are independently C1-C4 alkyl or hydroxy alkyl, benzyl and $(C_2H_4O)_xH$, where $x$ is from 1 to 5 and $X$ is an anion.

4. A handwash laundry detergent composition according to either of claims 1 and 2, wherein said surfactant system further comprises from 0.5% to 3% of a surfactant selected from zwitterionic, amphoteric surfactants and mixtures thereof.

5. A handwash laundry detergent composition according to claim 4, wherein said surfactant is a betaine.

6. A handwash laundry detergent composition according to any of the preceding claims, wherein said ratio of anionic surfactant to cationic surfactant is from 5:1 to 15:1 and wherein said ratio of cationic surfactant to nonionic surfactant is from 2:1 to 1:7.

7. A handwash laundry detergent composition according to any of the preceding claims, further comprising a detergent adjunct selected from bleaching agents, bleach activators, enzymes, polymeric anti-redeposition agents, polymeric dispersants, polymeric soil release
agents, chelants, builders, dye transfer inhibitors and mixtures thereof.

8. A handwash laundry detergent composition according to any of the preceding claims, wherein said composition is in granular form.

9. A handwash laundry detergent composition according to any of the preceding claims, wherein said composition is in liquid form.

10. A handwash laundry detergent composition according to any of the preceding claims, wherein said composition is in the form of a laundry bar.

11. A method of laundering soiled fabrics, whereby said fabrics are manually contacted with an effective amount of a laundering detergent composition according to claim 1, in an aqueous solution.
A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) : C11D 1/75, 1/94, 7/60
US CL. 252/541, 544, 548, 547, 174.21
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.: 252/541, 544, 548, 547, 174.21

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)
AUTOMATED PATENT SYSTEM

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US.A, 5,338,491 (Connor et al) 16 August 1994, see column 2, lines 40-60, column 8, lines 1-60 and column 12, lines 20-60.</td>
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[X] Further documents are listed in the continuation of Box C.       [ ] See patent family 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 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

+ 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
  + 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
  + 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

Date of the actual completion of the international search
14 SEPTEMBER 1995

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
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Washington, D.C. 20231
Facsimile No. (703) 305-3230

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