Abstract:

A cold-water cleaning method and laundry detergents useful therein are disclosed. The method comprises laundering one or more textile articles in water having a temperature less than or equal to 30°C in the presence of a detergent comprising a Cr
C14 dialkyl sulfosuccinate or sulfomethylsucinate, a linear alkylbenzene sulfonate, and an optional nonionic surfactant. We surprisingly found that combinations of C6-C14 dialkyl sulfosuccinates or sulfomethylsuccinates and linear alkylbenzene sulfonates provide outstanding performance in removing greasy stains such as beef tallow from soiled articles even at wash temperatures of 30°C or less.
COLD-WATER CLEANING METHOD

FIELD OF THE INVENTION

The invention relates to a cold-water cleaning method and laundry detergents useful therein.

BACKGROUND OF THE INVENTION

Surfactants are essential components of everyday products such as household and industrial cleaners, agricultural products, personal care products, laundry detergents, oilfield chemicals, specialty foams, and many others.

Modern laundry detergents perform well in removing many kinds of soils from fabrics when warm or hot water is used for the wash cycle. Warmer temperatures soften or melt even greasy soils, which helps the surfactant assist in removing the soil from the fabric. Hot or warm water is not always desirable for washing, however. Warm or hot water tends to fade colors and may accelerate deterioration of the fabric. Moreover, the energy costs of heating water for laundry make cold-water washing more economically desirable and more environmentally sustainable. In many parts of the world, only cold water is available for laundering articles.

Of course, laundry detergents have now been developed that are designed to perform well in hot, warm, or cold water. One popular cold-water detergent utilizes a combination of a nonionic surfactant (a fatty alcohol ethoxylate) and two anionic surfactants (a linear alkylbenzene sulfonate ("NaLAS") and a fatty alcohol ethoxylate sulfate ("NaAES")) among other conventional components. Commercially available cold-water detergents tend to perform well on many common kinds of stains, but they have difficulty removing greasy dirt, particularly bacon grease, beef tallow, cooked beef fat, and the like. These soils are often deposited as liquids but quickly solidify and adhere tenaciously to textile fibers. Particularly in a cold-water wash cycle, the surfactant can be overmatched in the challenge to wet, liquefy, and remove these greasy, hardened soils.

In describing suitable surfactant compositions for use in personal care, hard surface cleaning, liquid dish detergents, or laundry detergents, it is common to see a list
of every conceivable anionic surfactant (see, e.g., U.S. Publ. No. 2006/0030513 and U.S. Pat. No. 4,692,271). Among the popular classes of anionic surfactants are linear alkylbenzene sulfonates and dialkyi sulfosuccinates. It is less common to see a specific disclosure of NaLAS combined with dialkyi sulfosuccinates, particularly in a laundry detergent formulation. Often, dialkyi sulfosuccinates are used in formulations that avoid NaLAS (see, e.g., U.S. Pat. Nos. 4,247,424 and 8,246,696 and EP 365170). In other cases, the formulation is a dish detergent or other non-laundry formula (see, e.g., U.S. Pat. Nos. 4,680,143; 4,732,707; and 5,565,146).

U.S. Pat. No. 4,176,080 describes compositions useful for removing oily soils from fabric using aqueous laundering. These compositions include a dialkyi sulfosuccinate in combination with a C12-C14 paraffin (about 1 part of dialkyi sulfosuccinate to 8 parts of C12-C14 paraffin). Example V illustrates that delayed addition of a "solvent stripping agent" comprising a sodium linear alkylbenzene sulfonate, gelatinized cornstarch, and other components provides good cleaning of oily soils in 40°C water.

Improved detergents are always in need, especially laundry detergents that perform well in cold water. Of particular interest are detergents that can tackle greasy dirt such as bacon grease or beef tallow, because these stains solidify and adhere strongly to common textile fibers. Ideally, the kind of cleaning performance on greasy dirt that consumers are used to enjoying when using hot water could be realized even with cold water.

SUMMARY OF THE INVENTION

In one aspect, the invention relates to a method for laundering textiles. The method comprises laundering one or more textile articles in water having a temperature less than or equal to 30°C in the presence of a detergent. The detergent comprises a C4 to C14 dialkyi sulfosuccinate or sulfomethylsuccinate and a linear alkylbenzene sulfonate (NaLAS). Optionally, the detergent includes other surfactants, particularly one or more nonionic surfactants. When certain dialkyi sulfosuccinates or sulfomethylsuccinates are combined with a linear alkylbenzene sulfonate, outstanding performance in removing greasy stains such as beef tallow from soiled articles under
cold-water laundering conditions can be achieved. We found that similar formulations prepared with dialkyl sulfosuccinates or sulfomethylsuccinates and other common surfactants such as alcohol ether sulfates (NaAES) fail to deliver the same high level of stain-removal performance. The method is easy to practice, is energy-efficient, utilizes commercially available surfactants, and delivers exceptional cleaning results on greasy soils, even in cold water.

**DETAILED DESCRIPTION OF THE INVENTION**

In one aspect, the invention relates to a method which comprises laundering one or more textile articles in water having a temperature less than or equal to 30°C in the presence of a detergent comprising a C4 to Cu dialkyl sulfosuccinate or sulfomethylsuccinate, a linear alkylbenzene sulfonate, and an optional nonionic surfactant.

**Laundering methods**

Methods for laundering fabrics with combinations of C4 to Cu dialkyl sulfosuccinates or sulfomethylsuccinates and linear alkylbenzene sulfonates are contemplated. Such methods involve placing fabric articles to be laundered in a high efficiency washing machine or a regular (non-high efficiency) washing machine and placing an amount of the detergent composition sufficient to provide a concentration of the composition in water of from about 0.001% to about 5% by weight when the machine is operated in a wash cycle. A high efficiency machine is defined by the Soap and Detergent Association as any machine that uses 20% to 66% of the water, and as little as 20% - 50% of the energy, of a traditional, regular agitator washer (SDA "Washers and Detergents" publication 2005; see www.cleaning101.com). The wash cycle is actuated or started to launder the fabric articles. Hand washing using the detergent compositions is also contemplated.

As used herein, "cold water" refers to water having a temperature less than or equal to 30°C, preferably from 5°C to 30°C. Depending on climate, sourced water will have a temperature in this range without requiring added heat. Thus, in one aspect, the invention is a method which comprises laundering one or more textile articles in water
having a temperature less than 30°C, preferably from 5°C to 30°C, the presence of a detergent comprising a dialkyi sulfosuccinate or sulfomethylsuccinate and a linear alkylbenzene sulfonate as described herein.

"Laundering" may refer to using the detergent in the traditional sense of adding it and water to a washing machine (or a tub or other container for manual washing) along with textile articles and using the detergent as the principal cleaning agent. "Laundering" also includes using the detergent as a pre-spotter or pre-soaker composition for manual or machine washing.

Thus, in one aspect, the detergent is used in a laundry pre-spotter composition. In this application, greasy or oily soils on the garments or textile fabrics are contacted directly with the pre-spotter in advance of laundering either manually or by machine. Preferably, the fabric or garment is treated for 5-30 minutes. The pre-spotter composition will normally contain 0.5 to 50 wt.%, more preferably 1 to 30 wt.%, and most preferably 5 to 20 wt.% of combined C4-C14 dialkyi sulfosuccinate or sulfomethylsuccinate and linear alkylbenzene sulfonate actives. Treated fabric is machine laundered as usual, preferably at a temperature within the range of 5°C and 30°C, more preferably 10°C to 20°C, most preferably 12°C to 18°C.

In another aspect, the detergent is used in a pre-soaker composition for manual or machine washing. When used for manual washing, the pre-soaker composition is combined with cold water in a washing tub or other container. The pre-soaker composition comprises 0.5 to 100 wt.%, more preferably 1 to 80 wt.%, and most preferably 5 to 50 wt.% of combined C4-C14 dialkyi sulfosuccinate or sulfomethylsuccinate and linear alkylbenzene sulfonate actives. Garments or textile fabrics are preferably saturated with pre-soaker in the tub, allowed to soak for 15-30 minutes, and laundered as usual.

When used for machine washing, the pre-soaker composition is preferably added to a machine containing water at a temperature within the range of 5°C and 30°C, more preferably 10°C to 20°C, most preferably 12°C to 18°C. The pre-soaker composition preferably comprises 0.5 to 100 wt.%, more preferably 1 to 80 wt.%, and most preferably 5 to 50 wt.% of combined C4-C14 dialkyi sulfosuccinate or sulfomethylsuccinate and linear alkylbenzene sulfonate actives. Garments/textile
fabrics are added to the machine, allowed to soak (usually with a pre-soak cycle selected on the machine) for 5-10 minutes, and then laundered as usual.

In some aspects, the detergent is used as an additive for a laundry product or formulation. In such applications, the combined C4-C14 dialkyl sulfosuccinate or sulfomethylsuccinate and linear alkylbenzene sulfonate surfactants help to improve or boost the grease removal or grease cutting performance of the laundry product or formulation. Preferably, the amount of C4-C14 dialkyl sulfosuccinate or sulfomethylsuccinate and linear alkylbenzene sulfonate surfactant actives used will be within the range of 1 to 10 wt.%, more preferably 2 to 8 wt.%, and most preferably 3 to 5 wt.%. 

In yet another aspect, the detergent is used as an additive to produce a modified surfactant having improved grease removal or grease cutting properties. Preferably, the amount of C4-C14 dialkyl sulfosuccinate or sulfomethylsuccinate and linear alkylbenzene sulfonate surfactant actives used will be within the range of 1 to 10 wt.%, more preferably 2 to 8 wt.%, and most preferably 3 to 5 wt.% in the additive formulation. The resulting modified surfactant will help to achieve improved grease cutting/removal in commercial products. Such products may be used at a temperature within the range of 5°C and 30°C, preferably 10°C to 20°C, and more preferably 12°C to 18°C.

Detergent components

1. Dialkyl sulfosuccinates or sulfomethylsuccinates

Detergents suitable for use in the inventive method comprise a C4-C14 dialkyl sulfosuccinate or sulfomethylsuccinate. The sulfosuccinates are succinic acid dialkyl esters having a sulfonate salt group on a carbon alpha to an ester group. The sulfomethylsuccinates are dialkyl esters of methylsuccinic acid in which a sulfonate salt group replaces one hydrogen atom of the original methyl group. The alcohol portion of the alkyl sulfosuccinate or sulfomethylsuccinate ester can have the same or different numbers of carbons. In some aspects, the dialkyl sulfosuccinate or sulfomethylsuccinate is a C₆ to C₁₂ dialkyl sulfosuccinate or sulfomethylsuccinate. Preferably, the dialkyl sulfosuccinate or sulfomethylsuccinate is a C₆ to C₁₀ dialkyl
sulfosuccinate or sulfomethylsuccinate. In other preferred aspects, the dialkyi sulfosuccinate or sulfomethylsuccinate is a Cs dialkyi sulfosuccinate or sulfomethylsuccinate. A minor proportion of disulfonated material can be present; preferably, the alkyl sulfosuccinate or sulfomethylsuccinate is monosulfonated.

In some aspects, the C4-C14 alkyl sulfosuccinate has the formula:

\[
\begin{array}{c}
\text{SO}_3^\ominus \quad \text{M}^\oplus \\
\text{OR}^2 \quad \text{OR}^1
\end{array}
\]

wherein each of R\textsuperscript{1} and R\textsuperscript{2} is independently a linear, branched, or cyclic saturated or unsaturated C4-C14 alkyl group, and M is solubilizing cation, preferably an alkali metal or an ammonium ion. In other aspects, M may be an alkaline earth metal cation that is coordinated to two dialkyi sulfosuccinate anions (or both sulfonate groups of a disulfonated material):

In some aspects, the C4-C14 alkyl sulfomethylsuccinate has the formula:

\[
\begin{array}{c}
\text{R}^1 \quad \text{R}^2 \\
\text{SO}_3^\ominus \quad \text{M}^{2\ominus} \\
\end{array}
\]

In some aspects, the C4-C14 alkyl sulfomethylsuccinate has the formula:
wherein each of $R^1$ and $R^2$ is independently a linear, branched, or cyclic saturated or unsaturated C4-C14 alkyl group, and M is solubilizing cation, preferably an alkali metal or an ammonium ion. In other aspects, M may be an alkaline earth metal cation that is coordinated to two dialkyl sulfomethylsuccinate anions.

Suitable C4-C14 dialkyl sulfosuccinates are commercially available from Stepan Company under the Stepwet® mark (e.g., Stepwet® DOS 70), from Cytec under the Aerosol® mark, from Dow under the Triton™ mark, from AkzoNobel under the Lankropol® mark, and from Huntsman under the Surfonic® mark. Diocetyl sulfosuccinates such as sodium bis(2-ethylhexyl) sulfosuccinate are most commonly available and are preferred for use herein.

Dialkyl sulfosuccinates can also be synthesized using well-known methods. For instance, they can be made by directly esterifying sulfosuccinic acid (or its salts) with excess C4 to C14 alcohol (see, e.g., U.S. Pat. No. 2,028,091). In another approach, a maleate or fumarate diester is first made by reacting two equivalents of the C4-C14 alcohol with maleic anhydride or fumaric acid. This is converted to the dialkyl sulfosuccinate by reacting the maleate or fumarate diester with sodium bisulfite (NaHSO3) or sodium metabisulfite (Na2S2O5). See, e.g., U.S. Pat. Nos. 2,028,091 and 2,813,078; EP 8771 1; GB 565,675; GB 1,215,561; and GB 1,527,020. The teachings of U.S. Pat. Nos. 2,028,091 and 2,813,078 related to dialkyl sulfosuccinate preparation are incorporated herein by reference.

Suitable C4-C14 dialkyl sulfomethylsuccinates can be prepared using a modified version of the procedure described in U.S. Pat. No. 8,853,141, the teachings of which are incorporated herein by reference, for making monoalkyl sulfomethylsuccinates. For instance, itaconic acid or itaconic anhydride can be reacted with an excess of an alcohol to give a dialkyl itaconate ester, followed by sulfitation of the vinylidene group to give the desired dialkyl sulfomethylsuccinate.

2. Linear alkylbenzene sulfonates

Linear alkylbenzene sulfonates (and the sulfonic acid counterparts) are well-known surfactants for laundry detergents. They are commercially available from many sources such as Stepan Company (under the Bio-Soft®, Nacconol®, and Ninate®
marks), BASF (as "LAS"); Kao (under the Neopelex™ mark), Solvay (under the Rhodacal® mark), AkzoNobel (under the Witconate® mark), Pilot Chemical (under the Calsoft® mark), and other suppliers. Linear alkylbenzene sulfonates have a sulfonated aromatic ring that is also substituted with a linear alkyl chain. The alkyl chain usually has 8 to 20 carbons, more typically 10 to 14 carbons or 11 to 14 carbons. Because many suitable alkylbenzene sulfonate products are readily available, these will normally not require synthesis. Industrially, the linear alkylbenzene sulfonates are made by dehydrogenating normal paraffins to give olefins, followed by alkylation of benzene in a fixed-bed process, sulfonation of the benzene ring, and neutralization. In some processes, the alkylbenzenes are produced by HF-catalyzed alkylation of benzene with olefins or AlCl₃-catalyzed alkylation with alkyl halides.

In some aspects, the alkylbenzene sulfonate may be represented by the formula:

\[ R^6 ArSO₃M \]

where \( R^6 \) is an alkyl group of 8 to 18 carbon atoms, \( Ar \) is a benzene ring (-C₆H₄⁻) and \( M \) is a solubilizing cation. \( R^6 \) may be a mixture of chain lengths. A mixture of isomers is typically used, and different grades are commercially available for use depending on formulation needs.

It may be more desirable to formulate the detergent using the corresponding alkylbenzene sulfonic acid ("HLAS") and including enough sodium hydroxide or other hydroxide base to convert the sulfonic acid groups to sulfonate salts.

The C₄-C₁₄ alkyl sulfosuccinate or sulfomethylsuccinate and linear alkylbenzene sulfonate are the principal anionic surfactant components of detergents useful for the inventive method, although one or more other anionic surfactants can be included. Generally, the combined amount of C₄-C₁₄ alkyl sulfosuccinate or sulfomethylsuccinate and linear alkylbenzene sulfonate will make up at least 50 wt.%, at least 60 wt.%, at least 75 wt.% or at least 90 wt. % of the anionic surfactant component of a laundry detergent formulation.

In some aspects, the C₄-C₁₄ dialkyl sulfosuccinate or sulfomethylsuccinate will be used in an amount within the range of 20 to 80 wt.%, or 30 to 70 wt.%, or 40 to 60 wt.%, or 45 to 55 wt.% based on the combined amounts of C₄-C₁₄ dialkyl sulfosuccinate and linear alkylbenzene sulfonate in a laundry detergent formulation.
In some aspects, the anionic surfactant component of the detergent formulation will consist essentially of the C4-C14 dialkyi sulfosuccinate or sulfomethylsuccinate and the linear alkylbenzene sulfonate.

In some aspects, the detergent will comprise 1 to 70 wt.%, or 1 to 20 wt.%, or 2 to 15 wt.%, of the C4-C14 dialkyi sulfosuccinate or sulfomethylsuccinate and 1 to 70 wt.%, or 1 to 20 wt.%, or 2 to 15 wt.% of the linear alkylbenzene sulfonate (each based on 100% actives).

Preferably, the detergent comprises water in addition to the C4-C14 dialkyi sulfosuccinate or sulfomethylsuccinate, linear alkylbenzene sulfonate, and any other surfactants. The amount of water present may vary over a wide range and will normally depend on the intended application, the form in which the detergent is delivered, the desired actives level, and other factors. In actual use, the detergents will normally be diluted with a small, large, or very large proportion of water, depending on the equipment available for washing. Generally, the amount of water used will be effective to give 0.001 to 5 wt.% of active surfactant in the wash.

In some aspects the detergent comprises one or more nonionic surfactants in addition to the C4-C14 dialkyi sulfosuccinate or sulfomethylsuccinate and linear alkylbenzene sulfonate surfactants. Preferred nonionic surfactants are fatty alcohol ethoxylates, especially C9-C15 primary alcohol ethoxylates containing 3-12 moles of ethylene oxide per mole of alcohol, particularly C12-C15 primary alcohols containing 5-8 moles of ethylene oxide per mole of alcohol (e.g., Bio-Soft® N25-7, product of Stepan Company).

In some aspects, the detergent comprises 1 to 70 wt.% of the C4-C14 dialkyi sulfosuccinate or sulfomethylsuccinate, 1 to 70 wt.% of the linear alkylbenzene sulfonate, and 1 to 70 wt.% of the nonionic surfactant, all based on 100% actives. In other aspects, the detergent comprises 1 to 20 wt.% of the C4-C14 dialkyi sulfosuccinate or sulfomethylsuccinate, 1 to 20 wt.% of the linear alkylbenzene sulfonate, and 1 to 30 wt.% of the nonionic surfactant, all based on 100% actives. In other aspects, the detergent comprises 5 to 10 wt.% of the C4-C14 dialkyi sulfosuccinate or sulfomethylsuccinate, 5 to 10 wt.% of the linear alkylbenzene sulfonate, and 5 to 20 wt.% of the nonionic surfactant, all based on 100% actives.
The detergents may include other components, including, for example, other surfactants, hydrotropes, fatty acids or soaps, alkalinity adjusters, buffers, pH adjusters, or other components. These are described more completely in the paragraphs that follow.

General Considerations for Laundry Detergents

Desirable surfactant attributes for laundry detergents include having the ability to be formulated as heavy duty liquid (HDL) detergents, powders, bar soaps, sachets, pods, or other detergents forms.

For HDLs, this includes being in liquid form at room temperature, an ability to be formulated in cold-mix applications, and an ability to perform as well as or better than existing surfactants.

Desirable attributes for HDLs include, for example, the ability to emulsify, suspend or penetrate greasy or oily soils and suspend or disperse particulates, in order to clean surfaces; and then prevent the soils, grease, or particulates from re-depositing on the newly cleaned surfaces.

It is also desirable to have the ability to control the foaming. For use of an HDL in a high-efficiency washing machine, low foam is desired to achieve the best cleaning and to avoid excess foaming. Other desirable properties include the ability to clarify the formulation and to improve long-term storage stability under both extreme outdoor and normal indoor temperatures.

The skilled person will appreciate that combinations of a C4 to C14 dialkyl sulfosuccinate or sulfomethylsuccinate and a linear alkylbenzene sulfonate as described above may not be mere "drop-in" substitutions in an existing detergent formulation. Some amount of re-formulation is typically necessary to adjust the nature and amounts of other surfactants, hydrotropes, alkalinity control agents, and/or other components of the formulation in order to achieve a desirable outcome in terms of appearance, handling, solubility characteristics, and other physical properties and performance attributes. For example, a formulation might need to be adjusted by using, in combination with the C4 to Cu dialkyl sulfosuccinate or sulfomethylsuccinate and NaLAS surfactant, a more highly ethoxylated nonionic surfactant instead of one that has
fewer EO units. This kind of reformulating is considered to be within ordinary skill and is left to the skilled person's discretion.

A wide variety of detergent compositions can be made that include the C4 to Cu dialkyi sulfosuccinate or sulfomethylsuccinate and NaLAS surfactants, with or without other ingredients as specified below. Formulations are contemplated including 1% to 99% of combined C4 to Cu dialkyi sulfosuccinate or sulfomethylsuccinate and NaLAS surfactant, more preferably between 1% and 60%, even more preferably between 1% and 30%, with 99% to 1% water and, optionally, other ingredients as described here.

Additional Surfactants

The detergent compositions can contain co-surfactants, which can be anionic, cationic, nonionic, ampholytic, zwitterionic, or combinations of these.

Anionic Surfactants

Formulations useful for the inventive methods can include anionic surfactants in addition to the C4 to Cu dialkyi sulfosuccinate or sulfomethylsuccinate and NaLAS surfactants. "Anionic surfactants" are defined here as amphiphilic molecules with an average molecular weight of less than about 10,000, comprising one or more functional groups that exhibit a net anionic charge when present in aqueous solution at the normal wash pH, which can be a pH between 6 and 11. The anionic surfactant can be any anionic surfactant that is substantially water soluble. "Water soluble" surfactants are, unless otherwise noted, here defined to include surfactants which are soluble or dispersible to at least the extent of 0.01% by weight in distilled water at 25°C. At least one of the anionic surfactants used may be an alkali or alkaline earth metal salt of a natural or synthetic fatty acid containing between about 4 and about 30 carbon atoms. A mixture of carboxylic acid salts with one or more other anionic surfactants can also be used. Another important class of anionic compounds is the water soluble salts, particularly the alkali metal salts, of organic sulfur reaction products having in their molecular structure an alkyl radical containing from about 6 to about 24 carbon atoms and a radical selected from the group consisting of sulfonic and sulfuric acid ester radicals.
Specific types of anionic surfactants are identified in the following paragraphs.

Carboxylic acid salts are represented by the formula:

$$\text{R}^1\text{COOM}$$

where $\text{R}^1$ is a primary or secondary alkyl group of 4 to 30 carbon atoms and $\text{M}$ is a solubilizing cation. The alkyl group represented by $\text{R}^1$ may represent a mixture of chain lengths and may be saturated or unsaturated, although it is preferred that at least two thirds of the $\text{R}^1$ groups have a chain length of between 8 and 18 carbon atoms. Non-limiting examples of suitable alkyl group sources include the fatty acids derived from coconut oil, tallow, tall oil and palm kernel oil. For the purposes of minimizing odor, however, it is often desirable to use primarily saturated carboxylic acids. Such materials are well known to those skilled in the art, and are available from many commercial sources, such as Uniqema (Wilmington, DE) and Twin Rivers Technologies (Quincy, MA). The solubilizing cation, $\text{M}$, may be any cation that confers water solubility to the product, although monovalent such moieties are generally preferred. Examples of acceptable solubilizing cations for use with the present technology include alkali metals such as sodium and potassium, which are particularly preferred, and amines such as triethanolammonium, ammonium and morpholinium. Although, when used, the majority of the fatty acid should be incorporated into the formulation in neutralized salt form, it is often preferable to leave a small amount of free fatty acid in the formulation, as this can aid in the maintenance of product viscosity.

Primary alkyl sulfates are represented by the formula:

$$\text{R}^2\text{OSO}_3\text{M}$$

where $\text{R}^2$ is a primary alkyl group of 8 to 18 carbon atoms and can be branched or linear, saturated or unsaturated. $\text{M}$ is $\text{H}$ or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethylammonium cations and quaternary ammonium cations such as tetramethylammonium and dimethylpiperidinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). The alkyl group $\text{R}^2$ may have a mixture of chain lengths. It is preferred that at least two-thirds of the $\text{R}^2$ alkyl groups have a chain length of 8 to 18 carbon atoms. This will be the case if $\text{R}^2$ is coconut alkyl, for example. The
solubilizing cation may be a range of cations which are in general monovalent and confer water solubility. An alkali metal, notably sodium, is especially envisaged. Other possibilities are ammonium and substituted ammonium ions, such as trialkanolammonium or trialkylammonium.

Alkyl ether sulfates are represented by the formula:

\[ R^3O(CH_2CH_2O)_nSO_3M \]

where \( R^3 \) is a primary alkyl group of 8 to 18 carbon atoms, branched or linear, saturated or unsaturated, and \( n \) has an average value in the range from 1 to 6 and \( M \) is a solubilizing cation. The alkyl group \( R^3 \) may have a mixture of chain lengths. It is preferred that at least two-thirds of the \( R^3 \) alkyl groups have a chain length of 8 to 18 carbon atoms. This will be the case if \( R^3 \) is coconut alkyl, for instance. Preferably \( n \) has an average value of 2 to 5. Ether sulfates have been found to provide viscosity build in certain of the formulations of the present technology, and thus are considered a preferred ingredient.

Other suitable anionic surfactants that can be used are alkyl ester sulfonate surfactants including linear esters of Cs-C20 carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO3 (see, e.g., J. Am. Oil Chem. Soc. 52 (1975) 323). Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, and the like.

Preferred alkyl ester sulfonate surfactants, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:

\[ R^3-CH(SO_3M)-C(O)-OR^4 \]

where \( R^3 \) is a \( C_6-C_20 \) hydrocarbyl, preferably an alkyl or combination thereof \( R^4 \) is a \( C_1-C_6 \) hydrocarbyl, preferably an alkyl, or combination thereof, and \( M \) is a cation that forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. The group \( R^3 \) may have a mixture of chain lengths. Preferably at least two-thirds of these groups have 6 to 12 carbon atoms. This will be the case when the moiety \( R^3CH(-)CO_2(-) \) is derived from a coconut source, for instance. Preferably, \( R^3 \) is
Cio -Ci6 alkyl, and R^4 is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates where R^3 is C10 -C16 alkyl.

Paraffin sulfonates having about 8 to about 22 carbon atoms, preferably about 12 to about 16 carbon atoms, in the alkyl moiety, are contemplated for use here. They are usually produced by the sulfoxidation of petrochemically derived normal paraffins. These surfactants are commercially available as, for example, Hostapur SAS from Clariant (Charlotte, NC).

Olefin sulfonates having 8 to 22 carbon atoms, preferably 12 to 16 carbon atoms, are also contemplated for use in the present compositions. The olefin sulfonates are further characterized as having from 0 to 1 ethylenic double bonds; from 1 to 2 sulfonate moieties, of which one is a terminal group and the other is not; and 0 to 1 secondary hydroxyl moieties. U.S. Pat. No. 3,332,880 contains a description of suitable olefin sulfonates, and its teachings are incorporated herein by reference. Such materials are sold as, for example, Bio-Terge® AS-40, a product of Stepan.

Organic phosphate-based anionic surfactants include organic phosphate esters such as complex mono- or diester phosphates of hydroxyl-terminated alkoxide condensates, or salts thereof. Suitable organic phosphate esters include phosphate esters of polyoxyalkylated alkylaryl phenols, phosphate esters of ethoxylated linear alcohols, and phosphate esters of ethoxylated phenols. Also included are nonionic alkoxylates having a sodium alkylene carboxylate moiety linked to a terminal hydroxyl group of the nonionic through an ether bond. Counterions to the salts of all the foregoing may be those of alkali metal, alkaline earth metal, ammonium, alkanolammonium and alkylammonium types.

Other anionic surfactants useful for detersive purposes can also be included in the detergent compositions. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C8-C22 primary of secondary alkanesulfonates, C8-C24 olefin sulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British Pat. No. 1,082,179, C8-C24 alkyl poly glycol ether sulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleoyl glycerol
sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C12-C18 monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C6-C12 diesters), sulfates of alkylpolyglycosides such as the sulfates of alkylpolyglucoside (the nonionic non-sulfated compounds being described below), and alkyl polyethoxy carboxylates such as those of the formula RO(CH2CH2O)kCH2COO-M+ where R is a C8-C22 alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. 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 described 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. Pat. Nos. 3,929,678 and 6,949,498, the teachings of which are incorporated herein by reference.

Other anionic surfactants contemplated include isethionates, sulfated triglycerides, alcohol sulfates, ligninsulfonates, naphthlene sulfonates and alkyl naphthene sulfonates, and the like.

For a more general description of suitable anionic surfactants, see U.S. Pat. No. 5,929,022, the teachings of which are incorporated herein by reference.

**Nonionic or Ampholytic Surfactants**

Examples of suitable nonionic surfactants include alkyl polyglucosides ("APGs"), alcohol ethoxylates, nonylphenol ethoxylates, methyl ester ethoxylates ("MEEs"), and others. The nonionic surfactant may be used as from 1% to 90%, more preferably from 1 to 40% and most preferably between 1% and 32% of a detergent composition. Other suitable nonionic surfactants are described in U.S. Pat. No. 5,929,022, from which much of the following discussion comes.

One class of nonionic surfactants useful herein are condensates of ethylene oxide with a hydrophobic moiety to provide a surfactant having an average hydrophilic-lipophilic balance (HLB) in the range from 8 to 17, preferably from 9.5 to 14, more preferably from 12 to 14. The hydrophobic (lipophilic) moiety may be aliphatic or
aromatic and the length of the polyoxyethylene group which is condensed with any
particular hydrophobic group can be readily adjusted to yield a water-soluble compound
having the desired degree of balance between hydrophilic and hydrophobic elements.

For "low HLB" nonionics, low HLB can be defined as having an HLB of 8 or less
and preferably 6 or less. A "low level" of co-surfactant can be defined as 6% or less of
the HDL and preferably 4% or less of the HDL.

Especially preferred nonionic surfactants of this type are the C9-C15 primary
alcohol ethoxylates containing 3-12 moles of ethylene oxide per mole of alcohol, particularly the C12-C15 primary alcohols containing 5-8 moles of ethylene oxide per
mole of alcohol. One suitable example of such a surfactant is polyalkoxylated aliphatic
base, sold for example as Bio-Soft® N25-7 by Stepan Company.

Another class of nonionic surfactants comprises alkyl polyglucoside compounds of
general formula:

\[ \text{RO-}(\text{C}_n\text{H}_{2n}\text{O})_t\text{Z}_x \]

where z is a moiety derived from glucose; R is a saturated hydrophobic alkyl
group that contains from 12 to 18 carbon atoms; t is from 0 to 10 and n is 2 or 3; \( x \) has
an average value from 1.3 to 4. The compounds include less than 10% unreacted fatty
alcohol and less than 50% short chain alkyl polyglucosides. Compounds of this type
and their use in detergent compositions are disclosed in EP-B 0 070 077, EP 0 075 996
and EP 0 094 118.

Also suitable as nonionic surfactants are polyhydroxy fatty acid amide surfactants
of the formula:

\[ \text{R}^2\text{C(O)-N(R}^1\text{)}\text{Z}_x \]

where \( R^1 \) is H, or \( R^1 \) is C1-4 hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl or a
mixture thereof, \( R^2 \) is C5-C31 hydrocarbyl, and z is a polyhydroxyhydrocarbyl having a
linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an
alkoxylated derivative thereof. Preferably, \( R^1 \) is methyl, \( R^2 \) is a straight C11-15 alkyl or
alkenyl chain 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.
Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and where one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono (see U.S. Pat. Nos. 3,664,961 and 3,929,678, the teachings of which are incorporated herein by reference). Suitable ampholytic surfactants include fatty amine oxides, fatty amidopropylamine oxides, fatty betaines, and fatty amidopropylamine betaines. Examples of suitable betaines are coco betaine (CB) and cocoamidopropyl betaine (CAPB). Commercially available betaines include Amphosol® HCG or Amphosol® HCA (cocoamidopropyl betaine) surfactants (Stepan). Suitable amine oxides include laurylamine oxide, myristylamine oxide, lauryl amidopropylamine oxide, myristyl amidopropylamine oxide, and the like, and mixtures thereof. Commercially available amine oxides include Ammonyx® LO, Ammonyx® MO, and Ammonyx® LMDO surfactants (Stepan).

Ampholytic surfactants can be used at a level from 1% to 50%, more preferably from 1% to 10%, even more preferably between 1% and 5% of the formulation, by weight.

Amine oxide surfactants are suitable ampholytic surfactants. Compositions herein may comprise an amine oxide in accordance with the general formula:

\[ R^1(EO)x(PO)y(BO)zN(O)(CH2R')2 \cdot H2O \]

In general, it can be seen that the preceding formula provides one long-chain moiety \( R^1(EO)x(PO)y(BO)z \) and two short chain moieties, \(-CH2R': R' \) is preferably selected from hydrogen, methyl and \(-CH2OH \). In general \( R^1 \) is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, \( R^1 \) is a primary alkyl moiety. When \( x+y+z=0 \), \( R^1 \) is a hydrocarbyl moiety having a chain length of from about 8 to about 18. When \( x+y+z \) is different from 0, \( R^1 \) may be somewhat longer, having a chain length in the range C12-C24. The general formula also encompasses amine oxides where \( x+y+z=0 \), \( R^1 \) is C8-C18, \( R' \) is H and \( q= \) from 0 to 2, preferably 2. These amine oxides are illustrated by C12-14 alkyl dimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, especially the
dihydrates as disclosed in U.S. Pat. Nos. 5,075,501 and 5,071,594, the teachings of which are incorporated herein by reference.

Also suitable are amine oxides where x+y+z is different from zero. Specifically, x+y+z is from about 1 to about 10, and R₁ is a primary alkyl group containing about 8 to about 24 carbons, preferably from about 12 to about 16 carbon atoms. In these embodiments y+z is preferably 0 and x is preferably from about 1 to about 6, more preferably from about 2 to about 4; EO represents ethyleneoxy; PO represents propyleneoxy; and BO represents butyleneoxy. Such amine oxides can be prepared by conventional synthetic methods, e.g., by the reaction of alkylethoxysulfates with dimethylamine followed by oxidation of the ethoxylated amine with hydrogen peroxide.

Preferred amine oxides are solids at ambient temperature. More preferably, they have melting points in the range of 30°C to 90°C. Amine oxides suitable for use are made commercially by Stepan, AkzoNobel, Procter & Gamble, and others. See McCutcheon's compilation and a Kirk-Othmer review article for alternate amine oxide manufacturers.

Suitable detergents may include, e.g., hexadecyldimethylamine oxide dihydrate, octadecyldimethylamine oxide dihydrate, hexadecyltris(ethyleneoxy)dimethylamine oxide, and tetradecyldimethylamine oxide dihydrate.

In certain aspects in which R' is H, there is some latitude with respect to having R' slightly larger than H. Specifically, R' may be CH₂OH, as in hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbi(2-hydroxyethyl)amine oxide.

Zwitterionic Surfactants

Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium and phosphonium or tertiary sulfonium compounds, in which the cationic atom may be part of a heterocyclic ring, and in which the aliphatic radical may be straight chain or branched, and where one of the aliphatic substituents contains from about 3 to 18 carbon atoms, and at least one aliphatic substituent contains an anionic water-solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphonato (see U.S. Pat. No. 3,664,961, the teachings of which are incorporated...
herein by reference). Zwitterionic surfactants can be used as from 1% to 50%, more preferably from 1% to 10%, even more preferably from 1% to 5% by weight of the present formulations.

Mixtures of any two or more individually contemplated surfactants, whether of the same type or different types, are contemplated herein.

Formulation and Use

Four desirable characteristics of a laundry detergent composition, in particular a liquid composition (although the present disclosure is not limited to a liquid composition, or to a composition having any or all of these attributes) are that (1) a concentrated formulation is useful to save on shelf space of a retailer, (2) a "green" or environmentally friendly composition is useful, (3) a composition that works in modern high efficiency washing machines which use less energy and less water to wash clothes than previous machines is useful, and (4) a composition that cleans well in cold water, i.e., less than 30°C, preferably 5°C to 30°C.

To save a substantial amount of retailer shelf space, a concentrated formulation is contemplated having two or even three, four, five, six, or even greater (e.g., 8x) times potency per unit volume or dose as conventional laundry detergents. The use of less water complicates the formulation of a detergent composition, as it needs to be more soluble and otherwise to work well when diluted in relatively little water.

To make a "green" formula, the surfactants should be ultimately biodegradable and non-toxic. To meet consumer perceptions and reduce the use of petrochemicals, a "green" formula may also advantageously be limited to the use of renewable hydrocarbons, such as vegetable or animal fats and oils, in the manufacture of surfactants.

High efficiency (HE) washing machines present several challenges to the detergent formulation. As of January 2011, all washing machines sold in the U.S. must be HE, at least to some extent, and this requirement will only become more restrictive in the coming years. Front loading machines, all of which are HE machines, represent the highest efficiency, and are increasingly being used.
Heavy duty liquid detergent formulas are impacted by HE machines because the significantly lower water usage requires that less foam be generated during the wash cycle. As the water usage levels continue to decrease in future generations of HE machines, detergents may be required to transition to no foam. In addition, HE HDLs should also disperse quickly and cleanly at lower wash temperatures.

To work in a modern high efficiency washing machine, the detergent composition needs to work in relatively concentrated form in cold water, as these washing machines use relatively little water and cooler washing temperatures than prior machines. The sudsing of such high-efficiency formulations must also be reduced, or even eliminated, in a low-water environment to provide effective cleaning performance. The anti-redeposition properties of a high efficiency detergent formulation also must be robust in a low-water environment. In addition, formulations that allow the used wash water to be more easily rinsed out of the clothes or spun out of the clothes in a washing machine are also contemplated, to promote efficiency.

Liquid fabric softener formulations and "softergent" (fabric softener/detergent dual functional) single-add formulations also may need to change as water usage continues to decline in HE machines. A washer-added softener is dispensed during the rinse cycle in these machines. The combined C4 to Cu dialkyl sulfo succinate and linear alkylbenzene sulfonate surfactants can be used in formulations that provide softening in addition to cleaning.

Laundry detergents and additives containing the presently described combined C4 to Cu dialkyl sulfo succinate and linear alkylbenzene sulfonate surfactants are contemplated to provide high concentration formulations, or "green" formulations, or formulations that work well in high efficiency washing machines. Such detergents and additives are contemplated that have at least one of the advantages or desirable characteristics specified above, or combinations of two or more of these advantages, at least to some degree. The ingredients contemplated for use in such laundry detergents and additives are found in the following paragraphs.

In addition to the surfactants as previously described, a laundry detergent composition commonly contains other ingredients for various purposes. Some of those ingredients are also described below.
**Builders and Alkaline Agents**

Builders and other alkaline agents are contemplated for use in the present formulations.

Any conventional builder system is suitable for use here, including aluminosilicate materials, silicates, polycarboxylates and fatty acids, materials such as ethylenediamine tetraacetate, metal ion sequestrants such as aminopolyphosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylene phosphonic acid. Though less preferred for environmental reasons, phosphate builders could also be used here.

Suitable polycarboxylate builders for use here include citric acid, preferably in the form of a water-soluble salt, and derivatives of succinic acid of the formula:

\[ R \text{-CH(COOH)}CH_2 \text{(COOH)} \]

where \( R \) is C10-20 alkyl or alkenyl, preferably C12-C16, or where \( R \) can be substituted with hydroxyl, sulfo, sulfoxy, or sulfone substituents. Specific examples include lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenylsuccinate, or 2-tetradecenyl succinate. Succinate builders are preferably used in the form of their water-soluble salts, including sodium, potassium, ammonium, and alkanolammonium salts.

Other suitable polycarboxylates are oxodisuccinates and mixtures of tartrate monosuccinic and tartrate disuccinic acid, as described in U.S. Pat. No. 4,663,071.

Especially for a liquid detergent composition, suitable fatty acid builders for use here are saturated or unsaturated C10-C18 fatty acids, as well as the corresponding soaps. Preferred saturated species have from 12 to 16 carbon atoms in the alkyl chain. The preferred unsaturated fatty acid is oleic acid. Another preferred builder system for liquid compositions is based on dodecenyl succinic acid and citric acid.

Some examples of alkaline agents include alkali metal (Na, K, or NH₄) hydroxides, carbonates, citrates, and bicarbonates. Another commonly used builder is borax.

For powdered detergent compositions, the builder or alkaline agent typically comprises from 1% to 95% of the composition. For liquid compositions, the builder or alkaline agent typically comprises from 1% to 60%, alternatively between 1% and 30%.
alternatively between 2% and 15%. See U.S. Pat. No. 5,929,022, the teachings of which are incorporated by reference, from which much of the preceding discussion comes. Other builders are described in PCT Int. Publ. WO 99/05242, which is incorporated here by reference.

Enzymes
The detergent compositions may further comprise one or more enzymes, which provide cleaning performance and/or fabric care benefits. The enzymes include cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxigenases, ligninases, pullulanases, tannases, pentosanases, malanases, beta-glucanases, arabinosidases or mixtures thereof.

A preferred combination is a detergent composition having a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase and/or cellulase in conjunction with the lipolytic enzyme variant D96L at a level of from 50 LU to 8500 LU per liter of wash solution.

Suitable cellulases 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. Pat. No. 4,435,307, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2 075 028; GB-A-2 095 275 and DE-OS-2 247 832.

Examples of such cellulases are cellulases produced by a strain of *Humicola insolens* (*Humicola grisea var. thermoidea*), particularly the *Humicola* strain DSM 1800. Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50,000, an isoelectric point of 5.5 and containing 415 amino acid units. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in EP Appl. No. 91202879.2.

Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, and the like. 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 haloperoxidases such as chloro- and bromoperoxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT Int. Appl. WO 89/099813 and in EP Appl. No. 91202882.6.

The cellulases and/or peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of active enzyme by weight of the detergent composition.

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase®, Savinase®, Primase®, Durazym®, and Esperase® by Novo Nordisk A/S (Denmark), those sold under the tradename Maxatase®, Maxacal® and Maxapem® by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean® and Optimase® by Solvay Enzymes. Other proteases are described in U.S. Pat. No. 5,679,630 can be included in the detergent compositions. Protease enzyme may be incorporated into the detergent compositions at a level of from about 0.0001% to about 2% active enzyme by weight of the composition.

A preferred protease here referred to as “Protease D” is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for the amino acid residue at a position in the carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of Bacillus amyloliquefaciens subtilisin, as described in U.S. Pat. No. 5,679,630, the teachings of which are incorporated herein by reference.

Highly preferred enzymes that can be included in the detergent compositions include lipases. It has been found that the cleaning performance on greasy soils is synergistically improved by using lipases. Suitable lipase enzymes include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in British Pat. No. 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of
the lipase, produced by the microorganism *Pseudomonas fluorescens* 1AM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereafter referred to as "Amano-P." Further suitable lipases are lipases such as M1 Lipase® and Lipomax® (Gist-Brocades). Highly preferred lipases are the D96L lipolytic enzyme variant of the native lipase derived from *Humicola lanuginosa* as described in U.S. Pat. No. 6,017,871. Preferably, the *Humicola lanuginosa* strain DSM 4106 is used. This enzyme is incorporated into the detergent compositions at a level of from 50 LU to 8500 LU per liter wash solution. Preferably, the variant D96L is present at a level of from 100 LU to 7500 LU per liter of wash solution. A more preferred level is from 150 LU to 5000 LU per liter of wash solution.

By "D96L lipolytic enzyme variant," we mean the lipase variant as described in PCT Int. Appl. WO 92/05249, where the native lipase ex *Humicola lanuginosa* aspartic acid (D) residue at position 96 is changed to leucine (L). According to this nomenclature, the substitution of aspartic acid to leucine in position 96 is shown as: D96L.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases that do not require interfacial activation. Addition of cutinases to detergent compositions is described, e.g. in PCT Int. Appl. No. WO 88/09367.

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001 % to 2% of active enzyme by weight of the detergent composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. Suitable amylases are Termamyl® (Novo Nordisk), Fungamyl® and BAN® amylases (Novo Nordisk).

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and/or yeast origin. See U.S. Pat. No. 5,929,022, the teachings of which are incorporated herein by reference, from which much of the preceding discussion comes. Preferred compositions optionally contain a combination of enzymes or a single enzyme, with the amount of each enzyme commonly ranging from 0.0001 % to 2%.
Other enzymes and materials used with enzymes are described in PCT Int. Appl. No. WO99/05242, which is incorporated here by reference.

**Adjuvants**

The detergent compositions optionally contain one or more soil suspending agents or resoiling inhibitors in an amount from about 0.01% to about 5% by weight, alternatively less than about 2% by weight. Resoiling inhibitors include anti-redeposition agents, soil release agents, or combinations thereof. Suitable agents are described in U.S. Pat. No. 5,929,022, and include water-soluble ethoxylated amines having clay soil removal and anti-redeposition properties. Examples of such soil release and anti-redeposition agents include an ethoxylated tetraethylenepentamine. Further suitable ethoxylated amines are described in U.S. Pat. 4,597,898, the teachings of which are incorporated herein by reference. Another group of preferred clay soil removal/anti-redeposition agents are the cationic compounds disclosed in EP Appl. No. 111,965. Other clay soil removal/anti-redeposition agents which can be used include the ethoxylated amine polymers disclosed in EP Appl. No. 111,984; the zwitterionic polymers disclosed in EP Appl. No. 112,592; and the amine oxides disclosed in U.S. Pat. No. 4,548,744, the teachings of which are incorporated herein by reference.

Other clay soil removal and/or anti-redeposition agents known in the art can also be utilized in the compositions hereof. Another type of preferred anti-redeposition agent includes the carboxymethylcellulose (CMC) materials.

Anti-redeposition polymers can be incorporated into HDL formulations described herein. It may be preferred to keep the level of anti-redeposition polymer below about 2%. At levels above about 2%, the anti-redeposition polymer may cause formulation instability (e.g., phase separation) and or undue thickening.

Soil release agents are also contemplated as optional ingredients in the amount of about 0.1% to about 5% (see, e.g., U.S. Pat. No. 5,929,022).

Chelating agents in the amounts of about 0.1% to about 10%, more preferably about 0.5% to about 5%, and even more preferably from about 0.8% to about 3%, are also contemplated as an optional ingredient (see, e.g., U.S. Pat. No. 5,929,022).
Polymeric dispersing agents in the amount of 0% to about 6% are also contemplated as an optional component of the presently described detergent compositions (see, e.g., U.S. Pat. No. 5,929,022).

A suds suppressor is also contemplated as an optional component of the present detergent composition, in the amount of from about 0.1% to about 15%, more preferably between about 0.5% to about 10% and even more preferably between about 1% to about 7% (see, e.g., U.S. Pat. No. 5,929,022).

Other ingredients that can be included in a liquid laundry detergent include perfumes, which optionally contain ingredients such as aldehydes, ketones, esters, and alcohols. More compositions that can be included are: carriers, hydrorotropes, processing aids, dyes, pigments, solvents, bleaches, bleach activators, fluorescent optical brighteners, and enzyme stabilizing packaging systems.

The co-surfactants and fatty acids described in U.S. Pat. No. 4,561,998, the teachings of which are incorporated herein by reference, can be included in the detergent compositions. In conjunction with anionic surfactants, these improve laundering performance. Examples include chloride, bromide and methylsulfate Cs-Ci6 alkyl trimethylammonium salts, Cs-Ci6 alkyl di(hydroxyethyl) methylammonium salts, Cs-Ci6 alkyl hydroxyethylidimethylammonium salts, and Cs-Ci6 alkyl oxypropyl trimethylammonium salts.

Similar to what is taught in U.S. Pat. 4,561,998, the compositions herein can also contain from about 0.25% to about 12%, preferably from about 0.5% to about 8%, more preferably from about 1% to about 4%, by weight of a cosurfactant selected from the group of certain quaternary ammonium, diquaternary ammonium, amine, diamine, amine oxide and di(amine oxide) surfactants. The quaternary ammonium surfactants are particularly preferred.

Quaternary ammonium surfactants can have the following formula:

\[ [R^2(OR^3)_y][R^4(OR^3)_z]_2 R^6 N^+ X^- \]

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
-CH₂CH₂--, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, --CH₂CH₂CH₂--, and mixtures thereof; each R⁴ is selected from the group consisting of C1-C4 alkyl, C1-C4 hydroxyalkyl, benzyl, ring structures formed by joining the two R⁴ groups, ~CH₂CHOHCHOHCOR ⁶CHOHCH₂OH wherein R⁶ is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

Preferred of the above are the alkyl quaternary ammonium surfactants, especially the mono-long chain alkyl surfactants described in the above formula when R⁵ is selected from the same groups as R⁴. The most preferred quaternary ammonium surfactants are the chloride, bromide and methylsulfate Cs-Ci6 alkyl trimethylammonium salts, C₈-C₁₆ alkyl di(hydroxyethyl) methylammonium salts, Cs-Ci6 alkyl hydroxyethyldimethylammonium salts, and Cs-Ci6 alkyl oxypropyl trimethylammonium salts. Of the above, decyl trimethylammonium methylsulfate, lauryl trimethylammonium chloride, myristyl trimethylammonium bromide and coconut trimethylammonium chloride and methylsulfate are particularly preferred.

U.S. Pat. No. 4,561,998 also provides that under cold water washing conditions, in this case less than about 65°F (18.3°C), the Cs-C₁₀ alkyltrimethyl ammonium surfactants are particularly preferred since they have a lower Kraft boundary and, therefore, a lower crystallization temperature than the longer alkyl chain quaternary ammonium surfactants herein.

Diquaternary ammonium surfactants can be of the formula:

\[ [R²(OR₃)ₙ][R⁴(OR₃)ₙ]₂N⁺R³N⁺R⁵][R⁴(OR₃)ₙ]₂(X⁻)₂ \]

wherein the R², R³, R⁴, R⁵, y and X substituents are as defined above for the quaternary ammonium surfactants. These substituents are also preferably selected to provide diquaternary ammonium surfactants corresponding to the preferred quaternary ammonium surfactants. Particularly preferred are the Cs-16 alkyl pentamethylenediammonium chloride, bromide and methylsulfate salts.

Amine surfactants useful herein are of the formula:

\[ [R²(OR₃)ₙ][R⁴(OR₃)ₙ]R⁵N \]
wherein the \( R_2, R_3, R_4, R_5 \) and \( y \) substituents are as defined above for the quaternary ammonium surfactants. Particularly preferred are the C\textsubscript{12-16} alkyl dimethyl amines.

Diamine surfactants herein are of the formula

\[
[R^2(OR_3)^y][R^4(OR_3)^y]NR^3NR^5[R^4(OR_3)^y]
\]

wherein the \( R_2, R_3, R_4, R_5 \) and \( y \) substituents are as defined above. Preferred are the C\textsubscript{12-16} alkyl trimethylene diamines.

Amine oxide surfactants useful herein are of the formula:

\[
[R^2(OR_3)^y][R^4(OR_3)^y]R^5N^O
\]

wherein the \( R_2, R_3, R_4, R_5 \) and \( y \) substituents are also as defined above for the quaternary ammonium surfactants. Particularly preferred are the C\textsubscript{12-16} alkyl dimethyl amine oxides.

Di(amine oxide) surfactants herein are of the formula:

\[
[R^2(OR_3)^y][R^4(OR_3)^y]NR^3NR^5[R^4(OR_3)^y]
\]

wherein the \( R_2, R_3, R_4, R_5 \) and \( y \) substituents are as defined above, preferably is C\textsubscript{12-16} alkyl trimethylene di(amine oxide).

Other common cleaning adjuncts are identified in U.S. Pat. No. 7,326,675 and PCT Int. Publ. WO 99/05242. Such cleaning adjuncts are identified as including bleaches, bleach activators, suds boosters, dispersant polymers (e.g., from BASF Corp. or Dow Chemical) other than those described above, color speckles, silvercare, anti-tarnish and/or anti-corrosion agents, pigments, dyes, fillers, germicides, hydrotropes, anti-oxidants, enzyme stabilizing agents, pro-perfumes, carriers, processing aids, solvents, dye transfer inhibiting agents, brighteners, structure elasticizing agents, fabric softeners, anti-abrasion agents, and other fabric care agents, surface and skin care agents. Suitable examples of such other cleaning adjuncts and levels of use are found in U.S. Pat. Nos. 5,576,282, 6,306,812, 6,326,348 and PCT Int. Publ. WO99/05242, the teachings of which are incorporated herein by reference.
**Fatty Acids**

Similar to that disclosed in U.S. Pat. No. 4,561,998, the detergent compositions may contain a fatty acid containing from about 10 to about 22 carbon atoms. The fatty acid can also contain from about 1 to about 10 ethylene oxide units in the hydrocarbon chain. Suitable fatty acids are saturated and/or unsaturated and can be obtained from natural sources such as plant or animal esters (e.g., palm kernel oil, palm oil, coconut oil, babassu oil, safflower oil, tall oil, castor oil, tallow and fish oils, grease, and mixtures thereof) or synthetically prepared (e.g., via the oxidation of petroleum or by hydrogenation of carbon monoxide via the Fisher-Tropsch process). Examples of suitable saturated fatty acids for use in the detergent compositions include capric, lauric, myristic, palmitic, stearic, arachidic and behenic acid. Suitable unsaturated fatty acid species include: palmitoleic, oleic, linoleic, linolenic and ricinoleic acid. Examples of preferred fatty acids are saturated C₁₀-C₁₄ (coconut) fatty acids, from about 5:1 to about 1:1 (preferably about 3:1) weight ratio mixtures of lauric and myristic acid, and mixtures of the above lauric/myristic blends with oleic acid at a weight ratio of about 4:1 to about 1:4 mixed lauric/myristic:oleic.

U.S. Pat. No. 4,507,219 identifies various sulfonate surfactants as suitable for use with the above-identified co-surfactants. The disclosures of U.S. Pat. Nos. 4,561,998 and 4,507,219 with respect to co-surfactants are incorporated herein by reference.

**Softergents**

Softergent technologies as described in, for example, U.S. Pat. Nos. 6,949,498, 5,466,394 and 5,622,925 can be used in the detergent compositions. "Softergent" refers to a softening detergent that can be dosed at the beginning of a wash cycle for the purpose of simultaneously cleaning and softening fabrics. The combined C₄ to C₆ dialkyl sulfosuccinate and linear alkylbenzene sulfonate surfactants can be used to make stable, aqueous heavy duty liquid laundry detergent compositions containing a fabric-softening agent that provide exceptional cleaning as well as fabric softening and anti-static benefits.
Some suitable softergent compositions contain about 0.5% to about 10%, preferably from about 2% to about 7%, more preferably from about 3% to about 5% by weight of a quaternary ammonium fabric-softening agent having the formula:

\[
\begin{array}{c}
R_4 \\
N \\
R_3 \\
R_2 \\
R_1
\end{array}
\]

wherein \( R_1 \) and \( R_2 \) are individually selected from the group consisting of \( \text{C}_1-\text{C}_4 \) alkyi, \( \text{C}_1-\text{C}_4 \) hydroxy alkyi, benzyl, and \(-(\text{C}_2\text{H}_4\text{O})_x\text{H}\) where \( x \) has a value from 2 to 5; \( X \) is an anion; and \( (1) \) \( R_3 \) and \( R_4 \) are each a \( \text{C}_8-\text{C}_{22} \) alkyi and \( (2) \) \( R_4 \) is selected from the group consisting of \( \text{C}_1-\text{C}_{10} \) alkyi, \( \text{C}_{10} \) hydroxy alkyi, benzyl, and \( -(\text{C}_2\text{H}_4\text{O})_x\text{H} \) where \( x \) has a value from 2 to 5.

Preferred fabric-softening agents are the mono-long chain alkyi quaternary ammonium surfactants wherein in the above formula \( R_1, R_2, \) and \( R_3 \) are each methyl and \( R_4 \) is a \( \text{C}_8-\text{C}_{12} \) alkyi. The most preferred quaternary ammonium surfactants are the chloride, bromide and methylsulfate \( \text{Cs-Ci6} \) alkyi trimethyl ammonium salts, and \( \text{Cs-Ci6} \) alkyi di(hydroxyethyl)-methyl ammonium salts. Of the above, lauryl trimethyl ammonium chloride, myristyl trimethyl ammonium chloride and coconut trimethylammonium chloride and methylsulfate are particularly preferred.

Another class of preferred quaternary ammonium surfactants are the di-\( \text{Cs-Ci4} \) alkyi dimethyl ammonium chloride or methylsulfates; particularly preferred is di- \( \text{C12-C14} \) alkyi dimethyl ammonium chloride. This class of materials is particularly suited to providing antistatic benefits to fabrics.

A preferred softergent comprises the detergent composition wherein the weight ratio of anionic surfactant component to quaternary ammonium softening agent is from about 3:1 to about 40:1; a more preferred range is from about 5:1 to 20:1.

**Odor Control**

Odor control technologies as described in, for example, U.S. Pat. No. 6,878,695 can be used in the detergent compositions.
For example, a composition containing the combined C4 to C14 dialkyl sulfosuccinate and linear alkylbenzene sulfonate surfactants can further comprise a low-degree of substitution cyclodextrin derivative and a perfume material. The cyclodextrin is preferably functionally-available cyclodextrin. The compositions can further comprise optional cyclodextrin-compatible and -incompatible materials, and other optional components. Such a composition can be used for capturing unwanted molecules in a variety of contexts, preferably to control malodors including controlling malodorous molecules on inanimate surfaces, such as fabrics, including carpets, and hard surfaces including countertops, dishes, floors, garbage cans, ceilings, walls, carpet padding, air filters, and the like, and animate surfaces, such as skin and hair.

The low-degree of substitution cyclodextrin derivatives useful herein are preferably selected from low-degree of substitution hydroxyalkyi cyclodextrin, low-degree of substitution alkylated cyclodextrin, and mixtures thereof. Preferred low-degree of substitution hydroxyalkyi beta-cyclodextrins have an average degree of substitution of less than about 5.0, more preferably less than about 4.5, and still more preferably less than about 4.0. Preferred low-degree of substitution alkylated cyclodextrins have an average degree of substitution of less than about 6.0, more preferably less than about 5.5, and still more preferably less than about 5.0.

The detergent compositions can comprise a mixture of cyclodextrins and derivatives thereof such that the mixture effectively has an average degree of substitution equivalent to the low-degree of substitution cyclodextrin derivatives described hereinbefore. Such cyclodextrin mixtures preferably comprise high-degree of substitution cyclodextrin derivatives (having a higher average degree of substitution than the low-degree substitution cyclodextrin derivatives described herein) and non-derivatized cyclodextrin, such that the cyclodextrin mixture effectively has an average degree of substitution equivalent to the low-degree of substitution cyclodextrin derivative. For example, a composition comprising a cyclodextrin mixture containing about 0.1\% non-derivatized beta-cyclodextrin and about 0.4\% hydroxypropyl beta-cyclodextrin having an average degree of substitution of about 5.5, exhibits an ability to capture unwanted molecules similar to that of a similar composition comprising low-degree of substitution hydroxypropyl beta-cyclodextrin having an average degree of
substitution of about 3.3. Such cyclodextrin mixtures can typically absorb odors more broadly by complexing with a wider range of unwanted molecules, especially malodorous molecules, having a wider range of molecular sizes preferably at least a portion of a cyclodextrin mixture is alpha-cyclodextrin and its derivatives thereof, gamma-cyclodextrin and its derivatives thereof, and/or beta-cyclodextrin and its derivatives thereof; more preferably a mixture of alpha-cyclodextrin, or an alpha-cyclodextrin derivative, and derivatized beta-cyclodextrin, even more preferably a mixture of derivatised alpha-cyclodextrin and derivatized beta-cyclodextrin; and most preferably a mixture of hydroxypropyl alpha-cyclodextrin and hydroxypropyl beta-cyclodextrin, and/or a mixture of methylated alpha-cyclodextrin and methylated beta-cyclodextrin.

The cavities within the functionally-available cyclodextrin in the detergent compositions should remain essentially unfilled (i.e., the cyclodextrin remains uncomplexed and free) or filled with only weakly complexing materials when in solution, in order to allow the cyclodextrin to absorb (i.e., complex with) various unwanted molecules, such as malodor molecules, when the composition is applied to a surface containing the unwanted molecules. Non-derivatized (normal) beta-cyclodextrin can be present at a level up to its solubility limit of about 1.85% (about 1.85 g in 100 grams of water) at room temperature. Beta-cyclodextrin is not preferred in compositions which call for a level of cyclodextrin higher than its water solubility limit. Non-derivatized beta-cyclodextrin is generally not preferred when the composition contains surfactant since it affects the surface activity of most of the preferred surfactants that are compatible with the derivatized cyclodextrins.

The level of low-degree of substitution cyclodextrin derivatives that are functionally-available in the odor control compositions is typically at least about 0.001%, preferably at least about 0.01%, and more preferably at least about 0.1%, by weight of the detergent composition. The total level of cyclodextrin in the present composition will be at least equal to or greater than the level of functionally-available cyclodextrin. The level of functionally-available will typically be at least about 10%, preferably at least about 20%, and more preferably at least about 30%, by weight of the total level of cyclodextrin in the composition.
Concentrated compositions can also be used. When a concentrated product is used, i.e., when the total level of cyclodextrin used is from about 3% to about 60%, more preferably from about 5% to about 40%, by weight of the concentrated composition, it is preferable to dilute the concentrated composition before treating fabrics in order to avoid staining. Preferably, the concentrated cyclodextrin composition is diluted with about 50% to about 6000%, more preferably with about 75% to about 2000%, most preferably with about 100% to about 1000% by weight of the concentrated composition of water. The resulting diluted compositions have usage concentrations of total cyclodextrin and functionally-available cyclodextrin as discussed hereinbefore, e.g., from about 0.1% to about 5%, by weight of the diluted composition of total cyclodextrin and usage concentrations of functionally-available cyclodextrin of at least about 0.001%, by weight of the diluted composition.

Forms
The detergent compositions can take any of a number of forms and any type of delivery system, such as ready-to-use, dilutable, wipes, or the like.

For example, the detergent compositions can be a dilutable fabric detergent, which may be an isotropic liquid, a surfactant-structured liquid, a granular, spray-dried or dry-blended powder, a tablet, a paste, a molded solid, a water soluble sheet, or any other laundry detergent form known to those skilled in the art. A "dilutable" fabric detergent composition is defined, for the purposes of this disclosure, as a product intended to be used by being diluted with water or a non-aqueous solvent by a ratio of more than 100:1, to produce a liquor suitable for treating textiles. "Green concentrate" compositions like those on the market today for Fantastic®, Windex® and the like, can be formulated such that they could be a concentrate to be added to a bottle for final reconstitution.

The detergent compositions can also be formulated as a gel or a gel packet or pod like the dishwasher products on the market today. Water-soluble sheets, sachets, or pods such as those described in U.S. Pat. Appl. No. 2002/01 87909, the teachings of which are incorporated herein by reference, are also envisaged as a suitable form. The detergent composition can also be deposited on a wiper or other substrate.
Polymeric suds enhancers

In some aspects, polymeric suds enhancers such as those described in U.S. Pat. No. 6,903,064 can be used in the detergent compositions. For example, the compositions may further comprise an effective amount of polymeric suds volume and suds duration enhancers. These polymeric materials provide enhanced suds volume and suds duration during cleaning.

Examples of polymeric suds stabilizers suitable for use in the compositions:
(i) a polymer comprising at least one monomeric unit having the formula:

\[ \begin{array}{c}
\text{R}^2 \\
\text{R}^1 \\
\text{R}^3 \\
\text{L}
\end{array} \]

\[ \text{A} \rightarrow (Z)_2 \rightarrow O \]

wherein each of \( \text{R}^1 \), \( \text{R}^2 \) and \( \text{R}^3 \) are independently selected from the group consisting of hydrogen, \( \text{C}_1 \) to \( \text{C}_5 \) alkyl, and mixtures thereof; \( \text{L} \) is \( \text{O} \); \( \text{Z} \) is \( \text{CH}_2 \); \( z \) is an integer selected from about 2 to about 12; \( \text{A} \) is \( \text{N} \text{R}^4 \text{R}^5 \), wherein each of \( \text{R}^4 \) and \( \text{R}^5 \) is independently selected from the group consisting of hydrogen, \( \text{C}_1 \) to \( \text{C}_5 \) alkyl, and mixtures thereof, or \( \text{N} \text{R}^4 \text{R}^5 \) form an heterocyclic ring containing from 4 to 7 carbon atoms, optionally containing additional hetero atoms, optionally fused to a benzene ring, and optionally substituted by \( \text{C}_1 \) to \( \text{C}_5 \) hydrocarbyl;

(ii) a proteinaceous suds stabilizer having an isoelectric point from about 7 to about 11.5;

(iii) a zwitterionic polymeric suds stabilizer; or

(iv) mixtures thereof.

Preferably, the exemplary polymeric suds stabilizer described above has a molecular weight of from about 1,000 to about 2,000,000; more preferably the molecular weight is about 5,000 to about 1,000,000.

Other applications

Although we found that combinations of \( \text{C}_4 \) to \( \text{C}_{14} \) dialkyl sulfosuccinate or sulfomethylsuccinate and linear alkylbenzene sulfonate surfactants have considerable
value for laundry detergents, other end uses should benefit from their use. Thus, the surfactants should also be valuable in applications where greasy substances require removal or cleaning at low temperature. Such applications include, for example, household cleaners, degreasers, sanitizers and disinfectants, light-duty liquid detergents, hard and soft surface cleaners for household, autodish detergents, rinse aids, laundry additives, carpet cleaners, spot treatments, softergents, liquid and sheet fabric softeners, industrial and institutional cleaners and degreasers, oven cleaners, car washes, transportation cleaners, drain cleaners, industrial cleaners, oil dispersants, foamers, defoamers, institutional cleaners, janitorial cleaners, glass cleaners, graffiti removers, adhesive removers, concrete cleaners, metal/machine parts cleaners, and food service cleaners, and other similar applications for which removal of greasy soils is advantageously accomplished, particularly at room temperature or below. The detergents may also be beneficial for certain personal care applications such as hand soaps and liquid cleansers, shampoos, and other hair/scalp cleansing products, especially for oily/greasy hair, scalp, and skin, which are also beneficial when effective with lukewarm or cold water.

The following examples merely illustrate the invention; those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

**Sulfosuccinate surfactants**

A commercial sample of di-2-ethylhexyl sulfosuccinate is used (Stepwet® DOS 70). Other sulfosuccinates are prepared by first reacting the required C4-C14 alcohol (or alcohol mixture) with maleic anhydride, followed by sulfitation of the carbon-carbon double bond with sodium metabisulfite, then neutralization to afford the desired C4-C14 dialkyl sulfosuccinate, all by well-known methods.

**Test formulations**

Tables 1 and 2 summarize the laundry detergent formulations tested for the inventive and comparative examples, respectively.
Procedure for testing laundry detergent samples

Laundry detergent (to give 0.1% actives in washing solution) is charged to a washing machine, followed by soiled/stained fabric swatches that are attached to pillowcases. Wash temperature: 60°F. Rinse temperature: 60°F. The swatches are detached from pillowcases, dried, and ironed. Swatches are scanned to measure the L° a° b° values, which are used to calculate a soil removal index (SRI) for each type of swatch. Finally, the ASRI is calculated, which equals the experimental sample SRI minus the SRI of a pre-determined standard laundry detergent formula (or control). When |ASRI| > 0.5 differences are perceivable to the naked eye. If the value of ASRI is greater than or equal to 0.5, the sample is superior. If ASRI is less than or equal to -0.5, the sample is inferior. If ASRI is greater than -0.5 and less than 0.5, the sample is considered equal to the standard.

The following standard soiled/stained fabric swatches are used: bacon grease, cooked beef fat, and beef tallow. At least three of each kind of swatch are used per wash. Swatches are stapled to pillowcases for laundering, and extra pillowcases are included to complete a six-pound load.

The same procedure is used to launder all of the pillowcases/swatches, with care taken to ensure that water temperature, wash time, manner of addition, etc. are held constant for the cold-water wash process. When the cycle is complete, swatches are removed from the pillowcases, dried at low heat on a rack, and pressed gently and briefly with a dry iron.

A Hunter LabScan® XE spectrophotometer is used to determine the L° a° b° values to calculate the SRI for every type of swatch, and the stain removal index (SRI) is calculated as follows:

\[
SRI = 100 - \sqrt{(L°_{clean} - L°_{washed})^2 + (a°_{clean} - a°_{washed})^2 + (b°_{clean} - b°_{washed})^2}
\]

\[
\Delta SRI = SRI_{sample} - SRI_{standard}
\]

Performance results for cold-water cleaning of cotton fabric treated with bacon grease, cooked beef fat, and beef tallow greasy soils are compared. All formulations are tested at 0.1% actives levels. Wash cycles are 30 min in front-loading high-efficiency washing machines. The target performance (which corresponds to a ASRI
value of 0.0) is that of a commercial cold-water detergent or a control cold-water detergent used with a cold-water wash (60°F) and cold-water rinse (60°F).

Results

Table 3 summarizes cold-water cleaning results using detergents comprising C4-C14 dialkyl sulfosuccinates and either a linear alkylbenzene sulfonate ("NaLAS," inventive examples) or a sodium C12-C14 alcohol ethoxylate (3 EO) sulfate ("NaAES," comparative examples). As the table shows, the cleaning performance on these greasy soils is generally unremarkable when a combination of a C4-C14 dialkyl sulfosuccinate and NaAES is used (with the exception of the combination of a C10 dialkyl sulfosuccinate and NaAES, which provides enhanced performance compared with the control). However, when the C4-C14 dialkyl sulfosuccinate is combined with NaLAS, cold-water cleaning performance on greasy soils consistently improves when compared with the applicable control. In particular, the change in stain removal index versus the control across all three stains ("overall ASRI") improves for all of the C4-C14 dialkyl sulfosuccinate/NaLAS combinations. The results demonstrate that cold-water cleaning performance on greasy soils is unpredictable, and that the selection of anionic surfactant to be used in combination with the C4-C14 dialkyl sulfosuccinate matters: although NaLAS and NaAES are both well known for use in laundry detergent formulations in general, only NaLAS provides a benefit when combined with C4-C14 dialkyl sulfosuccinate for cold-water cleaning on these greasy soils. In cases where cold-water detergency performance is desired for both greasy soils and stains such as green grass, red wine, clay, and the like, both NaLAS and NaAES surfactants could be combined with the C4-C14 dialkyl sulfosuccinate or sulfomethylsuccinate.
## Table 1. Cold-Water Liquid Laundry Detergent Formulations

**INVENTIVE examples**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Control, wt.% active</th>
<th>Formulation, wt.% active</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>C</td>
</tr>
<tr>
<td>Sodium citrate dehydrate</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Bio-Soft® S-101, 96.85% (HLAS)</td>
<td>7.9</td>
<td>7.9</td>
</tr>
<tr>
<td>Monoethanolamine, 99%</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Neodol® 25-7, 100%</td>
<td>11.9</td>
<td>11.9</td>
</tr>
<tr>
<td>Stepanate® SCS, 44.9% (Na cumene sulfonate)</td>
<td>1.115</td>
<td>1.115</td>
</tr>
<tr>
<td>Coco fatty acid, Emry 622, 100%</td>
<td>2.95</td>
<td>2.95</td>
</tr>
<tr>
<td>Sodium C\textsubscript{12}-C\textsubscript{14} alcohol ethoxylate (3 EO) sulfate, 27.66%, (NaAES 3EO)</td>
<td>7.74</td>
<td>--</td>
</tr>
<tr>
<td>Diisobutylsulfosuccinate, 45.4%</td>
<td>--</td>
<td>7.74</td>
</tr>
<tr>
<td>Di-n-amylsulfosuccinate, 100.0%</td>
<td>--</td>
<td>7.74</td>
</tr>
<tr>
<td>Di-n-hexylsulfosuccinate, 79.6%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Di-2-ethylhexylsulfosuccinate, 99.0%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Di-n-decylsulfosuccinate, 95.2%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Di-n-C\textsubscript{12}C\textsubscript{14}sulfosuccinate, 96.2%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Deionized water</td>
<td>q.s. to 100%</td>
<td>q.s. to 100%</td>
</tr>
<tr>
<td>NaOH, 50%</td>
<td>q.s.</td>
<td>q.s.</td>
</tr>
<tr>
<td>adjusted pH</td>
<td>8.4</td>
<td>8.4</td>
</tr>
<tr>
<td></td>
<td>Control, wt.% active</td>
<td>Formulation, wt.% active</td>
</tr>
<tr>
<td>--------------------------</td>
<td>----------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>D</td>
</tr>
<tr>
<td>Sodium citrate dihydrate</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Bio-Soft® S-101, 96.85% (HLAS)</td>
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<td>2.95</td>
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<tr>
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<td>7.74</td>
</tr>
<tr>
<td>Diisobutylsulfosuccinate, 45.4%</td>
<td>--</td>
<td>7.9</td>
</tr>
<tr>
<td>Di-n-amylsulfosuccinate, 100.0%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Di-n-hexylsulfosuccinate, 79.6%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Di-2-ethylhexylsulfosuccinate, 99.0%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Di-n-decylsulfosuccinate, 95.2%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Di-n-C_{12-14}sulfosuccinate, 96.2%</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Deionized water</td>
<td>q.s. to 100%</td>
<td>q.s. to 100%</td>
</tr>
<tr>
<td>NaOH, 50%</td>
<td>q.s.</td>
<td>q.s.</td>
</tr>
<tr>
<td>adjusted pH</td>
<td>8.4</td>
<td>8.4</td>
</tr>
</tbody>
</table>
Table 3. Performance in Cold-Water Cleaning Greasy Soil Stain Set

<table>
<thead>
<tr>
<th>Test formulation (0.1% actives)</th>
<th>ASRI of Cleaning Data at 60°F wash/60°F rinse</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bacon Grease</td>
</tr>
<tr>
<td>Control</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Inventive examples**

<table>
<thead>
<tr>
<th></th>
<th>Bacon Grease</th>
<th>Beef Tallow</th>
<th>Cooked Beef Fat</th>
<th>Overall ASRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diisobutylsulfosuccinate/NaLAS /N25-7-(Formulation A)</td>
<td>4.58</td>
<td>0.17</td>
<td>-0.51</td>
<td>4.24</td>
</tr>
<tr>
<td>Di-n-amylsulfosuccinate/NaLAS /N25-7-(Formulation C)</td>
<td>3.92</td>
<td>3.48</td>
<td>-0.83</td>
<td>6.57</td>
</tr>
<tr>
<td>Di-n-hexylsulfosuccinate/NaLAS /N25-7-(Formulation E)</td>
<td>2.92</td>
<td>3.70</td>
<td>-1.75</td>
<td>4.87</td>
</tr>
<tr>
<td>Di-2-ethylhexylsulfosuccinate/NaLAS /N25-7-(Formulation G)</td>
<td>5.74</td>
<td>12.88</td>
<td>1.17</td>
<td>19.79</td>
</tr>
<tr>
<td>Di-n-decylsulfosuccinate/NaLAS /N25-7-(Formulation I)</td>
<td>1.27</td>
<td>7.74</td>
<td>2.41</td>
<td>11.42</td>
</tr>
<tr>
<td>Di-n-C_{12}/C_{14}sulfosuccinate/NaLAS /N25-7-(Formulation K)</td>
<td>0.1 1</td>
<td>1.65</td>
<td>-0.34</td>
<td>1.42</td>
</tr>
</tbody>
</table>

**Comparative examples**

<table>
<thead>
<tr>
<th></th>
<th>Bacon Grease</th>
<th>Beef Tallow</th>
<th>Cooked Beef Fat</th>
<th>Overall ASRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diisobutylsulfosuccinate/NaAES /N25-7-(Formulation B)</td>
<td>4.35</td>
<td>-2.54</td>
<td>-1.80</td>
<td>0.0</td>
</tr>
<tr>
<td>Di-n-amylsulfosuccinate/NaAES /N25-7-(Formulation D)</td>
<td>3.1 6</td>
<td>-2.85</td>
<td>-2.09</td>
<td>-1.78</td>
</tr>
<tr>
<td>Di-n-hexylsulfosuccinate/NaAES /N25-7-(Formulation F)</td>
<td>3.04</td>
<td>-4.82</td>
<td>-2.18</td>
<td>-3.96</td>
</tr>
<tr>
<td>Di-2-ethylhexylsulfosuccinate/NaAES /N25-7-(Formulation H)</td>
<td>2.81</td>
<td>0.73</td>
<td>-1.58</td>
<td>1.96</td>
</tr>
<tr>
<td>Di-n-decylsulfosuccinate/NaAES /N25-7-(Formulation J)</td>
<td>0.03</td>
<td>6.09</td>
<td>3.28</td>
<td>9.37</td>
</tr>
<tr>
<td>Di-n-C_{12}/C_{14}sulfosuccinate/NaAES /N25-7-(Formulation L)</td>
<td>0.29</td>
<td>-3.96</td>
<td>-2.18</td>
<td>-5.85</td>
</tr>
</tbody>
</table>

The preceding examples are meant only as illustrations; the following claims define the invention.
We claim:

1. A method which comprises laundering one or more textile articles in water having a temperature less than or equal to 30°C in the presence of a detergent comprising:
   (a) a C4 to C4 dialkyi sulfosuccinate or sulfomethylsuccinate;
   (b) a linear alkylbenzene sulfonate; and
   (c) optionally, a nonionic surfactant.

2. The method of claim 1 wherein the dialkyi sulfosuccinate or sulfomethylsuccinate is a C6 to C12 dialkyi sulfosuccinate or sulfomethylsuccinate.

3. The method of claim 1 wherein the dialkyi sulfosuccinate or sulfomethylsuccinate is a Cs to C10 dialkyi sulfosuccinate or sulfomethylsuccinate.

4. The method of claim 1 wherein the dialkyi sulfosuccinate or sulfomethylsuccinate is a Cs dialkyi sulfosuccinate or sulfomethylsuccinate.

5. The method of claim 1 wherein the nonionic surfactant is a fatty alcohol ethoxylate.

6. The method of claim 1 wherein the detergent comprises 1 to 70 wt.% of the dialkyi sulfosuccinate or sulfomethylsuccinate, 1 to 70 wt.% of the linear alkylbenzene sulfonate, and 1 to 70 wt.% of the nonionic surfactant, all based on 100% actives.

7. The method of claim 1 wherein the detergent comprises 1 to 20 wt.% of the dialkyi sulfosuccinate or sulfomethylsuccinate, 1 to 20 wt.% of the linear alkylbenzene sulfonate, and 1 to 30 wt.% of the nonionic surfactant, all based on 100% actives.

8. The method of claim 1 wherein the detergent comprises 5 to 10 wt.% of the dialkyi sulfosuccinate or sulfomethylsuccinate, 5 to 10 wt.% of the linear alkylbenzene sulfonate, and 5 to 20 wt.% of the nonionic surfactant, all based on 100% actives.

9. The method of claim 1 wherein the detergent is in the form of a liquid, powder, paste, granule, tablet, molded solid, water-soluble sheet, water-soluble sachet, or water-soluble pod.

10. The method of claim 1 wherein the water has a temperature within the range of 5°C to 30°C.

11. The method of claim 1 wherein the detergent is used as a pre-spotter or pre-soaker for cold-water manual or machine washing.
12. The method of claim 1 wherein the detergent is used as an additive or booster component to improve grease removal performance.

13. The method of claim 1 wherein the textile articles are soiled with a greasy soil.

14. The method of claim 13 wherein the greasy soil comprises beef tallow.

15. A method which comprises laundering one or more textile articles in water having a temperature within the range of 5°C to 30°C in the presence of a detergent comprising:
   
   (a) 1 to 20 wt.% actives of a Cs to Cio dialkyi sulfosuccinate or sulfomethylsuccinate;  
   
   (b) 1 to 20 wt.% actives of a linear alkylbenzene sulfonate; and  
   
   (c) 1 to 30 wt.% actives of the nonionic surfactant, all based on 100% actives.

16. The method of claim 15 wherein the detergent comprises:
   
   (a) 5 to 10 wt.% actives of a Cs dialkyi sulfosuccinate or sulfomethylsuccinate;  
   
   (b) 5 to 10 wt.% actives of the linear alkylbenzene sulfonate; and  
   
   (c) 5 to 20 wt.% actives of a fatty alcohol ethoxylate.
# INTERNATIONAL SEARCH REPORT

**PCT/US2016/035162**

## A. CLASSIFICATION OF SUBJECT MATTER

**INV. CII/D1/37 CII/D1/83 CII/D1/00**

**ADD.**

According to International Patent Classification (IPC) onto both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

CII/D

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)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>CN 102 333 853 A (FARIBORZ DEWUDIAN) 25 January 2012 (2012-01-25) pages 3-7; cl aims 13-6</td>
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**[X]** Further documents are listed in the continuation of Box C.  

**[X]** See patent family annex.

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Date of the actual completion of the international search: 5 August 2016

Date of mailing of the international search report: 12/08/2016

Name and mailing address of the ISA/

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Fax: (+31-70) 340-3016

Authorized officer: Kanbi er, Titia

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