AQUEOUS AND NON-AQUEOUS HEAVY DUTY LIQUID DETERGENT COMPOSITIONS COMPRISING MID-CHAIN BRANCHED SURFACTANTS

Abstract

Aqueous and non-aqueous, heavy duty liquid laundry detergent compositions which essentially include a branched surfactant mixture which comprises mid-chain branched and linear surfactant compounds, said linear compounds being greater than 25 % and less than about 70 %, by weight of the branched surfactant mixture. The mid-chain branched surfactant compounds are of the formula: \( A^b - B \). \( A^b \) is a hydrophobic moiety having from about 10 to about 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from about 9 to about 17 carbon atoms, there being one or more \( C_1-C_3 \) alkyl moieties branching from the longest chain, provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon 1 which is attached to the – B moiety, to position \( \omega - 2 \) carbon, wherein \( \omega \) is the terminal carbon. B is a hydrophilic moiety selected from the group consisting of S02M, (EO/PO)mSO2M, (EO/PO)mOH and mixtures thereof, wherein EO/PO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, wherein \( m \) is at least about 0.01 to about 30 and M is hydrogen or a salt forming cation. Provided that the average total number of carbon atoms in the \( A^b \) moiety in the branched surfactant mixture is within the range of greater than 12 to about 14.5.
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AQUEOUS AND NON-AQUEOUS HEAVY DUTY LIQUID DETERGENT COMPOSITIONS COMPRISING MID-CHAIN BRANCHED SURFACTANTS

FIELD OF THE INVENTION

This invention relates to heavy duty liquid laundry detergent products which are aqueous or non-aqueous in nature and which include mid-chain branched surfactants and which preferably also include additional surfactants and other conventional detergent composition adjuvants.

BACKGROUND OF THE INVENTION

Conventional detergents comprise molecules having a water-solubilizing substituent (hydrophilic group) and an oleophilic substituent (hydrophobic group). Such surfactants typically comprise hydrophilic groups such as carboxylate, sulfate, sulfonate, amine oxide, polyoxyethylene, and the like, attached to an alkyl, alkenyl or alkaryl hydrophobe usually containing from about 10 to about 20 carbon atoms.

The literature asserts that certain branched hydrophobes can be used to advantage in the manufacture of alkyl sulfate detergents; see, for example, U.S. 3,480,556 to deWitt, et al., November 25, 1969. However, it has been determined that the beta-branched surfactants described in the '556 patent are inferior with respect to certain solubility parameters, as evidenced by their Krafft temperatures. It has further been determined that surfactants having branching towards the center of carbon chain of the hydrophobe have much lower Krafft temperatures. See: "The Aqueous Phase Behavior of Surfactants", R.G. Laughlin, Academic Press, N.Y. (1994) p. 347. Accordingly, it has now been determined that such surfactants are preferred for use especially under cool or cold water washing conditions (e.g., 20°C-5°C).

Generally, alkyl sulfates are well known to those skilled in the art of detergents. Alkyl sulfates were developed as a functional improvement over traditional soap surfactants and have been found to possess improved solubility and surfactant characteristics. Linear alkyl sulfates are the most commonly used of the alkyl sulfate surfactants and are the easiest to obtain. For example, long-chain linear alkyl sulfates, such as tallow alkyl sulfate, have been used in laundry
detergents. However, these have significant cleaning performance limitations, especially with the trend to lower wash temperatures.

Also, as noted hereinbefore, the 2-alkyl or "beta" branched alkyl sulfate surfactants are known. In addition to U.S. 3,480,556 discussed above, more recently EP 439,316, published July 31, 1991, and EP 684,300, published November 29, 1995, describe these beta-branched alkyl sulfates. R.G. Laughlin in "The Aqueous Phase Behavior of Surfactants", Academic Press, N.Y. (1994) p. 347 observes that as branching moves away from the 2-alkyl position towards the center of the alkyl hydrophobe there is a lowering of Krafft temperatures (for a 15% solution), such solubility observations teach nothing about the surfactancy of these compounds or their utility for incorporation into detergent compositions. In fact, both commercial practice and the published literature are equivocal on the desirability of branching in the mid-chain region.

Thus, going beyond simple technical theories of how to achieve cleaning superiority of one pure surfactant compound versus another, the developer and formulator of surfactants for laundry detergents must consider a wide variety of possibilities with limited (sometimes inconsistent) information, and then strive to provide overall improvements in one or more of a whole array of criteria, including performance in the presence of complex mixtures of surfactants, trends to low wash temperatures, formulation changes including builders, enzymes and bleaches, various changes in consumer habits and practices, and the need for biodegradability. In the context provided by these preliminary remarks, the development of improved alkyl sulfates for use in laundry detergents and cleaning products is clearly a complex challenge. The present invention relates to improvements in such alkyl sulfate surfactant compositions.

As will be seen from the disclosures hereinafter, it has now unexpectedly been determined that certain relatively short-chain alkyl sulfate and alkylethoxylated sulfate compositions containing mid-chain branching are preferred for use in laundry products, especially under cool or cold water washing conditions (e.g., 20°C-5°C). Preferred are the combination of two or more of these mid-chain branched alkyl sulfate and alkylethoxylated sulfate surfactants which provide a surfactant mixture that is higher in surfactancy and has better low temperature water solubility than any single branched alkyl sulfate or alkylethoxylated sulfate. The mixtures as produced comprise the mid-chain branching desirable for use in the surfactant mixtures of the present invention or the surfactant mixtures disclosed herein can be formulated by mixing the desired amounts of individual mid-chain branched surfactants. Such superior mixtures are not limited to combinations with other mid-chain branched
surfactants but (preferably) they can be suitably combined with one or more other traditional detergent surfactants (e.g., other primary alkyl sulfates; linear alkyl benzene sulfonates; alkyl ethoxylated sulfates; nonionic surfactants; etc.) to provide improved surfactant systems.

It is therefore an object of the present invention to provide mid-chain branched primary alkyl sulfate and alkylethoxylated sulfate surfactants with an average of less than 14.5 carbon atoms which are useful in cleaning compositions. It is also an object of the present invention to provide mixtures of the mid-chain branched primary alkyl surfactants which are formulatable with other surfactants to provide cleaning compositions having one or more advantages, including greater surfactancy at low use temperatures, increased resistance to water hardness, greater efficacy in surfactant systems, improved removal of greasy or body soils from fabrics, improved compatibility with detergent enzymes, and the like.

BACKGROUND ART

U.S. 3,480,556 to deWitt, et al., November 25, 1969, EP 439,316, published by Lever July 31, 1991, and EP 684,300, published by Lever November 29, 1995, describe beta-branched alkyl sulfates. EP 439,316 describes certain laundry detergents containing a specific commercial C14/C15 branched primary alkyl sulfate, namely LIAL 145 sulfate. This is believed to have 61% branching in the 2-position; 30% of this involves branching with a hydrocarbon chain having four or more carbon atoms. U.S. 3,480,556 describes mixtures of from 10 to 90 parts of a straight chain primary alkyl sulfate and from 90 to 10 parts of a beta branched (2-position branched) primary alcohol sulfate of formula:

$$\text{R}^2\text{CHCH}_2\text{OSO}_3\text{X}$$

wherein the total number of carbon atoms ranges from 12 to 20 and R1 is a straight chain alkyl radical containing 9 to 17 carbon atoms and R2 is a straight chain alkyl radical containing 1 to 9 carbon atoms (67% 2-methyl and 33% 2-ethyl branching is exemplified).

EP 342,917 A, Unilever, published Nov. 23, 1989 describes laundry detergents containing a surfactant system in which the major anionic surfactant is an alkyl sulfate having an assertedly "wide range" of alkyl chain lengths (the experimental appears to involve mixing coconut and tallow chain length surfactants).

U.S. Patent 4,102,823 and GB 1,399,966 describe other laundry compositions containing conventional alkyl sulfates.

G.B. Patent 1,299,966, Matheson et al., published July 2, 1975, discloses a detergent composition in which the surfactant system is comprised of a mixture of sodium tallow alkyl sulfate and nonionic surfactants.

Methyl-substituted sulfates include the known "isostearyl" sulfates; these are typically mixtures of isomeric sulfates having a total of 18 carbon atoms. For example, EP 401,462 A, assigned to Henkel, published December 12, 1990, describes certain isostearyl alcohols and ethoxylated isostearyl alcohols and their sulfation to produce the corresponding alkyl sulfates such as sodium isostearyl sulfate. See also K.R. Wormuth and S. Zushma, Langmuir, Vol. 7, (1991), pp 2048-2053 (technical studies on a number of branched alkyl sulfates, especially the "branched Guerbet" type); R. Varadaraj et al., J. Phys. Chem., Vol. 95, (1991), pp 1671-1676 (which describes the surface tensions of a variety of "linear Guerbet" and "branched Guerbet"- class surfactants including alkyl sulfates); Varadaraj et al., J. Colloid and Interface Sci., Vol. 140, (1990), pp 31-34 (relating to foaming data for surfactants which include C12 and C13 alkyl sulfates containing 3 and 4 methyl branches, respectively); and Varadaraj et al., Langmuir, Vol. 6 (1990), pp 1376-1378 (which describes the micropolarity of aqueous micellar solutions of surfactants including branched alkyl sulfates).

"Linear Guerbet" alcohols are available from Henkel, e.g., EUTANOL G-16.

Primary alkyl sulfates derived from alcohols made by Oxo reaction on propylene or n-butylene oligomers are described in U.S. Patent 5,245,072 assigned to Mobil Corp. See also: U.S. Patent 5,284,989, assigned to Mobil Oil Corp. (a method for producing substantially linear hydrocarbons by oligomerizing a lower olefin at elevated temperatures with constrained intermediate pore siliceous acidic zeolite), and U.S. Patents 5,026,933 and 4,870,038, both to Mobil Oil Corp. (a process for producing substantially linear hydrocarbons by oligomerizing a lower olefin at elevated temperatures with siliceous acidic ZSM-23 zeolite).

See also: Surfactant Science Series, Marcel Dekker, N.Y. (various volumes include those entitled "Anionic Surfactants" and "Surfactant Biodegradation", the latter by R.D. Swisher, Second Edition, publ. 1987 as Vol. 18; see especially p.20-24

**SUMMARY OF THE INVENTION**

The present invention provides aqueous and non-aqueous heavy-duty liquid detergent compositions comprising mid-chain branched surfactants.

Specifically, the present invention comprises an aqueous heavy-duty liquid detergent composition. Additionally provided is a nonaqueous heavy-duty liquid detergent composition in the form of a stable suspension of solid, substantially insoluble particulate material dispersed throughout a structured, surfactant-containing liquid phase. Both the aqueous and non-aqueous heavy-duty liquid detergent compositions comprise mid-chain branched surfactants.

The nonaqueous detergent compositions comprise from about 55% to 98.9% by weight of the composition of a structured, surfactant-containing liquid phase formed by combining:

i) from about 1% to 80% by weight of said liquid phase of one or more nonaqueous organic diluents; and

ii) from about 20% to 99% by weight of said liquid phase of a surfactant system comprising surfactants selected from the group consisting of anionic, nonionic, cationic surfactants and combinations thereof.

The aqueous based heavy duty laundry detergent compositions herein preferably contain a surfactant system comprising surfactants selected from nonionic detersive surfactant, anionic detersive surfactant, zwitterionic detersive surfactant, amine oxide detersive surfactant, and mixtures thereof. The surfactant system typically comprises from about 0.01% to about 50%, preferably from about 0.2% to about 30%, by weight of the detergent composition.

The surfactant system further comprises at least about 10%, preferably at least about 20%, more preferably at least about 30% and most preferably at least about 50%, by weight of a branched surfactant mixture. The branched surfactant mixture comprises mid-chain branched and linear surfactant compounds, the linear compounds exceeding at least 25% and less than about 70%, preferably greater than 25% and less than about 60% and most preferably greater than 25% and less than
about 50%, by weight of the branched surfactant mixture and the mid-chain branched compounds being of the formula:

\[ A^b - B \]

wherein:

\( A^b \) is a hydrophobic C9 to C18, total carbons in the moiety, preferably from about C10 to about C15, mid-chain branched alkyl moiety having: (1) a longest linear carbon chain attached to the - B moiety in the range of from 8 to 17 carbon atoms; (2) one or more C1 - C3 alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position \( \omega - 2 \) carbon, the terminal carbon minus 2 carbons; and (4) the surfactant composition has an average total number of carbon atoms in the \( A^b \) moiety in the above formula within the range of greater than 12 to about 14.5; and

\( B \) is a hydrophilic moiety selected from the group consisting of \( \text{OSO}_3M \), \( (\text{EO}/\text{PO})m\text{OSO}_3M \), \( (\text{EO}/\text{PO})m\text{OH} \) and mixtures thereof. \( \text{EO}/\text{PO} \) are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, and \( m \) is at least about 0.01 to about 30. The average total number of carbon atoms in the \( A^b \) moiety in the branched surfactant mixture defined above should be within the range of greater than 12 to about 14.5, preferably greater than about 12.5 to about 14.5 and most preferably greater than about 13 to about 14.5. The "total" number of carbon atoms as used herein is intended to mean the number of carbon atoms in the longest chain, i.e. the backbone of the molecule, plus the number of carbon atoms in all of the short chains, i.e. the branches.

The detergent compositions defined herein also comprise from about 1% to 80% by weight of the composition of additional detergent ingredients such as builders, enzymes, colorants, bleaching agents, bleach activators, and other known ingredients. In the nonaqueous compositions adjuvants can be added in the form of particulate material which ranges in size from about 0.1 to 1500 microns, which is substantially insoluble in the liquid phase and which is selected from the group consisting of peroxygen bleaching agents, bleach activators, colored speckles, organic detergent builders, inorganic alkalinity sources and mixtures thereof.

**DETAILED DESCRIPTION OF THE INVENTION**

The aqueous and non-aqueous liquid detergent compositions of this invention comprise a surfactant system which comprises a branched surfactant mixture
comprising linear and mid-chain branched surfactants. The essential and optional components of the surfactant mixture and other optional materials of the detergent compositions herein, as well as composition form, preparation and use, are described in greater detail as follows: (All concentrations and ratios are on a weight basis unless otherwise specified.)

The surfactant system further comprises at least about 10%, preferably at least about 20%, more preferably at least about 30% and most preferably at least about 50%, by weight of a branched surfactant mixture. The branched surfactant mixture comprises mid-chain branched and linear surfactant compounds, the linear compounds exceeding at least 25% and less than about 70%, preferably greater than 25% and less than about 60% and most preferably greater than 25% and less than about 50%, by weight of the branched surfactant mixture and the mid-chain branched compounds being of the formula:

\[ A^b - B \]

wherein:

- \( A^b \) is a hydrophobic C9 to C18, total carbons in the moiety, preferably from about C10 to about C15, mid-chain branched alkyl moiety having: (1) a longest linear carbon chain attached to the - B moiety in the range of from 8 to 17 carbon atoms; (2) one or more \( C_1 \) - \( C_3 \) alkyl moieties branching from this longest linear carbon chain; (3) at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position \( \omega - 2 \) carbon, the terminal carbon minus 2 carbons; and (4) the surfactant composition has an average total number of carbon atoms in the \( A^b \) moiety in the above formula within the range of greater than 12 to about 14.5; and

- \( B \) is a hydrophilic moiety selected from the group consisting of \( \text{OSO}_3\text{M} \), \( \text{(EO/PO)}_m\text{OSO}_3\text{M} \), \( \text{(EO/PO)}_m\text{OH} \) and mixtures thereof. EO/PO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, and \( m \) is at least about 0.01 to about 30. The average total number of carbon atoms in the \( A^b \) moiety in the branched surfactant mixture defined above should be within the range of greater than 12 to about 14.5, preferably greater than about 12.5 to about 14.5 and most preferably greater than about 13 to about 14.5. The "total" number of carbon atoms as used herein is intended to mean the number of carbon atoms in the longest chain, i.e. the backbone of the molecule, plus the number of carbon atoms in all of the short chains, i.e. the branches.
The \( \text{A}^b \) moiety of the mid-chain branched surfactant components of the present claims is preferably a branched alkyl moiety having the formula:

\[
\text{CH}_3\text{CH}_2(\text{CH}_2)_w\text{CH}(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{CH}_2.
\]

Wherein the total number of carbon atoms in the branched alkyl moiety, including the \( R, R^1, \) and \( R^2 \) branching, is from about 10 to about 17. \( R, R^1, \) and \( R^2 \) are each independently selected from hydrogen and \( \text{C}_1-\text{C}_3 \) alkyl, preferably methyl, provided that \( R, R^1, \) and \( R^2 \) are not all hydrogen. Additionally, when \( z \) is 0, at least \( R \) or \( R^1 \) is not hydrogen. Moreover, \( w \) is an integer from 0 to 10; \( x \) is an integer from 0 to 10; \( y \) is an integer from 0 to 10; \( z \) is an integer from 0 to 10; and \( w + x + y + z \) is from 3 to 10.

In another preferred embodiment of the present claims, the \( \text{A}^b \) moiety of the mid-chain branched surfactant component is a branched alkyl moiety having the formula selected from the group consisting of:

\[
\text{CH}_3
\]

(\( \text{I} \))

\[
\text{CH}_3(\text{CH}_2)_a\text{CH}(\text{CH}_2)_b\text{H}^-
\]

(\( \text{II} \))

\[
\text{CH}_3(\text{CH}_2)_d\text{CH}(\text{CH}_2)_e\text{C}\text{H}^-
\]

and mixtures thereof.

Wherein \( a, b, d, \) and \( e \) are integers, and \( a + b \) is from 6 to 13, \( d + e \) is from 4 to 11.

Further,

- when \( a + b = 6 \), \( a \) is an integer from 2 to 5 and \( b \) is an integer from 1 to 4;
- when \( a + b = 7 \), \( a \) is an integer from 2 to 6 and \( b \) is an integer from 1 to 5;
- when \( a + b = 8 \), \( a \) is an integer from 2 to 7 and \( b \) is an integer from 1 to 6;
- when \( a + b = 9 \), \( a \) is an integer from 2 to 8 and \( b \) is an integer from 1 to 7;
- when \( a + b = 10 \), \( a \) is an integer from 2 to 9 and \( b \) is an integer from 1 to 8;
- when \( a + b = 11 \), \( a \) is an integer from 2 to 10 and \( b \) is an integer from 1 to 9;
- when \( a + b = 12 \), \( a \) is an integer from 2 to 11 and \( b \) is an integer from 1 to 10;
- when \( a + b = 13 \), \( a \) is an integer from 2 to 12 and \( b \) is an integer from 1 to 11;
- when \( d + e = 4 \), \( d \) is an integer from 2 to 3 and \( e \) is an integer from 1 to 2;
- when \( d + e = 5 \), \( d \) is an integer from 2 to 4 and \( e \) is an integer from 1 to 3;
- when \( d + e = 6 \), \( d \) is an integer from 2 to 5 and \( e \) is an integer from 1 to 4;
- when \( d + e = 7 \), \( d \) is an integer from 2 to 6 and \( e \) is an integer from 1 to 5;
- when \( d + e = 8 \), \( d \) is an integer from 2 to 7 and \( e \) is an integer from 1 to 6;
when \( d + e = 9 \), \( d \) is an integer from 2 to 8 and \( e \) is an integer from 1 to 7;
when \( d + e = 10 \), \( d \) is an integer from 2 to 9 and \( e \) is an integer from 1 to 8;
when \( d + e = 11 \), \( d \) is an integer from 2 to 10 and \( e \) is an integer from 1 to 9.

**Mid-chain Branched Primary Alkyl Sulfate Surfactants**

The mid-chain branched surfactant compositions of the present invention may comprise one or more mid-chain branched primary alkyl sulfate surfactants having the formula:

\[
R \quad R^1 \quad R^2
\]
\[
\text{CH}_3\text{CH}_2(\text{CH}_2)_w\text{CH}(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{CH}_2\text{OSO}_3\text{M}
\]

More specifically, the branched surfactant mixtures of the present invention comprise molecules having a linear primary alkyl sulfate chain backbone (i.e., the longest linear carbon chain which includes the sulfated carbon atom). These alkyl chain backbones comprise from about 9 to about 18 carbon atoms; and further the molecules comprise a branched primary alkyl moiety or moieties having at least about 1, but not more than 3, carbon atoms. In addition, the surfactant mixture has an average total number of carbon atoms for the branched primary alkyl moieties of from about 12 to about 14.5. Thus, the present invention mixtures comprise at least one branched primary alkyl sulfate surfactant compound having a longest linear carbon chain of not less than 8 carbon atoms or more than 17 carbon atoms, and the average total number of carbon atoms for the branched primary alkyl chains is within the range of greater than 12 to about 14.5, preferably greater than about 12.5 to about 14.5 and most preferably greater than about 13 to about 14.5.

For example, a C14 total carbon primary alkyl sulfate surfactant having 11 carbon atoms in the backbone must have 1, 2, or 3 branching units (i.e., \( R, R^1 \) and/or \( R^2 \)) whereby total number of carbon atoms in the molecule is 14. In this example, the C14 total carbon requirement may be satisfied equally by having, for example, one propyl branching unit or three methyl branching units.

\( R, R^1, \) and \( R^2 \) are each independently selected from hydrogen and \( C_1-C_3 \) alkyl (preferably hydrogen or \( C_1-C_2 \) alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided \( R, R^1, \) and \( R^2 \) are not all hydrogen. Further, when \( z \) is 0, at least \( R \) or \( R^1 \) is not hydrogen.

Although for the purposes of the present invention surfactant compositions the above formula does not include molecules wherein the units \( R, R^1, \) and \( R^2 \) are all hydrogen (i.e., linear non-branched primary alkyl sulfates), it is to be recognized that the present invention compositions may still further comprise some amount of
linear, non-branched primary alkyl sulfate. Further, this linear non-branched primary alkyl sulfate surfactant may be present as the result of the process used to manufacture the surfactant mixture having the requisite one or more mid-chain branched primary alkyl sulfates according to the present invention, or for purposes of formulating detergent compositions some amount of linear non-branched primary alkyl sulfate may be admixed into the final product formulation.

Further it is to be similarly recognized that non-sulfated mid-chain branched alcohol may comprise some amount of the present invention compositions. Such materials may be present as the result of incomplete sulfation of the alcohol used to prepare the alkyl sulfate surfactant, or these alcohols may be separately added to the present invention detergent compositions along with a mid-chain branched alkyl sulfate surfactant according to the present invention.

M is hydrogen or a salt forming cation depending upon the method of synthesis. Examples of salt forming cations are lithium, sodium, potassium, calcium, magnesium, quaternary alkyl amines having the formula

\[
\begin{align*}
R^3 & + \\
R^6-NR^4 & \\
R^5 &
\end{align*}
\]

wherein \(R^3\), \(R^4\), \(R^5\) and \(R^6\) are independently hydrogen, \(C_1-C_{22}\) alkylene, \(C_{4-22}\) branched alkylene, \(C_1-C_{6}\) alkanol, \(C_1-C_{22}\) alkenylene, \(C_{4-22}\) branched alkenylene, and mixtures thereof. Preferred cations are ammonium (\(R^3, R^4, R^5\) and \(R^6\) equal hydrogen), sodium, potassium, mono-, di-, and trialkanol ammonium, and mixtures thereof. The monoalkanol ammonium compounds of the present invention have \(R^3\) equal to \(C_1-C_{6}\) alkanol, \(R^4\), \(R^5\) and \(R^6\) equal to hydrogen; dialkanol ammonium compounds of the present invention have \(R^3\) and \(R^4\) equal to \(C_1-C_{6}\) alkanol, \(R^5\) and \(R^6\) equal to hydrogen; trialkanol ammonium compounds of the present invention have \(R^3\), \(R^4\) and \(R^5\) equal to \(C_1-C_{6}\) alkanol, \(R^6\) equal to hydrogen. Preferred alkanol ammonium salts of the present invention are the mono-, di- and tri- quaternary ammonium compounds having the formulas:

\[
H_3N^+(CH_2CH_2OH), \quad H_2N^+(CH_2CH_2OH)_2, \quad HN^+(CH_2CH_2OH)_3.
\]

Preferred M is sodium, potassium and the \(C_2\) alkanol ammonium salts listed above; the most M preferred is sodium.

Further regarding the above formula, w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10; and \(w + x + y + z\) is an integer from 2 to 11.
The preferred surfactant mixtures of the present invention have at least about 10%, more preferably at least about 20%, and even more preferably at least about 30% and most preferably at least about 50% by weight, of the mixture of one or more branched primary alkyl sulfates having the formula:

$$\text{R}^1 \text{R}^2\text{CH}_3\text{CH}_2(\text{CH}_2)x\text{yCH}(\text{CH}_2)z\text{CH}_2\text{OSO}_3\text{M}$$

Wherein the total number of carbon atoms, including branching, is from 10 to 16, and the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than 12 to about 14. R$^1$ and R$^2$ are each independently hydrogen or C$_1$-C$_3$ alkyl. M is a water soluble cation, and x is from 0 to 10, y is from 0 to 10, z is from 0 to 10 and x + y + z is from 4 to 10. Further, R$^1$ and R$^2$ are not both hydrogen. More preferred are compositions having at least 5% of the mixture comprising one or more mid-chain branched primary alkyl sulfates wherein x + y is equal to 6 and z is at least 1.

Preferably, the mixtures of surfactant comprise at least 5% of a mid chain branched primary alkyl sulfate having R$^1$ and R$^2$ independently hydrogen or methyl, provided R$^1$ and R$^2$ are not both hydrogen. It is further provided that x + y is equal to 5, 6 or 7 and z is at least 1. More preferably the mixtures of surfactant comprise at least 20% of a mid chain branched primary alkyl sulfate having R$^1$ and R$^2$ independently hydrogen or methyl, provided R$^1$ and R$^2$ are not both hydrogen, and x + y is equal to 5, 6 or 7 and z is at least 1.

Preferred mid-chain branched primary alkyl sulfate surfactants for use in the detergent compositions defined herein are selected from the group of compounds having the formula:

(I)$$\text{CH}_3\text{CH}_3(\text{CH}_2)a\text{CH}(\text{CH}_2)b\text{CH}_2\text{OSO}_3\text{M}$$

(II)$$\text{CH}_3\text{CH}_3(\text{CH}_2)d\text{CH}(\text{CH}_2)e\text{CHCH}_2\text{OSO}_3\text{M}$$

and mixtures thereof.

Wherein a, b, d, and e are integers, and a+b is from 6 to 13, d+e is from 4 to 11.

Further,
when a + b = 6, a is an integer from 2 to 5 and b is an integer from 1 to 4;
when a + b = 7, a is an integer from 2 to 6 and b is an integer from 1 to 5;
when a + b = 8, a is an integer from 2 to 7 and b is an integer from 1 to 6;
when a + b = 9, a is an integer from 2 to 8 and b is an integer from 1 to 7;
when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8; 
when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9; 
when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10; 
when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11; 
when d + e = 4, d is an integer from 2 to 3 and e is an integer from 1 to 2; 
when d + e = 5, d is an integer from 2 to 4 and e is an integer from 1 to 3; 
when d + e = 6, d is an integer from 2 to 5 and e is an integer from 1 to 4; 
when d + e = 7, d is an integer from 2 to 6 and e is an integer from 1 to 5; 
when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6; 
when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7; 
when d + e = 10, d is an integer from 2 to 9 and e is an integer from 1 to 8; 
when d + e = 11, d is an integer from 2 to 10 and e is an integer from 1 to 9.

Wherein the average total number of carbon atoms in the branched primary alkyl moieties having the above formulas is within the range of greater than about 12 to about 14.5.

Especially preferred mid-chain branched surfactants are those comprising a mixture of compounds having the general formulas from Groups I and II, wherein the molar ratio of compounds according to Group I to Group II is greater than 4:1, preferably greater than 9:1 and most preferably greater than 20:1.

Further, the present invention surfactant composition may comprise a mixture of linear and branched surfactants wherein the branched primary alkyl sulfates have the formula:

$$\text{CH}_3\text{CH}_2(\text{CH}_2)_w\text{CH}(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{CH}_2\text{OSO}_3\text{M}$$

Wherein the total number of carbon atoms per molecule, including branching, is from about 10 to about 17, and the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than about 12 to about 14.5. R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl, provided R, R¹, and R² are not all hydrogen. M is a water soluble cation, and w is an integer from 0 to 10, x is an integer from 0 to 10, y is an integer from 0 to 10, z is an integer from 0 to 10 and w + x + y + z is from 3 to 10. Provided that when R² is a C₁-C₃ alkyl the ratio of surfactants having z equal to 0 to surfactants having z of 1 or greater is at least about 1:1, preferably at least about 1:5, more preferably at least about 1:10, and most preferably at least about 1:20. Also preferred are surfactant compositions, when R² is a C₁-C₃ alkyl, comprising less than about 20%, preferably less than 10%, more preferably less than
5%, most preferably less than 1%, of branched primary alkyl sulfates having the above formula wherein z equals 0.

Preferred mono-methyl branched primary alkyl sulfates are selected from the group consisting of: 3-methyl dodecanol sulfate, 4-methyl dodecanol sulfate, 5-methyl dodecanol sulfate, 6-methyl dodecanol sulfate, 7-methyl dodecanol sulfate, 8-methyl dodecanol sulfate, 9-methyl dodecanol sulfate, 10-methyl dodecanol sulfate, 3-methyl tridecanol sulfate, 4-methyl tridecanol sulfate, 5-methyl tridecanol sulfate, 6-methyl tridecanol sulfate, 7-methyl tridecanol sulfate, 8-methyl tridecanol sulfate, 9-methyl tridecanol sulfate, 10-methyl tridecanol sulfate, 11-methyl tridecanol sulfate, and mixtures thereof.

The following branched primary alkyl sulfates comprising 13 carbon atoms and having one branching unit are examples of preferred branched surfactants useful in the present invention compositions:

5-methyl dodecyl sulfate having the formula:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{OSO}_3 \text{M}
\end{array}
\]

6-methyl dodecyl sulfate having the formula

\[
\begin{array}{c}
\text{CH}_3 \\
\text{OSO}_3 \text{M}
\end{array}
\]

7-methyl dodecyl sulfate having the formula

\[
\begin{array}{c}
\text{CH}_3 \\
\text{OSO}_3 \text{M}
\end{array}
\]

8-methyl dodecyl sulfate having the formula

\[
\begin{array}{c}
\text{CH}_3 \\
\text{OSO}_3 \text{M}
\end{array}
\]

9-methyl dodecyl sulfate having the formula

\[
\begin{array}{c}
\text{CH}_3 \\
\text{OSO}_3 \text{M}
\end{array}
\]

10-methyl dodecyl sulfate having the formula

\[
\begin{array}{c}
\text{CH}_3 \\
\text{OSO}_3 \text{M}
\end{array}
\]

wherein M is preferably sodium.
Preferred di-methyl branched primary alkyl sulfates are selected from the group consisting of: 2,3-dimethyl undecanol sulfate, 2,4-dimethyl undecanol sulfate, 2,5-dimethyl undecanol sulfate, 2,6-dimethyl undecanol sulfate, 2,7-dimethyl undecanol sulfate, 2,8-dimethyl undecanol sulfate, 2,9-dimethyl undecanol sulfate, 2,3-dimethyl dodecanol sulfate, 2,4-dimethyl dodecanol sulfate, 2,5-dimethyl dodecanol sulfate, 2,6-dimethyl dodecanol sulfate, 2,7-dimethyl dodecanol sulfate, 2,8-dimethyl dodecanol sulfate, 2,9-dimethyl dodecanol sulfate, 2,10-dimethyl dodecanol sulfate, and mixtures thereof.

The following branched primary alkyl sulfates comprising 14 carbon atoms and having two branching units are examples of preferred branched surfactants according to the present invention:

2,5-dimethyldodecylsulfate having the formula:

```
CH3
CH3
CH3

OSO3M
```

2,6-dimethyldodecylsulfate having the formula

```
CH3
CH3

OSO3M
```

2,7-dimethyldodecylsulfate having the formula

```
CH3

OSO3M
```

2,8-dimethyldodecylsulfate having the formula

```
CH3
CH3

OSO3M
```

2,9-dimethyldodecylsulfate having the formula

```
CH3

OSO3M
```

2,10-dimethyldodecylsulfate having the formula

```
CH3

OSO3M
```
wherein M is preferably sodium.

**Mid-chain Branched Primary Alkyl Alkoxylated Sulfate Surfactants**

The mid-chain branched surfactant components of the present invention may comprise one or more (preferably a mixture of two or more) mid-chain branched primary alkyl alkoxylated sulfates having the formula:

\[
R \quad R^1 \quad R^2
\]

\[
\text{CH}_3\text{CH}_2(\text{CH}_2)_w\text{CH}(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{CH}_2 (\text{EO/PO})_m\text{OSO}_3 \text{M}.
\]

The surfactant mixtures of the present invention comprise molecules having a linear primary alkoxylated sulfate chain backbone (i.e., the longest linear carbon chain which includes the alkoxy-sulfated carbon atom). These alkyl chain backbones comprise from about 9 to about 18 carbon atoms; and further the molecules comprise a branched primary alkyl moiety or moieties having at least about 1, but not more than 3, carbon atoms. In addition, the surfactant mixture has an average total number of carbon atoms for the branched primary alkyl moieties of from about 12 to about 14.5. Thus, the present invention mixtures comprise at least one branched primary alkyl sulfate surfactant compound having a longest linear carbon chain of not less than 9 carbon atoms or more than 17 carbon atoms, and the average total number of carbon atoms for the branched primary alkyl chains is within the range of greater than 12 to about 14.5, preferably greater than about 12.5 to about 14.5 and most preferably greater than about 13 to about 14.5.

For example, a C14 total carbon primary alkyl sulfate surfactant having 11 carbon atoms in the backbone must have 1, 2, or 3 branching units (i.e., R, R^1 and/or R^2) whereby total number of carbon atoms in the molecule is 14. In this example, the C14 total carbon requirement may be satisfied equally by having, for example, one propyl branching unit or three methyl branching units.

R, R^1, and R^2 are each independently selected from hydrogen and C1-C3 alkyl (preferably hydrogen or C1-C2 alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided R, R^1, and R^2 are not all hydrogen. Further, when z is 0, at least R or R^1 is not hydrogen.

Although for the purposes of the present invention surfactant components according to the above formula do not include molecules wherein the units R, R^1, and R^2 are all hydrogen (i.e., linear non-branched primary alkoxylated sulfates), it is
to be recognized that the present invention compositions may still further comprise some amount of linear, non-branched primary alkoxylated sulfate. Further, this linear non-branched primary alkoxylated sulfate surfactant may be present as the result of the process used to manufacture the surfactant mixture having the requisite mid-chain branched primary alkoxylated sulfates according to the present invention, or for purposes of formulating detergent compositions some amount of linear non-branched primary alkoxylated sulfate may be admixed into the final product formulation.

It is also to be recognized that some amount of mid-chain branched alkyl sulfate may be present in the compositions. This is typically the result of sulfation of non-alkoxylated alcohol remaining following incomplete alkoxylation of the mid-chain branched alcohol used to prepare the alkoxylated sulfate useful herein. It is to be recognized, however, that separate addition of such mid-chain branched alkyl sulfates is also contemplated by the present invention compositions.

Further it is to be similarly recognized that non-sulfated mid-chain branched alcohol (including polyoxyalkylene alcohols) may comprise some amount of the present invention alkoxylated sulfate-containing compositions. Such materials may be present as the result of incomplete sulfation of the alcohol (alkoxylated or non-alkoxylated) used to prepare the alkoxylated sulfate surfactant, or these alcohols may be separately added to the present invention detergent compositions along with a mid-chain branched alkoxylated sulfate surfactant according to the present invention.

M is as described hereinbefore.

Further regarding the above formula, w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10; and w + x + y + z is an integer from 2 to 11.

EO/PO are alkoxy moieties, preferably selected from ethoxy, propoxy, and mixed ethoxy/propano groups, wherein m is at least about 0.01, preferably within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10, and most preferably from about 1 to about 5. The \((EO/PO)_m\) moiety may be either a distribution with average degree of alkoxylation (e.g., ethoxylation and/or propoxylation) corresponding to m, or it may be a single specific chain with alkoxylation (e.g., ethoxylation and/or propoxylation) of exactly the number of units corresponding to m.

The preferred surfactant mixtures of the present invention have at least about 10%, more preferably at least about 20%, even more preferably at least about 30% and most preferably at least about 50%, by weight, of the mixture of one or more mid-chain branched primary alkyl alkoxylated sulfates having the formula:
$$\text{R}^1 \quad \text{R}^2$$

$$\text{CH}_3\text{CH}_2(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{CH}_2(\text{EO/PO})_m\text{OSO}_3\text{M}$$

Wherein the total number of carbon atoms, including branching, is from 10 to 16, and the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than 12 to about 14. $\text{R}^1$ and $\text{R}^2$ are each independently hydrogen or C$_1$-C$_3$ alkyl; M is a water soluble cation; x is from 0 to 10; y is from 0 to 10; z is from 0 to 10 and $x + y + z$ is from 4 to 10. Further, $\text{R}^1$ and $\text{R}^2$ are not both hydrogen and EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propano groups. Wherein m is at least about 0.01, preferably within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10, and most preferably from about 1 to about 5. More preferred are compositions having at least 5% of the mixture comprising one or more mid-chain branched primary alkyl alkoxy sulfates wherein $x + y$ is equal to 6 and $z$ is at least 1.

Preferably, the mixtures of surfactant comprise at least 5% of a mid chain branched primary alkyl sulfate having $\text{R}^1$ and $\text{R}^2$ independently hydrogen or methyl, provided $\text{R}^1$ and $\text{R}^2$ are not both hydrogen. Additionally, $x + y$ is equal to 5, 6 or 7 and $z$ is at least 1. More preferably the mixtures of surfactant comprise at least 20% of a mid chain branched primary alkyl sulfate having $\text{R}^1$ and $\text{R}^2$ independently hydrogen or methyl, provided $\text{R}^1$ and $\text{R}^2$ are not both hydrogen and with $x + y$ equal to 5, 6 or 7 and $z$ is at least 1.

Preferred mixtures of mid-chain branched primary alkyl alkoxylated sulfate and linear alkyl alkoxylated sulfate surfactants comprise at least about 5% by weight of one or more mid-chain branched alkyl alkoxylated sulfates having the formula:

(I)

$$\text{CH}_3\text{CH}_2(\text{CH}_2)_a\text{CH}(\text{CH}_2)_b\text{CH}_2(\text{EO/PO})_m\text{OSO}_3\text{M}$$

(II)

$$\text{CH}_3\text{CH}_2(\text{CH}_2)_d\text{CH}(\text{CH}_2)_e\text{CH}_2(\text{EO/PO})_m\text{OSO}_3\text{M}$$

and mixtures thereof. Wherein a, b, d, and e are integers, and $a+b$ is from 6 to 13, $d+e$ is from 4 to 11. Further, when $a + b = 6$, a is an integer from 2 to 5 and b is an integer from 1 to 4; when $a + b = 7$, a is an integer from 2 to 6 and b is an integer from 1 to 5; when $a + b = 8$, a is an integer from 2 to 7 and b is an integer from 1 to 6; when $a + b = 9$, a is an integer from 2 to 8 and b is an integer from 1 to 7; when $a + b = 10$, a is an integer from 2 to 9 and b is an integer from 1 to 8;
when \(a + b = 11\), \(a\) is an integer from 2 to 10 and \(b\) is an integer from 1 to 9;
when \(a + b = 12\), \(a\) is an integer from 2 to 11 and \(b\) is an integer from 1 to 10;
when \(a + b = 13\), \(a\) is an integer from 2 to 12 and \(b\) is an integer from 1 to 11;
when \(d + e = 4\), \(d\) is an integer from 2 to 3 and \(e\) is an integer from 1 to 2;
when \(d + e = 5\), \(d\) is an integer from 2 to 4 and \(e\) is an integer from 1 to 3;
when \(d + e = 6\), \(d\) is an integer from 2 to 5 and \(e\) is an integer from 1 to 4;
when \(d + e = 7\), \(d\) is an integer from 2 to 6 and \(e\) is an integer from 1 to 5;
when \(d + e = 8\), \(d\) is an integer from 2 to 7 and \(e\) is an integer from 1 to 6;
when \(d + e = 9\), \(d\) is an integer from 2 to 8 and \(e\) is an integer from 1 to 7;
when \(d + e = 10\), \(d\) is an integer from 2 to 9 and \(e\) is an integer from 1 to 8;
when \(d + e = 11\), \(d\) is an integer from 2 to 10 and \(e\) is an integer from 1 to 9.

The average total number of carbon atoms in the branched primary alkyl moieties having the above formulas is within the range of greater than about 12 to about 14.5 and EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein \(m\) is at least about 0.01, preferably within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10, and most preferably from about 1 to about 5.

Especially preferred mid-chain branched surfactants are those comprising a mixture of compounds having the general formulas from Groups I and II, wherein the molar ratio of compounds according to Group I to Group II is greater than 4:1, preferably greater than 9:1 and most preferably greater than 20:1.

Further, the present invention surfactant composition may comprise a mixture of linear and branched surfactants wherein the branched primary alkyl alkoxyxylated sulfates has the formula:

\[
\text{CH}_3\text{CH}_2(\text{CH}_2)_w\text{CH}(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{CH}_2(\text{EO}/\text{PO})_m\text{OSO}_3\text{M}.
\]

Wherein the total number of carbon atoms per molecule, including branching, is from about 10 to about 17, and the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than about 12 to about 14.5. \(R\), \(R^1\), and \(R^2\) are each independently selected from hydrogen and C\(_1\)-C\(_3\) alkyl, provided \(R\), \(R^1\), and \(R^2\) are not all hydrogen. \(M\) is a water soluble cation and \(w\) is an integer from 0 to 10; \(x\) is an integer from 0 to 10; \(y\) is an integer from 0 to 10; \(z\) is an integer from 0 to 10; \(w + x + y + z\) is from 3 to 10. EO/PO are alkoxy moieties, preferably selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein \(m\) is at least about 0.01, preferably within the range of from about 0.1 to about 30, more preferably from about 0.5 to about 10.
and most preferably from about 1 to about 5. When R² is a C₁-C₃ alkyl the ratio of surfactants having z equal to 0 to surfactants having z of 1 or greater is at least about 1:1, preferably at least about 1:5, more preferably at least about 1:10, and most preferably at least about 1:20. Also preferred are surfactant compositions, when R² is a C₁-C₃ alkyl, comprising less than about 20%, preferably less than 10%, more preferably less than 5%, most preferably less than 1%, of branched primary alkyl alkoxylated sulfate having the above formula wherein z equals 0.

Preferred mono-methyl branched primary alkyl ethoxylated sulfates are selected from the group consisting of: 3-methyl dodecanol ethoxylated sulfate, 4-methyl dodecanol ethoxylated sulfate, 5-methyl dodecanol ethoxylated sulfate, 6-methyl dodecanol ethoxylated sulfate, 7-methyl dodecanol ethoxylated sulfate, 8-methyl dodecanol ethoxylated sulfate, 9-methyl dodecanol ethoxylated sulfate, 10-methyl dodecanol ethoxylated sulfate, 3-methyl tridecanol ethoxylated sulfate, 4-methyl tridecanol ethoxylated sulfate, 5-methyl tridecanol ethoxylated sulfate, 6-methyl tridecanol ethoxylated sulfate, 7-methyl tridecanol ethoxylated sulfate, 8-methyl tridecanol ethoxylated sulfate, 9-methyl tridecanol ethoxylated sulfate, 10-methyl tridecanol ethoxylated sulfate, 11-methyl tridecanol ethoxylated sulfate, and mixtures thereof, wherein the compounds are ethoxylated with an average degree of ethoxylation of from about 0.1 to about 10.

Preferred di-methyl branched primary alkyl ethoxylated sulfates selected from the group consisting of: 2,3-dimethyl undecanol ethoxylated sulfate, 2,4-dimethyl undecanol ethoxylated sulfate, 2,5-dimethyl undecanol ethoxylated sulfate, 2,6-dimethyl undecanol ethoxylated sulfate, 2,7-dimethyl undecanol ethoxylated sulfate, 2,8-dimethyl undecanol ethoxylated sulfate, 2,9-dimethyl undecanol ethoxylated sulfate, 2,3-dimethyl dodecanol ethoxylated sulfate, 2,4-dimethyl dodecanol ethoxylated sulfate, 2,5-dimethyl dodecanol ethoxylated sulfate, 2,6-dimethyl dodecanol ethoxylated sulfate, 2,7-dimethyl dodecanol ethoxylated sulfate, 2,8-dimethyl dodecanol ethoxylated sulfate, 2,9-dimethyl dodecanol ethoxylated sulfate, 2,10-dimethyl dodecanol ethoxylated sulfate, and mixtures thereof, wherein the compounds are ethoxylated with an average degree of ethoxylation of from about 0.1 to about 10.

Mid-chain Branched Primary Alkyl Polyoxyalkylene Surfactants

The present invention branched surfactant compositions may comprise one or more mid-chain branched primary alkyl polyoxyalkylene surfactants having the formula:
The surfactant mixtures of the present invention comprise molecules having a linear primary polyoxyalkylene chain backbone (i.e., the longest linear carbon chain which includes the alkoxylated carbon atom). These alkyl chain backbones comprise from 9 to 18 carbon atoms; and further the molecules comprise a branched primary alkyl moiety or moieties having at least about 1, but not more than 3, carbon atoms. In addition, the surfactant mixture has an average total number of carbon atoms for the branched primary alkyl moieties within the range of from greater than about 12 to about 14.5. Thus, the present invention mixtures comprise at least one polyoxyalkylene compound having a longest linear carbon chain of not less than 9 carbon atoms or more than 17 carbon atoms, and further the average total number of carbon atoms for the branched primary alkyl chains is within the range of greater than 12 to about 14.5, preferably greater than about 12.5 to about 14.5 and most preferably greater than about 13 to about 14.5.

For example, a C14 total carbon primary polyoxyalkylene surfactant having 11 carbon atoms in the backbone must have 1, 2 or 3 branching units (i.e. R, R₁ and R²) whereby the total number of carbon atoms in the molecule is 14. In this example, the C14 total carbon requirement may be satisfied equally by having, for example, one propyl branching unit or three methyl branching units.

R, R₁, and R² are each independently selected from hydrogen and C₁⁻C₃ alkyl (preferably hydrogen or C₁⁻C₂ alkyl, more preferably hydrogen or methyl, and most preferably methyl), provided R, R₁, and R² are not all hydrogen. Further, when z is 0, at least R or R₁ is not hydrogen.

Although for the purposes of the present invention surfactant compositions the above formula does not include molecules wherein the units R, R₁, and R² are all hydrogen (i.e., linear non-branched primary polyoxyalkylenes), it is to be recognized that the present invention compositions may still further comprise some amount of linear, non-branched primary polyoxyalkylene. Further, this linear non-branched primary polyoxyalkylene surfactant may be present as the result of the process used to manufacture the surfactant mixture having the requisite mid-chain branched primary polyoxyalkylenes according to the present invention, or for purposes of formulating detergent compositions some amount of linear non-branched primary polyoxyalkylene may be admixed into the final product formulation.

Further it is to be similarly recognized that non-alkoxylated mid-chain branched alcohol may comprise some amount of the present invention
polyoxyalkylene-containing compositions. Such materials may be present as the result of incomplete alkyoxylation of the alcohol used to prepare the polyoxyalkylene surfactant, or these alcohols may be separately added to the present invention detergent compositions along with a mid-chain branched polyoxyalkylene surfactant according to the present invention.

Further regarding the above formula, w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10; and w + x + y + z is an integer from 2 to 11.

EO/PO are alkoxy moieties, preferably selected from ethoxy, propoxy, and mixed ethoxy/propanoxy groups, more preferably ethoxy, wherein m is at least about 1, preferably within the range of from about 3 to about 30, more preferably from about 5 to about 20, and most preferably from about 5 to about 15. The (EO/PO)_m moiety may be either a distribution with average degree of alkyoxylation (e.g., ethoxylation and/or propoxylation) corresponding to m, or it may be a single specific chain with alkyoxylation (e.g., ethoxylation and/or propoxylation) of exactly the number of units corresponding to m.

The preferred surfactant mixtures of the present invention have at least about 10%, more preferably at least about 20%, even more preferably at least about 30% and most preferably at least about 50%, by weight, of the mixture of one or more mid-chain branched primary alkyl polyoxyalkylenes having the formula:

\[
\begin{align*}
&\text{CH}_3\text{CH}_2(\text{CH}_2)_x(\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{CH}_2(\text{EO}/\text{PO})_m\text{OH},
\end{align*}
\]

Wherein the total number of carbon atoms, including branching, is from 10 to 16, and the average total number of carbon atoms in the branched primary alkyl moieties is within the range of greater than 12 to about 14. R¹ and R² are each independently hydrogen or C₁-C₃ alkyl; x is from 0 to 10; y is from 0 to 10; z is from 0 to 10; and x + y + z is from 4 to 10. Provided R¹ and R² are not both hydrogen. EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propanoxy groups, more preferably ethoxy, wherein m is at least about 1, preferably within the range of from about 3 to about 30, more preferably from about 5 to about 20, and most preferably from about 5 to about 15. More preferred are compositions having at least 5% of the mixture comprising one or more mid-chain branched primary polyoxyalkylenes wherein z is at least 1.

Preferably, the mixtures of surfactant comprise at least 5%, preferably at least about 20%, of a mid chain branched primary alkyl polyoxyalkylene having R¹ and
R\textsuperscript{2} independently hydrogen or methyl. Provided R\textsuperscript{1} and R\textsuperscript{2} are not both hydrogen and x + y is equal to 5, 6 or 7 and z is at least 1.

Preferred detergent compositions according to the present invention, for example one useful for laundering fabrics, comprise from about 0.001\% to about 99\% of a mixture of mid-chain branched primary alkyl polyoxyalkylene surfactants, said mixture comprising at least about 5 \% by weight of one or more mid-chain branched alkyl polyoxyalkylenes having the formula:

(I)

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{CH}_3 (\text{CH}_2)_b \text{CH} (\text{CH}_2)_d \text{CH}_2 (\text{EO/PO})_m \text{OH} & ,
\end{align*}
\]

(II)

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{CH}_3 (\text{CH}_2)_d \text{CH} (\text{CH}_2)_e \text{CH}_2 (\text{EO/PO})_m \text{OH} & ,
\end{align*}
\]

and mixtures thereof.

Wherein a, b, d, and e are integers, and a+b is from 6 to 13, d+e is from 4 to 11.

Further,

when a + b = 6, a is an integer from 2 to 5 and b is an integer from 1 to 4;
when a + b = 7, a is an integer from 2 to 6 and b is an integer from 1 to 5;
when a + b = 8, a is an integer from 2 to 7 and b is an integer from 1 to 6;
when a + b = 9, a is an integer from 2 to 8 and b is an integer from 1 to 7;
when a + b = 10, a is an integer from 2 to 9 and b is an integer from 1 to 8;
when a + b = 11, a is an integer from 2 to 10 and b is an integer from 1 to 9;
when a + b = 12, a is an integer from 2 to 11 and b is an integer from 1 to 10;
when a + b = 13, a is an integer from 2 to 12 and b is an integer from 1 to 11;
when d + e = 4, d is an integer from 2 to 3 and e is an integer from 1 to 2;
when d + e = 5, d is an integer from 2 to 4 and e is an integer from 1 to 3;
when d + e = 6, d is an integer from 2 to 5 and e is an integer from 1 to 4;
when d + e = 7, d is an integer from 2 to 6 and e is an integer from 1 to 5;
when d + e = 8, d is an integer from 2 to 7 and e is an integer from 1 to 6;
when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7;
when d + e = 10, d is an integer from 2 to 9 and e is an integer from 1 to 8;
when d + e = 11, d is an integer from 2 to 10 and e is an integer from 1 to 9.

Further, the average total number of carbon atoms in the branched primary alkyl moieties having the above formulas is within the range of greater than about 12 to about 14.5. EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propanoxy groups. Wherein m is at least about 1, preferably within the range of from about 3 to about 30, more preferably from about 5 to about 20, and most preferably from about 5 to about 15.
Further, the present invention surfactant composition may comprise a mixture of branched primary alkyl polyoxyalkylenes having the formula:

\[
\begin{array}{c}
\text{CH}_3\text{CH}_2(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{CH}_2(\text{EO/PO})_m\text{OH}
\end{array}
\]

Wherein the total number of carbon atoms per molecule, including branching, is from about 10 to about 17, and the average total number of carbon atoms in the branched primary alkyl moieties having the above formula is within the range of greater than about 12 to about 14.5. \( R, R^1, \) and \( R^2 \) are each independently selected from hydrogen and \( C_1-C_3 \) alkyl, provided \( R, R^1, \) and \( R^2 \) are not all hydrogen. \( w \) is an integer from 0 to 10; \( x \) is an integer from 0 to 10; \( y \) is an integer from 0 to 10; \( z \) is an integer from 0 to 10; \( w + x + y + z \) is from 3 to 10. EO/PO are alkoxy moieties, preferably selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein \( m \) is at least about 1, preferably within the range of from about 3 to about 30, more preferably from about 5 to about 20, and most preferably from about 5 to about 15. Provided when \( R^2 \) is \( C_1-C_3 \) alkyl the ratio of surfactants having \( z \) equal to 2 or greater to surfactants having \( z \) of 1 is at least about 1:1, preferably at least about 1.5:1, more preferably at least about 3:1, and most preferably at least about 4:1. Also preferred are surfactant compositions when \( R^2 \) is \( C_1-C_3 \) alkyl comprising less than about 50%, preferably less than about 40%, more preferably less than about 25%, most preferably less than about 20%, of branched primary alkyl polyoxyalkylene having the above formula wherein \( z \) equals 0.

Preferred mono-methyl branched primary alkyl ethoxylates are selected from the group consisting of: 3-methyl dodecanol ethoxylate, 4-methyl dodecanol ethoxylate, 5-methyl dodecanol ethoxylate, 6-methyl dodecanol ethoxylate, 7-methyl dodecanol ethoxylate, 8-methyl dodecanol ethoxylate, 9-methyl dodecanol ethoxylate, 10-methyl dodecanol ethoxylate, 3-methyl tridecanol ethoxylate, 4-methyl tridecanol ethoxylate, 5-methyl tridecanol ethoxylate, 6-methyl tridecanol ethoxylate, 7-methyl tridecanol ethoxylate, 8-methyl tridecanol ethoxylate, 9-methyl tridecanol ethoxylate, 10-methyl tridecanol ethoxylate, 11-methyl tridecanol ethoxylate, and mixtures thereof, wherein the compounds are ethoxylated with an average degree of ethoxylation of from about 5 to about 15.

Preferred di-methyl branched primary alkyl ethoxylates selected from the group consisting of: 2,3-dimethyl undecanol ethoxylate, 2,4-dimethyl undecanol ethoxylate, 2,5-dimethyl undecanol ethoxylate, 2,6-dimethyl undecanol ethoxylate, 2,7-dimethyl undecanol ethoxylate, 2,8-dimethyl undecanol ethoxylate, 2,9-dimethyl undecanol ethoxylate, 2,3-dimethyl dodecanol ethoxylate, 2,4-dimethyl dodecanol
ethoxylate, 2,5-dimethyl dodecanol ethoxylate, 2,6-dimethyl dodecanol ethoxylate, 
2,7-dimethyl dodecanol ethoxylate, 2,8-dimethyl dodecanol ethoxylate, 2,9-dimethyl 
dodecanol ethoxylate, 2,10-dimethyl dodecanol ethoxylate, and mixtures thereof, 
wherein the compounds are ethoxylated with an average degree of ethoxylolation of 
from about 1 to about 15.

**Preparation of Mid-chain Branched Surfactants**

The following reaction scheme outlines a general approach to the preparation 
of the mid-chain branched primary alcohol useful for alkoxylating and/or sulfating 
to prepare the mid-chain branched primary alkyl surfactants of the present invention. 
Linear alcohol can be added to the branched alcohol prior to alkoxylating and/or 
sulfating.

\[
\begin{align*}
  R\text{Cl} & \xrightarrow{\text{Mg}} R\text{MgCl} & & \xrightarrow{\text{Ac}_2\text{O}} \xrightarrow{\Delta} R\text{Ac} \\
  \text{Cl}(\text{CH}_2)_n: & \xrightarrow{\text{H}_3\text{O}^+} \xrightarrow{\text{Ac}_2\text{O}} \xrightarrow{\Delta} \xrightarrow{\text{H}_2 \xrightarrow{\text{cat}}} \text{Ac}
\end{align*}
\]

An alkyl halide is converted to a Grignard reagent and the Grignard is 
reacted with a haloketone. After conventional acid hydrolysis, acetylation and 
thermal elimination of acetic acid, an intermediate olefin is produced (not shown in 
the scheme) which is hydrogenated forthwith using any convenient hydrogenation 
catalyst such as Pd/C.

This route is favorable over others in that the branch, in this illustration a 5-
methyl branch, is introduced early in the reaction sequence.

Formulation of the alkyl halide resulting from the first hydrogenation step 
yields alcohol product, as shown in the scheme. This can be alkoxylated using 
standard techniques and/or sulfated using any convenient sulfating agent, e.g., 
chlorosulfonic acid, SO₃/air, or oleum, to yield the final branched primary alkyl 
surfactant. There is flexibility to extend the branching one additional carbon beyond 
that which is achieved by a single formulation. Such extension can, for example, be 
accomplished by reaction with ethylene oxide. See “Grignard Reactions of

In variations of the above procedure, alternate haloketones or Grignard reagents may be used. PBr3 halogenation of the alcohol from formulation or ethoxylation can be used to accomplish an iterative chain extension.

The preferred mid-chained branched primary alkyl alkoxylated sulfates (as well as the polyoxyalkylene and alkyl sulfates, by choosing to only alkoxylate or sulfate the intermediate alcohol produced) of the present invention can also be readily prepared as follows:

A conventional bromoalcohol is reacted with triphenylphosphine followed by sodium hydride, suitably in dimethylsulfoxide/tetrahydrofuran, to form a Wittig adduct. The Wittig adduct is reacted with an alpha methyl ketone, forming an internally unsaturated methyl-branched alcoholate. Hydrogenation followed by alkoxylation and/or sulfation yields the desired mid-chain branched primary alkyl surfactant. Although the Wittig approach does not allow the practitioner to extend the hydrocarbon chain, as in the Grignard sequence, the Wittig typically affords higher yields. See Agricultural and Biological Chemistry, M. Horiiike et al., vol. 42 (1978), pp 1963-1965 included herein by reference.

Any alternative synthetic procedure in accordance with the invention may be used to prepare the branched primary alkyl surfactants. The mid-chain branched primary alkyl surfactants may, in addition be synthesized or formulated in the presence of the conventional homologs, for example linear homologues or any of those which may be formed in an industrial process which produces 2-alkyl branching as a result of hydroformylation.
In certain preferred embodiments of the surfactant mixtures of the present invention, especially those derived from fossil fuel sources involving commercial processes, said surfactant mixtures comprise at least 1 mid-chain branched primary alkyl surfactant, preferably at least 2, more preferably at least 5, most preferably at least 8. Particularly suitable for preparation of certain surfactant mixtures of the present invention are "oxo" reactions wherein a branched chain olefin is subjected to catalytic isomerization and hydroformylation prior to alkoxylation and/or sulfation. The preferred processes resulting in such mixtures utilize fossil fuels as the starting material feedstock. Preferred processes utilize Oxo reaction on olefins (alpha or internal) with a limited amount of branching. Suitable olefins may be made by dimerization of linear alpha or internal olefins, by controlled oligomerization of low molecular weight linear olefins, by skeletal rearrangement of detergent range olefins, by dehydrogenation/skeletal rearrangement of detergent range paraffins, or by Fischer-Tropsch reaction. These reactions will in general be controlled to:

1) give a large proportion of olefins in the desired detergent range (while allowing for the addition of a carbon atom in the subsequent Oxo reaction),
2) produce a limited number of branches, preferably mid-chain,
3) produce C1-C3 branches, more preferably ethyl, most preferably methyl,
4) limit or eliminate gem dialkyl branching i.e. to avoid formation of quaternary carbon atoms.

The linear olefin content can be controlled in various ways, e.g., by controlling the extent to which skeletal rearrangement is allowed to proceed or by blending of branched and linear olefins. The suitable olefins can undergo Oxo reaction to give primary alcohols either directly or indirectly through the corresponding aldehydes. When an internal olefin is used, an Oxo catalyst is normally used which is capable of prior pre-isomerization of internal olefins primarily to alpha olefins. While a separately catalyzed (i.e. non-Oxo) internal to alpha isomerization could be effected, this is optional. On the other hand, if the olefin-forming step itself results directly in an alpha olefin (e.g. with high pressure Fischer-Tropsch olefins of detergent range), then use of a non-isomerizing Oxo catalyst is not only possible, but preferred.

A preferred embodiment of the surfactant mixtures of the present invention involves those materials derived from commercial processes wherein an olefin-rich feedstock containing branched chain olefins, linear olefins and other olefins, e.g., olefins containing cyclical structures, substituted cyclical olefins, and the like, is subjected to carbon monoxide and hydrogen in the presence of a catalytic amount of a hydroformylation catalyst prior to alkoxylation and/or sulfation. In this
embodiment, the olefin-rich feedstock is obtained by subjecting a synthesis gas comprising carbon monoxide (CO) and hydrogen (H₂) to Fischer-Tropsch reaction conditions in the presence of an iron-based, a cobalt-based, or an iron/cobalt-based Fischer-Tropsch catalyst. An exemplification of the alcohols and olefin mixtures of this embodiment are those described by WO 97/01521 and in the Sasol R&D technical product bulletin dated October 1, 1996 entitled SASOL DETERGENT ALCOHOLS, incorporated herein by reference.

The following two analytical methods for characterizing branching in the present invention surfactant compositions are useful:


2) Identification of Separated Fatty Alcohol Alkoxy Sulfate Components by MS/MS. The position and length of branching is also determinable by Ion Spray-MS/MS or FAB-MS/MS techniques on previously isolated fatty alcohol sulfate components.

The average total carbon atoms of the branched primary alkyl surfactants herein can be calculated from the hydroxyl value of the precursor fatty alcohol mix or from the hydroxyl value of the alcohols recovered by extraction after hydrolysis of the alcohol sulfate mix according to common procedures, such as outlined in "Balley's Industrial Oil and Fat Products", Volume 2, Fourth Edition, edited by Daniel Swern, pp. 440-441.

NON-AQUEOUS BASED HEAVY DUTY LIQUID DETERGENTS
SURFACTANT-CONTAINING LIQUID PHASE

The present invention comprises non-aqueous, liquid, heavy-duty detergent compositions in the form of a stable suspension of solid, substantially insoluble particulate material dispersed throughout a structured, surfactant-containing liquid phase. The detergent composition comprises from about 49% to 99.95% by weight of the composition of a structured, surfactant-containing liquid phase formed by combining:

i) from about 1% to 80% by weight of said liquid phase of one or more nonaqueous organic diluents; and
ii) from about 20% to 99% by weight of said liquid phase of a surfactant system comprising surfactants selected from the group consisting of anionic, nonionic, cationic surfactants and combinations thereof.

The surfactant-containing, non-aqueous liquid phase of the present invention will generally comprise from about 52% to about 98.9% by weight of the detergent compositions herein. More preferably, this liquid phase is surfactant-structured and will comprise from about 55% to 98% by weight of the compositions. Most preferably, this non-aqueous liquid phase will comprise from about 55% to 70% by weight of the compositions herein. Such a surfactant-containing liquid phase will frequently have a density of from about 0.6 to 1.4 g/cc, more preferably from about 0.9 to 1.3 g/cc. The liquid phase of the detergent compositions herein is preferably formed from one or more non-aqueous organic diluents into which is mixed a surfactant structuring agent which is preferably a specific type of anionic surfactant-containing powder.

Non-aqueous Organic Diluents

The major component of the liquid phase of the detergent compositions herein comprises one or more non-aqueous organic diluents. The non-aqueous organic diluents used in this invention may be either surface active, i.e., surfactant, liquids or non-aqueous, non-surfactant liquids referred to herein as non-aqueous solvents. The term "solvent" is used herein to connote the non-surfactant, non-aqueous liquid portion of the compositions herein. While some of the essential and/or optional components of the compositions herein may actually dissolve in the "solvent"-containing liquid phase, other components will be present as particulate material dispersed within the "solvent"-containing liquid phase. Thus the term "solvent" is not meant to require that the solvent material be capable of actually dissolving all of the detergent composition components added thereto.

The non-aqueous liquid diluent component will generally comprise from about 50% to 100%, more preferably from about 50% to 80%, most preferably from about 55% to 75%, of a structured, surfactant-containing liquid phase. Preferably the liquid phase of the compositions herein, i.e., the non-aqueous liquid diluent component, will comprise both non-aqueous liquid surfactants and non-surfactant non-aqueous solvents.

i) **Non-aqueous Surfactant Liquids**

Suitable types of non-aqueous surfactant liquids which can be used to form the liquid phase of the compositions herein include the alkoxyolated alcohols,
ethylene oxide (EO)-propylene oxide (PO) block polymers, polyhydroxy fatty acid amides, alkyl polysaccharides, and the like. Such normally liquid surfactants are those having an HLB ranging from 10 to 16. Most preferred of the surfactant liquids are the alcohol alkoxylate nonionic surfactants.

Alcohol alkoxylates are materials which correspond to the general formula:

$$R^1(C_mH_{2m}O)_nOH$$

wherein $R^1$ is a C$_8$ - C$_{16}$ alkyl group, $m$ is from 2 to 4, and $n$ ranges from about 2 to 12. Preferably $R^1$ is an alkyl group, which may be primary or secondary, that contains from about 9 to 15 carbon atoms, more preferably from about 10 to 14 carbon atoms. Preferably also the alkoxylated fatty alcohols will be ethoxylated materials that contain from about 2 to 12 ethylene oxide moieties per molecule, more preferably from about 3 to 10 ethylene oxide moieties per molecule.

The alkoxylated fatty alcohol materials useful in the liquid phase will frequently have a hydrophilic-lipophilic balance (HLB) which ranges from about 3 to 17. More preferably, the HLB of this material will range from about 6 to 15, most preferably from about 8 to 15.

Examples of fatty alcohol alkoxylates useful in or as the non-aqueous liquid phase of the compositions herein will include those which are made from alcohols of 12 to 15 carbon atoms and which contain about 7 moles of ethylene oxide. Such materials have been commercially marketed under the trade names Neodol 25-7 and Neodol 23-6.5 by Shell Chemical Company. Other useful Neodols include Neodol 1-5, an ethoxylated fatty alcohol averaging 11 carbon atoms in its alkyl chain with about 5 moles of ethylene oxide; Neodol 23-9, an ethoxylated primary C$_{12}$ - C$_{13}$ alcohol having about 9 moles of ethylene oxide and Neodol 91-10, an ethoxylated C$_9$-C$_{11}$ primary alcohol having about 10 moles of ethylene oxide. Alcohol ethoxylates of this type have also been marketed by Shell Chemical Company under the Dobanol tradename. Dobanol 91-5 is an ethoxylated C$_9$-C$_{11}$ fatty alcohol with an average of 5 moles ethylene oxide and Dobanol 25-7 is an ethoxylated C$_{12}$-C$_{15}$ fatty alcohol with an average of 7 moles of ethylene oxide per mole of fatty alcohol.

Other examples of suitable ethoxylated alcohols include Tergitol 15-S-7 and Tergitol 15-S-9 both of which are linear secondary alcohol ethoxylates that have been commercially marketed by Union Carbide Corporation. The former is a mixed ethoxylation product of C$_{11}$ to C$_{15}$ linear secondary alkanol with 7 moles of ethylene oxide and the latter is a similar product but with 9 moles of ethylene oxide being reacted.

Other types of alcohol ethoxylates useful in the present compositions are higher molecular weight nonionics, such as Neodol 45-11, which are similar
ethylene oxide condensation products of higher fatty alcohols, with the higher fatty alcohol being of 14-15 carbon atoms and the number of ethylene oxide groups per mole being about 11. Such products have also been commercially marketed by Shell Chemical Company.

If alcohol alkoxylate nonionic surfactant is utilized as part of the non-aqueous liquid phase in the detergent compositions herein, it will preferably be present to the extent of from about 1% to 60% of the composition structured liquid phase. More preferably, the alcohol alkoxylate component will comprise about 5% to 40% of the structured liquid phase. Most preferably, an alcohol alkoxylate component will comprise from about 5% to 35% of the detergent composition structured liquid phase. Utilization of alcohol alkoxylate in these concentrations in the liquid phase corresponds to an alcohol alkoxylate concentration in the total composition of from about 1% to 60% by weight, more preferably from about 2% to 40% by weight, and most preferably from about 5% to 25% by weight, of the composition.

Another type of non-aqueous surfactant liquid which may be utilized in this invention are the ethylene oxide (EO) - propylene oxide (PO) block polymers. Materials of this type are well known nonionic surfactants which have been marketed under the tradename Pluronic. These materials are formed by adding blocks of ethylene oxide moieties to the ends of polypropylene glycol chains to adjust the surface active properties of the resulting block polymers. EO-PO block polymer nonionics of this type are described in greater detail in Davidsohn and Milwidsky; Synthetic Detergents, 7th Ed.; Longman Scientific and Technical (1987) at pp. 34-36 and pp. 189-191 and in U.S. Patents 2,674,619 and 2,677,700. All of these publications are incorporated herein by reference. These Pluronic type nonionic surfactants are also believed to function as effective suspending agents for the particulate material which is dispersed in the liquid phase of the detergent compositions herein.

Another possible type of non-aqueous surfactant liquid useful in the compositions herein comprises polyhydroxy fatty acid amide surfactants. If present, the polyhydroxy fatty acid amide surfactants are preferably present in a concentration of from about 0.1 to about 8%. Materials of this type of nonionic surfactant are those which conform to the formula:

\[ \text{O} \quad \text{C}_p\text{H}_{2p+1} \]
\[ \text{R} \quad \text{C} \quad \text{N} \quad \text{Z} \]
wherein R is a C₉₋₁₇ alkyl or alkenyl, p is from 1 to 6, and Z is glycicyl derived from a reduced sugar or alkoxyalted derivative thereof. Such materials include the C₁₂⁻C₁₈ N-methyl glucamides. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucitory oleamide. Processes for making polyhydroxy fatty acid, amides are known and can be found, for example, in Wilson, U.S. Patent 2,965,576 and Schwartz, U.S. Patent 2,703,798, the disclosures of which are incorporated herein by reference. The materials themselves and their preparation are also described in greater detail in Honsa, U.S. Patent 5,174,937, Issued December 26, 1992, which patent is also incorporated herein by reference.

The amount of total liquid surfactant in the preferred surfactant-structured, non-aqueous liquid phase herein will be determined by the type and amounts of other composition components and by the desired composition properties. Generally, the liquid surfactant can comprise from about 35% to 70% of the non-aqueous liquid phase of the compositions herein. More preferably, the liquid surfactant will comprise from about 50% to 65% of a non-aqueous structured liquid phase. This corresponds to a non-aqueous liquid surfactant concentration in the total composition of from about 15% to 70% by weight, more preferably from about 20% to 50% by weight, of the composition.

ii) Non-surfactant Non-aqueous Organic Solvents

The liquid phase of the detergent compositions herein may also comprise one or more non-surfactant, non-aqueous organic solvents. Such non-surfactant non-aqueous liquids are preferably those of low polarity. For purposes of this invention, "low-polarity" liquids are those which have little, if any, tendency to dissolve one of the preferred types of particulate material used in the compositions herein, i.e., the peroxonium bleaching agents, sodium perborate or sodium percarbonate. Thus relatively polar solvents such as ethanol are preferably not utilized. Suitable types of low-polarity solvents useful in the non-aqueous liquid detergent compositions herein do include non-vicinal C₄⁻C₈ alkylene glycols, alkylene glycol mono lower alkyl ethers, lower molecular weight polyethylene glycols, lower molecular weight methyl esters and amides, and the like.

A preferred type of non-aqueous, low-polarity solvent for use in the compositions herein comprises the non-vicinal C₄⁻C₈ branched or straight chain alkylene glycols. Materials of this type include hexylene glycol (4-methyl-2,4-pentanediol), 1,6-hexanediol, 1,3-butylen glycol and 1,4-butylene glycol. Hexylene glycol is the most preferred.
Another preferred type of non-aqueous, low-polarity solvent for use herein comprises the mono-, di-, tri-, or tetra- C₂-C₃ alkylene glycol mono C₂-C₆ alkyl ethers. The specific examples of such compounds include diethylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, dipropylene glycol monoethyl ether, and dipropyylene glycol monobutyl ether. Diethylene glycol monobutyl ether, dipropylene glycol monobutyl ether and butoxy-propoxy-propanol (BPP) are especially preferred. Compounds of the type have been commercially marketed under the tradenames Dowanol, Carbitol, and Cellosolve.

Another preferred type of non-aqueous, low-polarity organic solvent useful herein comprises the lower molecular weight polyethylene glycols (PEGs). Such materials are those having molecular weights of at least about 150. PEGs of molecular weight ranging from about 200 to 600 are most preferred.

Yet another preferred type of non-polar, non-aqueous solvent comprises lower molecular weight methyl esters. Such materials are those of the general formula: R¹-C(O)-OCH₃ wherein R¹ ranges from 1 to about 18. Examples of suitable lower molecular weight methyl esters include methyl acetate, methyl propionate, methyl octanoate, and methyl dodecanoate.

The non-aqueous, generally low-polarity, non-surfactant organic solvent(s) employed should, of course, be compatible and non-reactive with other composition components, e.g., bleach and/or activators, used in the liquid detergent compositions herein. Such a solvent component is preferably utilized in an amount of from about 1% to 70% by weight of the liquid phase. More preferably, a non-aqueous, low-polarity, non-surfactant solvent will comprise from about 10% to 60% by weight of a structured liquid phase, most preferably from about 20% to 50% by weight, of a structured liquid phase of the composition. Utilization of non-surfactant solvent in these concentrations in the liquid phase corresponds to a non-surfactant solvent concentration in the total composition of from about 1% to 50% by weight, more preferably from about 5% to 40% by weight, and most preferably from about 10% to 30% by weight, of the composition.

iii) Blends of Surfactant and Non-surfactant Solvents

In systems which employ both non-aqueous surfactant liquids and non-aqueous non-surfactant solvents, the ratio of surfactant to non-surfactant liquids, e.g., the ratio of alcohol alkoxide to low polarity solvent, within a structured, surfactant-containing liquid phase can be used to vary the rheological properties of the detergent compositions eventually formed. Generally, the weight ratio of surfactant liquid to non-surfactant organic solvent will range about 50:1 to 1:50. More
preferably, this ratio will range from about 3:1 to 1:3, most preferably from about 2:1 to 1:2.

**Surfactant Structurant**

The non-aqueous liquid phase of the detergent compositions of this invention is prepared by combining with the non-aqueous organic liquid diluents hereinbefore described a surfactant which is generally, but not necessarily, selected to add structure to the non-aqueous liquid phase of the detergent compositions herein. Structuring surfactants can be of the anionic, nonionic, cationic, and/or amphoteric types.

Preferred structuring surfactants are the anionic surfactants such as the alkyl sulfates, the alkyl polyalkoxylate sulfates and the linear alkyl benzene sulfonates. Another common type of anionic surfactant material which may be optionally added to the detergent compositions herein as structurant comprises carboxylate-type anionics. Carboxylate-type anionics include the C_{10} - C_{18} alkyl alkoxy carboxylates (especially the EO 1 to 5 ethoxycarboxylates) and the C_{10} - C_{18} sarcosinates, especially oleoyl sarcosinate. Yet another common type of anionic surfactant material which may be employed as a structurant comprises other sulfonated anionic surfactants such as the C_{8} - C_{18} paraffin sulfonates and the C_{8} - C_{18} olefin sulfonates. Structuring anionic surfactants will generally comprise from about 1% to 30% by weight of the compositions herein.

As indicated, one preferred type of structuring anionic surfactant comprises primary or secondary alkyl sulfate anionic surfactants. Such surfactants are those produced by the sulfation of higher C_{8} - C_{20} fatty alcohols.

Conventional primary alkyl sulfate surfactants have the general formula

$$\text{ROSO}_3^-\text{M}^+$$

wherein R is typically a linear C_{8} - C_{20} hydrocarbyl group, which may be straight chain or branched chain, and M is a water-solubilizing cation. Preferably R is a C_{10} - C_{14} alkyl, and M is alkali metal. Most preferably R is about C_{12} and M is sodium.

Conventional secondary alkyl sulfates may also be utilized as a structuring anionic surfactant for the liquid phase of the compositions herein. Conventional secondary alkyl sulfate surfactants are those materials which have the sulfate moiety distributed randomly along the hydrocarbyl "backbone" of the molecule. Such materials may be depicted by the structure:

$$\text{CH}_3(\text{CH}_2)_n(\text{CHOSO}_3^-\text{M}^+)(\text{CH}_2)_m\text{CH}_3$$
wherein m and n are integers of 2 or greater and the sum of m + n is typically about 9 to 15, and M is a water-solubilizing cation.

If utilized, alkyl sulfates will generally comprise from about 1% to 30% by weight of the composition, more preferably from about 5% to 25% by weight of the composition. Non-aqueous liquid detergent compositions containing alkyl sulfates, peroxxygen bleaching agents, and bleach activators are described in greater detail in Kong-Chan et al.; WO 96/10073; Published April 4, 1996, which application is incorporated herein by reference.

Another preferred type of anionic surfactant material which may be optionally added to the non-aqueous cleaning compositions herein as a structurant comprises the alkyl polyalkoxylate sulfates. Alkyl polyalkoxylate sulfates are also known as alkoxylated alkyl sulfates or alkyl ether sulfates. Such materials are those which correspond to the formula

\[ R^2-\text{O-}(\text{C}_m\text{H}_{2m}\text{O})_n\text{-SO}_3\text{M} \]

wherein \( R^2 \) is a C\(_{10}\)-C\(_{22}\) alkyl group, m is from 2 to 4, n is from about 1 to 15, and M is a salt-forming cation. Preferably, \( R^2 \) is a C\(_{12}\)-C\(_{18}\) alkyl, m is 2, n is from about 1 to 10, and M is sodium, potassium, ammonium, alkylammonium or alkanolammonium. Most preferably, \( R^2 \) is a C\(_{12}\)-C\(_{16}\), m is 2, n is from about 1 to 6, and M is sodium. Ammonium, alkylammonium and alkanolammonium counterions are preferably avoided when used in the compositions herein because of incompatibility with peroxxygen bleaching agents.

If utilized, alkyl polyalkoxylate sulfates can also generally comprise from about 1% to 30% by weight of the composition, more preferably from about 5% to 25% by weight of the composition. Non-aqueous liquid detergent compositions containing alkyl polyalkoxylate sulfates, in combination with polyhydroxy fatty acid amides, are described in greater detail in Boutique et al; PCT Application No. PCT/US96/04223, which application is incorporated herein by reference.

The most preferred type of anionic surfactant for use as a structurant in the compositions herein comprises the linear alkyl benzene sulfonate (LAS) surfactants. In particular, such LAS surfactants can be formulated into a specific type of anionic surfactant-containing powder which is especially useful for incorporation into the non-aqueous liquid detergent compositions of the present invention. Such a powder comprises two distinct phases. One of these phases is insoluble in the non-aqueous organic liquid diluents used in the compositions herein; the other phase is soluble in the non-aqueous organic liquids. It is the insoluble phase of this preferred anionic
surfactant-containing powder which can be dispersed in the non-aqueous liquid phase of the preferred compositions herein and which forms a network of aggregated small particles that allows the final product to stably suspend other solid particulate materials in the composition.

Such a preferred anionic surfactant-containing powder is formed by co-drying an aqueous slurry which essentially contains a) one of more alkali metal salts of C_{10-16} linear alkyl benzene sulfonic acids; and b) one or more non-surfactant diluent salts. Such a slurry is dried to a solid material, generally in powder form, which comprises both the soluble and insoluble phases.

The linear alkyl benzene sulfonate (LAS) materials used to form the preferred anionic surfactant-containing powder are well known materials. Such surfactants and their preparation are described for example in U.S. Patents 2,220,099 and 2,477,383, incorporated herein by reference. Especially preferred are the sodium and potassium linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to 14. Sodium C_{11-14}, e.g., C_{12}, LAS is especially preferred. The alkyl benzene surfactant anionic surfactants are generally used in the powder-forming slurry in an amount from about 20 to 70% by weight of the slurry, more preferably from about 20% to 60% by weight of the slurry.

The powder-forming slurry also contains a non-surfactant, organic or inorganic salt component that is co-dried with the LAS to form the two-phase anionic surfactant-containing powder. Such salts can be any of the known sodium, potassium or magnesium halides, sulfates, citrates, carbonates, sulfates, borates, succinates, sulfo-succinates and the like. Sodium sulfate, which is generally a by-product of LAS production, is the preferred non-surfactant diluent salt for use herein. Salts which function as hydrotropes such as sodium sulfo-succinate may also usefully be included. The non-surfactant salts are generally used in the aqueous slurry, along with the LAS, in amounts ranging from about 1 to 50% by weight of the slurry, more preferably from about 5% to 40% by weight of the slurry. Salts that act as hydrotropes can preferably comprise up to about 3% by weight of the slurry.

The aqueous slurry containing the LAS and diluent salt components hereinbefore described can be dried to form the anionic surfactant-containing powder preferably added to the non-aqueous diluents in order to prepare a structured liquid phase within the compositions herein. Any conventional drying technique, e.g., spray drying, drum drying, etc., or combination of drying techniques, may be employed. Drying should take place until the residual water content of the solid
material which forms is within the range of from about 0.5% to 4% by weight, more preferably from about 1% to 3% by weight.

The anionic surfactant-containing powder produced by the drying operation constitutes two distinct phases, one of which is soluble in the inorganic liquid diluents used herein and one of which is insoluble in the diluents. The insoluble phase in the anionic surfactant-containing powder generally comprises from about 10% to 45% by weight of the powder, more preferably from about 15% to 35% by weight of a powder.

The anionic surfactant-containing powder that results after drying can comprise from about 45% to 94%, more preferably from about 60% to 94%, by weight of the powder of alkyl benzene sulfonic acid salts. Such concentrations are generally sufficient to provide from about 0.5% to 60%, more preferably from about 15% to 60%, by weight of the total detergent composition that is eventually prepared, of the alkyl benzene sulfonic acid salts. The anionic surfactant-containing powder itself can comprise from about 0.45% to 45% by weight of the total composition that is eventually prepared. After drying, the anionic surfactant-containing powder will also generally contain from about 2% to 50%, more preferably from about 2% to 25% by weight of the powder of the non-surfactant salts.

After it is dried to the requisite extent, the combined LAS/salt material can be converted to flakes or powder form by any known suitable milling or comminution process. Generally at the time such material is combined with the non-aqueous organic solvents to form the structured liquid phase of the compositions herein, the particle size of this powder will range from 0.1 to 2000 microns, more preferably from about 0.1 to 1000 microns.

A structured, surfactant-containing liquid phase of the preferred detergent compositions herein can be prepared by combining the non-aqueous organic diluents hereinbefore described with the anionic surfactant-containing powder as hereinbefore described. Such combination results in the formation of a structured surfactant-containing liquid phase. Conditions for making this combination of preferred structured liquid phase components are described more fully hereinafter in the "Composition Preparation and Use" section. As previously noted, the formation of a structured, surfactant-containing liquid phase permits the stable suspension of colored speckles and additional functional particulate solid materials within the preferred detergent compositions of this invention.

Additional suitable surfactants for use in the present invention included nonionic surfactants, specifically, polyhydroxy fatty acid amides of the formula:
wherein R is a C_{9-17} alkyl or alkenyl, R_1 is a methyl group and Z is glycyl derived from a reduced sugar or alkoxylated derivative thereof. Examples are N-methyl N-1-deoxyglucityl cocomamide and N-methyl N-1-deoxyglucityl oleamide. Processes for making polyhydroxy fatty acid amides are known and can be found in Wilson, U.S. Patent 2,965,576 and Schwartz, U.S. Patent 2,703,798, the disclosures of which are incorporated herein by reference.

Preferred surfactants for use in the detergent compositions described herein are amine based surfactants of the general formula:

\[
\begin{array}{c}
R_3 \\
R_1-X-(\text{CH}_2)_n-N \\
R_4
\end{array}
\]

wherein R_1 is a C_{6-12} alkyl group; n is from about 2 to about 4, X is a bridging group which is selected from NH, CONH, COO, or O or X can be absent; and R_3 and R_4 are individually selected from H, C_1-C_4 alkyl, or \((\text{CH}_2-\text{CH}_2-O(R_5))\) wherein R_5 is H or methyl. Especially preferred amines based surfactants include the following:

\[
\begin{align*}
\text{R}_1-(\text{CH}_2)_2-\text{NH}_2 \\
\text{R}_1-O-(\text{CH}_2)_3-\text{NH}_2 \\
\text{R}_1-\text{C(O)}-\text{NH}-(\text{CH}_2)_3-N(\text{CH}_3)_2 \\
\text{CH}_2-\text{CH(OH)}-\text{R}_5 \\
\text{R}_1-N \\
\text{CH}_2-\text{CH(OH)}-\text{R}_5
\end{align*}
\]

wherein R_1 is a C_{6-12} alkyl group and R_5 is H or CH_3. Particularly preferred amines for use in the surfactants defined above include those selected from the group consisting of octyl amine, hexyl amine, decyl amine, dodecyl amine, C_8-C_{12} bis(hydroxyethyl)amine, C_8-C_{12} bis(hydroxyisopropyl)amine, C_8-C_{12} amido-propyl dimethyl amine, or mixtures thereof.
In a highly preferred embodiment, the amine based surfactant is described by the formula:

\[ R_1\text{-}C(O)\text{-}NH\text{-}(CH_2)_3\text{-}N(CH_3)_2 \]

wherein \( R_1 \) is \( C_8\text{-}C_{12} \) alkyl.

**SOLID PARTICULATE MATERIALS**

The non-aqueous detergent compositions herein preferably comprise from about 0.01% to 50% by weight, more preferably from about 0.2% to 30% by weight, of solid phase particulate material which is dispersed and suspended within the liquid phase. Generally such particulate material will range in size from about 0.1 to 1500 microns, more preferably from about 0.1 to 900 microns. Most preferably, such material will range in size from about 5 to 200 microns.

The particulate material utilized herein can comprise one or more types of detergent composition components which in particulate form are substantially insoluble in the non-aqueous liquid phase of the composition. The types of particulate materials which can be utilized are described in detail as follows:

**Peroxygen Bleaching Agent With Optional Bleach Activators**

The most preferred type of particulate material useful in the detergent compositions herein comprises particles of a peroxygen bleaching agent. Such peroxygen bleaching agents may be organic or inorganic in nature. Inorganic peroxygen bleaching agents are frequently utilized in combination with a bleach activator.

Useful organic peroxygen bleaching agents include percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monopersyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxidodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, Issued November 20, 1984; European Patent Application EP-A-133,354, Banks et al., Published February 20, 1985; and U.S. Patent 4,412,934, Chung et al., Issued November 1, 1983. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid (NAPAA) as described in U.S. Patent 4,634,551, Issued January 6, 1987 to Burns et al.

Inorganic peroxygen bleaching agents may also be used in particulate form in the detergent compositions herein. Inorganic bleaching agents are in fact preferred. Such inorganic peroxygen compounds include alkali metal perborate and percarbonate materials, most preferably the percarbonates. For example, sodium
perborate (e.g. mono- or tetra-hydrate) can be used. Suitable inorganic bleaching agents can also include sodium or potassium carbonate peroxycarbonate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxycarbonate, urea peroxycarbonate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used. Frequently inorganic peroxygen bleaches will be coated with silicate, borate, sulfate or water-soluble surfactants. For example, coated percarbonate particles are available from various commercial sources such as FMC, Solvay Interox, Tokai Denka and Degussa.

Inorganic peroxygen bleaching agents, e.g., the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the in situ production in aqueous solution (i.e., during use of the compositions herein for fabric laundering/bleaching) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. Patent 4,915,854, Issued April 10, 1990 to Mao et al.; and U.S. Patent 4,412,934 Issued November 1, 1983 to Chung et al. The nonanoyloxybenzene sulfonate (NOBS) and tetraacetyl ethylene diamine (TAED) activators are typical. Mixtures thereof can also be used. See also the hereinbefore referenced U.S. 4,634,551 for other typical bleaches and activators useful herein.

Other useful amido-derived bleach activators are those of the formulae:

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

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

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl) oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate and mixtures thereof as described in the hereinbefore referenced U.S. Patent 4,634,551. Such mixtures are characterized herein as (6-C8-C10 alkamido-caproyl)oxybenzenesulfonate.

Another class of useful bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al. in U.S. Patent 4,966, 723, Issued October 30,
1990, incorporated herein by reference. A highly preferred activator of the benzoxazin-type is:

![Chemical structure](image)

Still another class of useful bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:

![Chemical structures](image)

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

If peroxxygen bleaching agents are used as all or part of the particulate material, they will generally comprise from about 0.1% to 30% by weight of the composition. More preferably, peroxxygen bleaching agent will comprise from about 1% to 20% by weight of the composition. Most preferably, peroxxygen bleaching agent will be present to the extent of from about 5% to 20% by weight of the composition. If utilized, bleach activators can comprise from about 0.5% to 20%, more preferably from about 3% to 10%, by weight of the composition. Frequently, activators are employed such that the molar ratio of bleaching agent to activator ranges from about 1:1 to 10:1, more preferably from about 1.5:1 to 5:1. In addition, it has been found that bleach activators, when agglomerated with certain acids such as citric acid, are more chemically stable.

**Organic Builder Material**

Another possible type of particulate material which can be suspended in the non-aqueous liquid detergent compositions herein comprises an organic detergent
builder material which serves to counteract the effects of calcium, or other ion, water hardness encountered during laundering/bleaching use of the compositions herein. Examples of such materials include the alkali metal, citrates, succinates, malonates, fatty acids, carboxymethyl succinates, carboxylates, polycarboxylates and polyacetyl carboxylates. Specific examples include sodium, potassium and lithium salts of oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids and citric acid. Other examples of organic phosphonate type sequestering agents such as those which have been sold by Monsanto under the Dequest tradename and alkanedioxy phosphonates. Citrate salts are highly preferred.

Other suitable organic builders include the higher molecular weight polymers and copolymers known to have builder properties. For example, such materials include appropriate polyacrylic acid, polymaleic acid, and polyacrylic/polymaleic acid copolymers and their salts, such as those sold by BASF under the Sokalan trademark which have molecular weight ranging from about 5,000 to 100,000.

Another suitable type of organic builder comprises the water-soluble salts of higher fatty acids, i.e., "soaps". These include alkali metal soaps such as the sodium, potassium, ammonium, and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, and preferably from about 12 to about 18 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

If utilized as all or part of the particulate material, insoluble organic detergent builders can generally comprise from about 2% to 20% by weight of the compositions herein. More preferably, such builder material can comprise from about 4% to 10% by weight of the composition.

**Inorganic Alkalinity Sources**

Another possible type of particulate material which can be suspended in the non-aqueous liquid detergent compositions herein can comprise a material which serves to render aqueous washing solutions formed from such compositions generally alkaline in nature. Such materials may or may not also act as detergent builders, i.e., as materials which counteract the adverse effect of water hardness on detergency performance.

Examples of suitable alkalinity sources include water-soluble alkali metal carbonates, bicarbonates, borates, silicates and metasilicates. Although not preferred for ecological reasons, water-soluble phosphate salts may also be utilized as
alkalinity sources. These include alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Of all of these alkalinity sources, alkali metal carbonates such as sodium carbonate are the most preferred.

The alkalinity source, if in the form of a hydratable salt, may also serve as a desiccant in the non-aqueous liquid detergent compositions herein. The presence of an alkalinity source which is also a desiccant may provide benefits in terms of chemically stabilizing those composition components such as the peroxxygen bleaching agent which may be susceptible to deactivation by water.

If utilized as all or part of the particulate material component, the alkalinity source will generally comprise from about 1% to 25% by weight of the compositions herein. More preferably, the alkalinity source can comprise from about 2% to 15% by weight of the composition. Such materials, while water-soluble, will generally be insoluble in the non-aqueous detergent compositions herein. Thus such materials will generally be dispersed in the non-aqueous liquid phase in the form of discrete particles.

(D) Colored Speckles

The non-aqueous liquid detergent compositions herein also essentially contain from about 0.05% to 2%, more preferably 0.1% to 1%, of the composition of colored speckles. Such colored speckles themselves are combinations of a conventional dye or pigment material with a certain kind of carrier material that imparts specific characteristics to the speckles. For purposes of this invention, "colored" speckles are those which have a color that is visibly distinct from the color of the liquid detergent composition in which they are dispersed.

The colorant materials which can be used to form the colored speckles can comprise any of the conventional dyes and pigments known and approved for use in detergent products for use in the home. Such materials can include, for example, Ultramarine Blue dye, Acid 80 Blue dye, Red HP Liquitint, Blue Liquitint and the like.

Dye or pigment material can be combined with a specific type of carrier material to form the colored speckles for use in the detergent compositions herein. The carrier material is selected to impart to the speckles certain specific density and solubility characteristics. Materials which have been found to be suitable as carriers for the colored speckles include polyacrylates; polysaccharides such as starches, celluloses, gums and derivatives thereof; and polyethylene glycols. Especially preferred carrier material comprises polyethylene glycol having a molecular weight from about 4,000 to 20,000, more preferably from about 4,000 to 10,000.
The colored speckles can be produced by dispersing the dye or pigment material within the carrier material. This can be done, for example, by a) melting the carrier and dispersing the dye or pigment therein under mixing, b) mixing the dye/pigment powder and carrier powder together, or c) by dissolving the dye/pigment and the carrier in aqueous solution. The colorant/carrer mixture can then be formed into particles by flaking, spray drying, prilling, extruding or other conventional techniques. Generally the colored speckles will contain from about 0.1% to 5% by weight of the speckles of the colorant (dye or pigment) material.

The colored speckles produced in this manner will generally range in size from about 400 to 1,500 microns, more preferably from about 400 to 1,200 microns. Speckles made from the carrier materials specified will have a density less than about 1.4 g/cc, preferably from about 1.0 to 1.4 g/cc. Such speckles will also be substantially insoluble in the non-aqueous liquid phase of the liquid detergent compositions herein. Thus, the colored speckles can be stably suspended in the non-aqueous matrix of the liquid detergent compositions of this invention without dissolving therein. Such speckles, however, rapidly dissolve in the aqueous wash liquors prepared from the liquid detergent compositions herein.

AQUEOUS BASED HEAVY DUTY LIQUID DETERGENTS SURFACTANTS

The present invention also comprises aqueous based liquid detergent compositions. The aqueous liquid detergent compositions preferably comprise from about 10% to about 98%, preferably from about 30% to about 95%, by weight of an aqueous liquid carrier which is preferably water. Additionally, the aqueous liquid detergent compositions of the present invention comprise a surfactant system which preferably contains one or more detersive co-surfactants in addition to the branched surfactants disclosed above. The additional co-surfactants can be selected from nonionic detersive surfactant, anionic detersive surfactant, zwitterionic detersive surfactant, amine oxide detersive surfactant, and mixtures thereof. The surfactant system typically comprises from about 5% to about 70%, preferably from about 15% to about 30%, by weight of the detergent composition.

Anionic Surfactant

Anionic surfactants include \( C_{11-18} \) alkyl benzene sulfonates (LAS) and primary, branched-chain and random \( C_{10-20} \) alkyl sulfates (AS), the \( C_{10-18} \) secondary \( (2,3) \) alkyl sulfates of the formula \( \text{CH}_3(\text{CH}_2)_x(\text{CHOSO}_3^+ \text{M}^-) \text{CH}_3 \) and \( \text{CH}_3(\text{CH}_2)_y(\text{CHOSO}_3^+ \text{M}^-) \text{CH}_2\text{CH}_3 \) where \( x \) and \( (y + 1) \) are integers of at least
about 7, preferably at least about 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C_{10-18} alkyl alkoxy sulfates ("AE_{x}S"; especially EO 1-7 ethoxy sulfates), C_{10-18} alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C_{10-18} glycerol ethers, the C_{10-18} alkyl polyglycosides and their corresponding sulfated polyglycosides, and C_{12-18} alpha-sulfonated fatty acid esters.


Useful anionic surfactants include the water-soluble salts, particularly the alkali metal, ammonium and alkylammonium (e.g., monoethanolammonium or triethanolammonium) salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of aryl groups.) Examples of this group of synthetic surfactants are the alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_{8-18} carbon atoms) such as those produced by reducing the glycerides of tallow or coconut oil.

Other anionic surfactants herein are the water-soluble salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 4 units of ethylene oxide per molecule and from about 8 to about 12 carbon atoms in the alkyl group.

Other useful anionic surfactants herein include the water-soluble salts of esters of a-sulfonated fatty acids containing from about 6 to 20 carbon atoms in the fatty acid group and from about 1 to 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; water-soluble salts of olefin sulfonates containing from about 12 to 24 carbon atoms; and b-acyloxy alkane sulfonates containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Particularly preferred anionic surfactants herein are the alkyl polyethoxylate sulfates of the formula
\[ RO(C_{2}H_{4}O)_{x}SO_{3}^{-}M^{+} \]
wherein R is an alkyl chain having from about 10 to about 22 carbon atoms, saturated or unsaturated, M is a cation which makes the compound water-soluble, especially an alkali metal, ammonium or substituted ammonium cation, and x averages from about 1 to about 15.
Preferred alkyl sulfate surfactants are the non-ethoxylated C_{12-15} primary and secondary alkyl sulfates. Under cold water washing conditions, i.e., less than about 65 °F (18.3°C), it is preferred that there be a mixture of such ethoxylated and non-ethoxylated alkyl sulfates. Examples of fatty acids include capric, lauric, myristic, palmitic, stearic, arachidic, and behenic acid. Other fatty acids include palmitoleic, oleic, linoleic, linolenic, and ricinoleic acid.

Nonionic Surfactant

Conventional nonionic and amphoteric surfactants include C_{12-C_{18}} alkyl ethoxylates (AE) including the so-called narrow peaked alkyl ethoxylates and C_{6-C_{12}} alkyl phenol alkoxylates (especially ethoxylates and mixed ethoxy/propanoate). The C_{10-C_{18}} N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C_{12-C_{18}} N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C_{10-C_{18}} N-(3-methoxypropyl) glucamides. The N-propyl through N-hexyl C_{12-C_{18}} glucamides can be used for low sudsing. C_{10-C_{20}} conventional soaps may also be used. If high sudsing is desired, the branched-chain C_{10-C_{16}} soaps may be used. Examples of nonionic surfactants are described in U.S. Patent No. 4,285,841, Barrat et al, issued August 25, 1981.

Preferred examples of these surfactants include ethoxylated alcohols and ethoxylated alkyl phenols of the formula R(OC_{2}H_{4})_{n}OH, wherein R is selected from the group consisting of aliphatic hydrocarbon radicals containing from about 8 to about 15 carbon atoms and alkyl phenyl radicals in which the alkyl groups contain from about 8 to about 12 carbon atoms, and the average value of n is from about 5 to about 15. These surfactants are more fully described in U.S. Patent No. 4,284,532, Leikhim et al, issued August 18, 1981. Particularly preferred are ethoxylated alcohols having an average of from about 10 to about 15 carbon atoms in the alcohol and an average degree of ethoxylation of from about 6 to about 12 moles of ethylene oxide per mole of alcohol. Mixtures of anionic and nonionic surfactants are especially useful.

Other conventional useful surfactants are listed in standard texts, including C_{12-C_{18}} betaines and sulfobetaines (sultaines).

Amine Oxide Surfactants

The compositions herein also contain amine oxide surfactants of the formula:
\[ R^{1}(EO)_{x}(PO)_{y}(BO)_{z}N(O)(CH_{2}R')_{2}.qH_{2}O \]
In general, it can be seen that the structure (I) provides one long-chain moiety 
$R^1(EO)^x(PO)^y(BO)^z$ and two short chain moieties, $CH_2R'$. $R'$ is preferably selected 
from hydrogen, methyl and $-CH_2OH$. 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 
chainlength of from about 8 to about 18. When $x+y+z$ is different from 0, $R^1$ may be 
somewhat longer, having a chainlength in the range $C_{12}-C_{24}$. The general formula 
also encompasses amine oxides wherein $x+y+z = 0$, $R^1 = C_8-C_{18}$, $R'$ is H and q is 0-
2, preferably 2. These amine oxides are illustrated by $C_{12}-14$ alkylidimethyl amine 
oxide, hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, 
especially the dihydrates as disclosed in U.S. Patents 5,075,501 and 5,071,594, incorporated herein by reference.

The invention also encompasses amine oxides wherein $x+y+z$ is different from 
zero, specifically $x+y+z$ is from about 1 to about 10, $R^1$ is a primary alkyl group 
containing 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.

Highly preferred amine oxides herein are solids at ambient temperature, more 
preferably they have melting-points in the range $30^\circ C$ to $90^\circ C$. Amine oxides 
suitable for use herein are made commercially by a number of suppliers, including 
Akzo Chemie, Ethyl Corp., and Procter & Gamble. See McCutcheon's compilation 
and Kirk-Othmer review article for alternate amine oxide manufacturers. Preferred 
commercially available amine oxides are the solid, dihydrate ADMOX 16 and 
ADMOX 18, ADMOX 12 and especially ADMOX 14 from Ethyl Corp.

Preferred embodiments include dodecylidimethylamine oxide dihydrate, 
hexadecylidimethylamine oxide dihydrate, octadecylidimethylamine oxide dihydrate, 
hexadecyltris(ethyleneoxy)dimethyl-amine oxide, tetradecylidimethylamine oxide 
dihydrate, and mixtures thereof.

Whereas in certain of the preferred embodiments $R'$ is H, there is some latitude 
with respect to having $R'$ slightly larger than H. Specifically, the invention further 
comprises embodiments wherein $R'$ is $CH_2OH$, such as hexadecylbis(2-
hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-
hydroxyethyl)amine oxide and oleyl bis(2-hydroxyethyl)amine oxide.
Builders

The compositions herein also optionally, but preferably, contain up to about 50%, more preferably from about 1% to about 40%, even more preferably from about 5% to about 30%, by weight of a detergent builder material. Lower or higher levels of builder, however, are not meant to be excluded. Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils. Detergent builders are described in U.S. Patent No. 4,321,165, Smith et al, issued March 23, 1982. Preferred builders for use in liquid detergents herein are described in U.S. Patent No. 4,284,532, Leikhim et al, issued August 18, 1981.

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

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

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders can be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula: M$_2$(zAlO$_2$)$_y$·xH$_2$O

wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.
Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:

$$\text{Na}_2[(\text{AlO}_2)\text{Si}_2\text{O}_5]_2\cdot x\text{H}_2\text{O}$$

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

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

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

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxyxsuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellite acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxyxsuccinic acid, and soluble salts thereof.
Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Oxydisuccinates are also especially useful in such compositions and combinations.

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


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

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

**OTHER OPTIONAL COMPOSITION COMPONENTS**

In addition to the liquid and solid phase components as hereinbefore described, the aqueous and non-aqueous based detergent compositions can, and preferably will, contain various other optional components. Such optional components may be in either liquid or solid form. The optional components may either dissolve in the liquid phase or may be dispersed within the liquid phase in the form of fine particles or droplets. Some of the other materials which may optionally be utilized in the compositions herein are described in greater detail as follows:
Optional Inorganic Detergent Builders

The detergent compositions herein may also optionally contain one or more types of inorganic detergent builders beyond those listed hereinbefore that also function as alkalinity sources. Such optional inorganic builders can include, for example, aluminosilicates such as zeolites. Aluminosilicate zeolites, and their use as detergent builders are more fully discussed in Corkill et al., U.S. Patent No. 4,605,509; Issued August 12, 1986, the disclosure of which is incorporated herein by reference. Also crystalline layered silicates, such as those discussed in this '509 U.S. patent, are also suitable for use in the detergent compositions herein. If utilized, optional inorganic detergent builders can comprise from about 2% to 15% by weight of the compositions herein.
Optional Enzymes

The detergent compositions herein may also optionally contain one or more types of detergent enzymes. Such enzymes can include proteases, amylases, cellulases and lipases. Such materials are known in the art and are commercially available. They may be incorporated into the non-aqueous liquid detergent compositions herein in the form of suspensions, "marumes" or "prills". Another suitable type of enzyme comprises those in the form of slurries of enzymes in nonionic surfactants, e.g., the enzymes marketed by Novo Nordisk under the tradename "SL" or the microencapsulated enzymes marketed by Novo Nordisk under the tradename "LDP."

Enzymes added to the compositions herein in the form of conventional enzyme prills are especially preferred for use herein. Such prills will generally range in size from about 100 to 1,000 microns, more preferably from about 200 to 800 microns and will be suspended throughout the non-aqueous liquid phase of the composition. Prills in the compositions of the present invention have been found, in comparison with other enzyme forms, to exhibit especially desirable enzyme stability in terms of retention of enzymatic activity over time. Thus, compositions which utilize enzyme prills need not contain conventional enzyme stabilizing such as must frequently be used when enzymes are incorporated into aqueous liquid detergents.

If employed, enzymes will normally be incorporated into the non-aqueous liquid compositions herein at levels sufficient to provide up to about 10 mg by weight, more typically from about 0.01 mg to about 5 mg, of active enzyme per gram of the composition. Stated otherwise, the non-aqueous liquid detergent compositions herein will typically comprise from about 0.001% to 5%, preferably from about 0.01% to 1% by weight, of a commercial enzyme preparation. Protease enzymes, for example, are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition.

Optional Chelating Agents

The detergent compositions herein may also optionally contain a chelating agent which serves to chelate metal ions, e.g., iron and/or manganese, within the non-aqueous detergent compositions herein. Such chelating agents thus serve to form complexes with metal impurities in the composition which would otherwise tend to deactivate composition components such as the peroxycyan bleaching agent. Useful chelating agents can include amino carboxylates, phosphonates, amino
phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethyl-ethylenediaminetriacetates, nitrilotriacetates, ethylene-diamine tetrapropionates, triethylenetetraminehexacetates, diethylenetriaminepentaacetates, ethylenediaminedisuccinates and ethanol diglycines. The alkali metal salts of these materials are preferred.

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

Preferred chelating agents include hydroxy-ethylidiphosphonic acid (HEDP), diethylene triamine penta acetic acid (DTPA), ethylenediamine disuccinic acid (EDDS) and dipicolinic acid (DPA) and salts thereof. The chelating agent may, of course, also act as a detergent builder during use of the compositions herein for fabric laundering/bleaching. The chelating agent, if employed, can comprise from about 0.1% to 4% by weight of the compositions herein. More preferably, the chelating agent will comprise from about 0.2% to 2% by weight of the detergent compositions herein.

Optional Thickening, Viscosity Control and/or Dispersing Agents

The detergent compositions herein may also optionally contain a polymeric material which serves to enhance the ability of the composition to maintain its solid particulate components in suspension. Such materials may thus act as thickeners, viscosity control agents and/or dispersing agents. Such materials are frequently polymeric polycarboxylates but can include other polymeric materials such as polyvinylpyrrolidone (PVP) or polyamide resins.

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

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 100,000, more preferably from about 2,000 to 10,000, even more preferably from about 4,000 to 7,000, and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, salts. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, Diehl, U.S. Patent 3,308,067, issued March 7, 1967. Such materials may also perform a builder function.

If utilized, the optional thickening, viscosity control and/or dispersing agents should be present in the compositions herein to the extent of from about 0.1% to 4% by weight. More preferably, such materials can comprise from about 0.5% to 2% by weight of the detergents compositions herein.

Optional Clay Soil Removal/Anti-redeposition Agents

The compositions of the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and anti-redeposition properties. If used, soil materials can contain from about 0.01% to about 5% by weight of the compositions herein.

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

The detergent compositions herein may also optionally contain bleach activators which are liquid in form at room temperature and which can be added as liquids to the non-aqueous liquid phase of the detergent compositions herein. One such liquid bleach activator is acetyl triethyl citrate (ATC). Other examples include glycerol triacetate and nonanoyl valerolactam. Liquid bleach activators can be dissolved in the non-aqueous liquid phase of the compositions herein.

Optional Bleach Catalysts

If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include MnIV\(2\)(u-O)\(3\)(1,4,7-trimethyl-1,4,7-triazacyclononane)\(2\)-(PF\(6\))\(2\), MnIII\(2\)(u-O)\(1\)(u-OAc)\(2\)(1,4,7-trimethyl-1,4,7-triazacyclononane)\(2\)(ClO\(4\))\(2\), MnIV\(4\)(u-O)\(6\)(1,4,7-triazacyclononane)\(4\)(ClO\(4\))\(4\), MnIIIMnIV\(4\)(u-O)\(1\)(u-OAc)\(2\)(1,4,7-trimethyl-1,4,7-triazacyclononane)\(2\)(ClO\(4\))\(3\), MnIV\(1\)(1,4,7-trimethyl-1,4,7-triazacyclononane)- (OCH\(3\))\(3\)(PF\(6\)), and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

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

Cobalt bleach catalysts useful herein are known, and are described, for example, in M. L. Tobe, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94. The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula [Co(NH\(3\))\(_5\)OAc] \(T_y\), wherein "OAc" represents an acetate moiety and "\(T_y\)" is an anion, and especially cobalt pentaamine acetate chloride, [Co(NH\(3\))\(_5\)OAc]Cl\(2\); as well as [Co(NH\(3\))\(_5\)OAc](OAc)\(2\); [Co(NH\(3\))\(_5\)OAc](PF\(6\))\(2\); [Co(NH\(3\))\(_5\)OAc](SO\(4\)); [Co(NH\(3\))\(_5\)OAc](BF\(4\))\(2\); and [Co(NH\(3\))\(_5\)OAc](NO\(3\))\(2\) (herein "PAC").
These cobalt catalysts are readily prepared by known procedures, such as
taught for example in the Tobe article and the references cited therein, in U.S. Patent
1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly

As a practical matter, and not by way of limitation, the compositions and
cleaning processes herein can be adjusted to provide on the order of at least one part
per hundred million of the active bleach catalyst species in the aqueous washing
medium, and will preferably provide from about 0.01 ppm to about 25 ppm, more
preferably from about 0.05 ppm to about 10 ppm, and most preferably from about
0.1 ppm to about 5 ppm, of the bleach catalyst species in the wash liquor. In order to
obtain such levels in the wash liquor of an automatic washing process, typical
compositions herein will comprise from about 0.0005% to about 0.2%, more
preferably from about 0.004% to about 0.08%, of bleach catalyst, especially
manganese or cobalt catalysts, by weight of the cleaning compositions.

Optional Brighteners, Suds Suppressors, Dyes and/or Perfumes

The detergent compositions herein may also optionally contain conventional
brighteners, sud suppressors, dyes and/or perfume materials. Such brighteners, sud
suppressors, silicone oils, dyes and perfumes must, of course, be compatible and
non-reactive with the other composition components in a non-aqueous environment.
If present, brighteners sud suppressors, dyes and/or perfumes will typically
comprise from about 0.0001% to 2% by weight of the compositions herein.

Structure Elasticizing Agents

The non-aqueous liquid detergent compositions herein can also contain from
about 0.1% to 5%, preferably from about 0.1% to 2% by weight of a finely divided,
solid particulate material which can include silica, e.g., fumed silica, titanium
dioxide, insoluble carbonates, finely divided carbon or combinations of these
materials. Fine particulate material of this type functions as a structure elasticizing
agent in the products of this invention. Such material has an average particle size
ranging from about 7 to 40 nanometers, more preferably from about 7 to 15
nanometers. Such material also has a specific surface area which ranges from about
40 to 400m$^2$/g.
The finely divided elasticizing agent material can improve the shipping stability of the non-aqueous liquid detergent products herein by increasing the elasticity of the surfactant-structured liquid phase without increasing product viscosity. This permits such products to withstand high frequency vibration which may be encountered during shipping without undergoing undesirable structure breakdown which could lead to sedimentation in the product.

In the case of titanium dioxide, the use of this material also imparts whiteness to the suspension of particulate material within the detergent compositions herein. This effect improves the overall appearance of the product.

Polymeric Soil Release Agent

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

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

Chelating Agents

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

Amino carboxylates useful as optional chelating agents include ethylenediamine-tetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

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

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


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

Clay Soil Removal/Anti-redeposition Agents

The compositions of the present invention can also optionally contain watersoluble ethoxylated amines having clay soil removal and antiredeposition properties.
Liquid detergent compositions typically contain about 0.01% to about 5% of these compositions.

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

Polymeric Dispersing Agents

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

Polymeric polycarboxylate materials can be prepared by polymerizing or copolymerizing suitable unsaturated monomers, preferably in their acid form. Unsaturated monomeric acids that can be polymerized to form suitable polymeric polycarboxylates include acrylic acid, maleic acid (or maleic anhydride), fumaric acid, itaconic acid, acconic acid, mesaconic acid, citraconic acid and methylenemalonic acid. The presence in the polymeric polycarboxylates herein or monomeric segments, containing no carboxylate radicals such as vinylmethyl ether, styrene, ethylene, etc. is suitable provided that such segments do not constitute more than about 40% by weight.
Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. Such acrylic acid-based polymers which are useful herein are the water-soluble salts of polymerized acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from about 2,000 to 10,000, more preferably from about 4,000 to 7,000 and most preferably from about 4,000 to 5,000. Water-soluble salts of such acrylic acid polymers can include, for example, the alkali metal, ammonium and substituted ammonium salts. Soluble polymers of this type are known materials. Use of polycarboxylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Patent 3,308,067, issued March 7, 1967.

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

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

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

**Dye Transfer Inhibiting Agents**

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

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

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

\[
\begin{aligned}
&O \\
&\text{(R}_1\text{)}_x\text{N}-(\text{R}_2)_y\text{O} \\
&\text{(R}_3\text{)}_z
\end{aligned}
\]

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

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

The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

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

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

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

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:

![Chemical Structure](attachment:image.png)
wherein \( R_1 \) is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; \( R_2 \) is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and \( M \) is a salt-forming cation such as sodium or potassium.

When in the above formula, \( R_1 \) is anilino, \( R_2 \) is N-2-bis-hydroxyethyl and \( M \) is a cation such as sodium, the brightener is 4,4′-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2′-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein.

When in the above formula, \( R_1 \) is anilino, \( R_2 \) is N-2-hydroxyethyl-N-2-methylamino and \( M \) is a cation such as sodium, the brightener is 4,4′-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2′-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, \( R_1 \) is anilino, \( R_2 \) is morphilino and \( M \) is a cation such as sodium, the brightener is 4,4′-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2′-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

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

COMPOSITION FORM

As indicated, the non-aqueous liquid detergent compositions herein are in the form of bleaching agent and/or other materials in particulate form as a solid phase suspended in and dispersed throughout a surfactant-containing, preferably structured non-aqueous liquid phase. Generally, the structured non-aqueous liquid phase will comprise from about 45% to 95%, more preferably from about 50% to 90%, by weight of the composition with the dispersed additional solid materials comprising from about 5% to 55%, more preferably from about 10% to 50%, by weight of the composition.

The particulate-containing liquid detergent compositions of this invention are substantially non-aqueous (or anhydrous) in character. While very small amounts of water may be incorporated into such compositions as an impurity in the essential or optional components, the amount of water should in no event exceed about 5% by weight of the compositions herein. More preferably, water content of the non-aqueous detergent compositions herein will comprise less than about 1% by weight.

The particulate-containing non-aqueous liquid detergent compositions herein will be relatively viscous and phase stable under conditions of commercial marketing and use of such compositions. Frequently the viscosity of the compositions herein will range from about 300 to 5,000 cps, more preferably from about 500 to 3,000 cps. For purposes of this invention, viscosity is measured with a Carriem CSL2 Rheometer at a shear rate of 20 s⁻¹.

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

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.5 and 11. Techniques for
controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

**COMPOSITION PREPARATION AND USE**

The aqueous based heavy-duty liquid detergent compositions of the present invention can be made by mixing and blending the desired ingredients with the desired solvent. The non-aqueous liquid detergent compositions herein can be prepared by first forming the surfactant-containing, preferably structured non-aqueous liquid phase and by thereafter adding to this structured phase the particulate components in any convenient order and by mixing, e.g., agitating, the resulting component combination to form the phase stable compositions herein. In a typical process for preparing such compositions, essential and certain preferred optional components will be combined in a particular order and under certain conditions.

In a first step of a preferred preparation process, the anionic surfactant-containing powder used to form the structured, surfactant-containing liquid phase is prepared. This pre-preparation step involves the formation of an aqueous slurry containing from about 30% to 60% of one or more alkali metal salts of linear C_{10-16} alkyl benzene sulfonic acid and from about 2% to 30% of one or more diluent non-surfactant salts. In a subsequent step, this slurry is dried to the extent necessary to form a solid material containing less than about 4% by weight of residual water.

After preparation of this solid anionic surfactant-containing material, this material can be combined with one or more of the non-aqueous organic diluents to form a structured, surfactant-containing liquid phase of the detergent compositions herein. This is done by reducing the anionic surfactant-containing material formed in the previously described pre-preparation step to powdered form and by combining such powdered material with an agitated liquid medium comprising one or more of the non-aqueous organic diluents, either surfactant or non-surfactant or both, as hereinbefore described. This combination is carried out under agitation conditions which are sufficient to form a thoroughly mixed dispersion of particles of the insoluble fraction of the co-dried LAS/salt material throughout a non-aqueous organic liquid diluent.

In a subsequent processing step, the non-aqueous liquid dispersion so prepared can then be subjected to milling or high shear agitation under conditions which are sufficient to provide a structured, surfactant-containing liquid phase of the detergent compositions herein. Such milling or high shear agitation conditions will generally include maintenance of a temperature between about 10°C and 90°C, preferably between about 20°C and 60°C; and a processing time that is sufficient to form a
network of aggregated small particles of the insoluble fraction of the anionic surfactant-containing powdered material. Suitable equipment for this purpose includes: stirred ball mills, co-ball mills (Fryma), colloid mills, high pressure homogenizers, high shear mixers, and the like. The colloid mill and high shear mixers are preferred for their high throughput and low capital and maintenance costs. The small particles produced in such equipment will generally range in size from about 0.4 to 2 microns. Milling and high shear agitation of the liquid/solids combination will generally provide an increase in the yield value of the structured liquid phase to within the range of from about 1 Pa to 8 Pa, more preferably from about 1 Pa to 4 Pa.

After formation of the dispersion of LAS/salt co-dried material in the non-aqueous liquid, either before or after such dispersion is milled or agitated to increase its yield value, the particulate material to be used in the detergent compositions herein can be added. Such components which can be added under high shear agitation include a silica or titanium dioxide elasticizing agent; particles of substantially all of an organic builder, e.g., citrate and/or fatty acid, and/or an alkalinity source, e.g., sodium carbonate, can be added while continuing to maintain this admixture of composition components under shear agitation. Agitation of the mixture is continued, and if necessary, can be increased at this point to form a uniform dispersion of insoluble solid phase particulates within the liquid phase.

After some or all of the foregoing solid materials have been added to this agitated mixture, the particles of the colored speckles and the highly preferred peroxycgen bleaching agent can be added to the composition, again while the mixture is maintained under shear agitation. By adding the peroxycgen bleaching agent material last, or after all or most of the other components, and especially after alkalinity source particles, have been added, desirable stability benefits for the peroxycgen bleach can be realized. If enzyme prills are incorporated, they are preferably added to the non-aqueous liquid matrix last.

As a final process step, after addition of all of the particulate material, agitation of the mixture is continued for a period of time sufficient to form compositions having the requisite viscosity, yield value and phase stability characteristics. Frequently this will involve agitation for a period of from about 1 to 30 minutes.

In adding solid components to non-aqueous liquids in accordance with the foregoing procedure, it is advantageous to maintain the free, unbound moisture content of these solid materials below certain limits. Free moisture in such solid materials is frequently present at levels of 0.8% or greater. By reducing free moisture content, e.g., by fluid bed drying, of solid particulate materials to a free
moisture level of 0.5% or lower prior to their incorporation into the detergent composition matrix, significant stability advantages for the resulting composition can be realized.

The compositions of this invention, prepared as hereinbefore described, can be used to form aqueous washing solutions for use in the laundering and bleaching of fabrics. Generally, an effective amount of such compositions is added to water, preferably in a conventional fabric laundering automatic washing machine, to form such aqueous laundering/bleaching solutions. The aqueous washing/bleaching solution so formed is then contacted, preferably under agitation, with the fabrics to be laundered and bleached therewith.

An effective amount of the liquid detergent compositions herein added to water to form aqueous laundering/bleaching solutions can comprise amounts sufficient to form from about 500 to 7,000 ppm of composition in aqueous solution. More preferably, from about 800 to 3,000 ppm of the detergent compositions herein will be provided in aqueous washing/bleaching solution.

The following Examples provide methods for synthesizing various compounds useful in the present compositions.

**EXAMPLE I**

**Preparation of sodium 7-methyltridecyl ethoxylated (E2) and sulfate**

**Synthesis of (6-hydroxyhexyl) triphenylphosphonium bromide**

Into a 5L, 3 neck round bottom flask fitted with nitrogen inlet, condenser, thermometer, mechanical stirring and nitrogen outlet is added 6-bromo-1-hexanol (500g, 2.76 mol), triphenylphosphine (768g, 2.9mol) and acetonitrile (1800 ml) under nitrogen. The reaction mixture is heated to reflux for 72 hrs. The reaction mixture is cooled to room temperature and transferred into a 5L beaker. The product is recrystallized from anhydrous ethyl ether (1.5L) at 10°C. Vacuum filtration followed by washing with ethyl ether and drying in a vacuum oven at 50°C for 2 hrs. gives 1140g of the desired product as white crystals.

**Synthesis of 7-methyltridecene-1-ol**

Into a dried 5L, 3 neck round bottom flask fitted with mechanical stirring, nitrogen inlet, dropping funnel, thermometer and nitrogen outlet is added 70.2g of 60% sodium hydride (1.76 mol) in mineral oil. The mineral oil is removed by washing with hexanes. Anhydrous dimethyl sulfoxide (500ml) is added to the flask and the mixture is heated to 70°C until evolution of hydrogen stops. The reaction
mixture is cooled to room temperature followed by addition of 1L of anhydrous tetrahydrofuran. (6-hydroxyhexyl) triphenylphosphonium bromide (443.4g, 1 mol) is slurried with warm anhydrous dimethyl sulfoxide (50°C, 500ml) and slowly added to the reaction mixture through the dropping funnel while keeping it at 25-30°C. The mixture is stirred for 30 minutes at room temperature at which time 2-octanone (140.8g, 1.1 mol) is slowly added through a dropping funnel. Reaction is slightly exothermic and cooling is needed to maintain 25-30°C. The mixture is stirred for 18 hr. and then poured into a 5L beaker containing 1L purified water with stirring. The oil phase (top) is allowed to separate out in a separatory funnel and the water phase is removed. The water phase is washed with hexanes (500ml) and the organic phase is separated and combined with the oil phase from the water wash. The organic mixture is then extracted with water 3 times (500ml each) followed by vacuum distillation to collect the clear, oily product (110g) at 140°C and 1mm Hg.

Hydrogenation of 7-methyltridecene-1-ol

Into a 3L rocking autoclave liner is added 7-methyltridecene-1-ol (108g, 0.508mol), methanol (300ml) and platinum on carbon (10% by weight, 35g). The mixture is hydrogenated at 180°C under 1200 psig of hydrogen for 13 hrs., cooled and vacuum filtered through Celite 545 with washing of the Celite 545, suitably with methylene chloride. If needed, the filtration can be repeated to eliminate traces of Pt catalyst, and magnesium sulfate can be used to dry the product. The solution of product is concentrated on a rotary evaporator to obtain a clear oil (104g).

Alkoxylaon of 7-methyltridecanol

Into a dried 1L 3 neck round bottom flask fitted with a nitrogen inlet, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added the alcohol from the preceding step. For purposes of removing trace amounts of moisture, the alcohol is sparged with nitrogen for about 30 minutes at 80-100°C. Continuing with a nitrogen sweep, sodium metal is added as the catalyst and allowed to melt with stirring at 120-140°C. With vigorous stirring, ethylene oxide gas is added in 140 minutes while keeping the reaction temperature at 120-140°C. After the correct weight (equal to two equivalents of ethylene oxide) has been added, nitrogen is swept through the apparatus for 20-30 minutes as the sample is allowed to cool. The desired 7-methyltridecy1 ethoxylate (average of 2 ethoxylates per molecule) product is then collected. The 7-methyl tridecyl ethoxylate is blended with n-tetradecanol ethoxylate (E2) to yield a composition containing at least 25% linear alcohol.
Sulfation of 7-methyltridecyl and n-tetradecanol ethoxylate (E2)

Into a dried 1L 3 neck round bottom flask fitted with a nitrogen inlet, dropping funnel, thermometer, mechanical stirring and nitrogen outlet is added chloroform and the blend of 7-methyltridecyl ethoxylate (E2) and n-tetradecanol ethoxylate (E2) from the preceding step. Chlorosulfonic acid is slowly added to the stirred mixture while maintaining 25-30°C temperature with an ice bath. Once HCl evolution has stopped slowly add sodium methoxide (25% in methanol) while keeping temperature at 25-30°C until a aliquot at 5% concentration in water maintains a pH of 10.5. To the mixture is added hot ethanol (55°C) and vacuum filtered immediately. The filtrate is concentrated to a slurry on a rotary evaporator, cooled and then poured into ethyl ether. The mixture is chilled to 50°C and vacuum filtered to provide the desired blend of 7-methyltridecyl / n-tetradecyl ethoxylate (average of 2 ethoxylates per molecule) sulfate, sodium salt, product.

EXAMPLE II

Preparation of mid-chain branched C12,13 and C14,15 sodium alcohol sulfate, alcohol ethoxylate, and sodium alcohol ethoxy sulfate from Sasol alcohol samples.

Alcohol samples containing from about 35% to about 45%, by weight linear surfactant concentration, were received from Sasol and had been prepared by hydroformylation of alpha olefins produced by a Fischer Tropsch process as described by patents WO 97/01521 and according to the Sasol R&D technical product bulletin dated October 1, 1996 entitled SASOL DETERGENT ALCOHOLS. Sodium alkyl sulfates, alcohol ethoxylates and sodium alkyl ethoxy sulfates were synthesized from both the C12,13 and C14,15 alcohols.

Sulfation of Sasol C12,13 Alcohol

Into a dried 2L 3 neck round bottom flask fitted with a gas inlet, dropping funnel, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added Sasol C12,13 Alcohol (234.0 g , 1.2 mol) and diethyl ether (250 ml). Chlorosulfonic acid (146.8 g , 1.26 mol) is slowly added to the stirred mixture while maintaining a reaction temperature of 5-15°C with an ice water bath. After the chlorosulfonic acid is added a slow nitrogen sweep and a vacuum (10-15 inches Hg) is begun to remove HCl. Also the reaction is warmed to 30-40°C with the addition of a warm water bath. After about 45 minutes the vacuum in increased to 25-30 inches Hg and maintained for an additional 45 minutes. The acidic reaction mixture is slowly poured into a vigorously stirred beaker of 25% sodium methoxide (285.1 g
, 1.32 mol) and methanol (600ml) that is cooled in an ice water bath. After pH >12 is confirmed the solution is allowed to stir about 30 minutes then poured into a stainless pan. Most of the solvent is allowed to evaporate overnight in the fume hood. The next morning the sample is transferred to a glass dish and placed in a vacuum drying oven. The sample is allowed to dry all day and overnight at 40-60°C with 25-30 inches Hg vacuum. After bottling 321g of yellow tacky solid, the cat SO3 analysis shows the sample is about 93% active. The pH of the sample is about 9.5.

Ethoxylation of Sasol C12,13 Alcohol to E3

Into a dried 1L 3 neck round bottom flask fitted with a gas inlet, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added Sasol C12,13 Alcohol (195.0 g, 1.0 mol). For the purpose of removing trace amounts of moisture, the alcohol is sparged with nitrogen for about 30 minutes at 60-80°C. Continuing with a nitrogen sweep, sodium metal (1.2 g, 0.05 mol) is added as the catalyst and allowed to melt with stirring at 120-140°C. With vigorous stirring, ethylene oxide gas (132.0 g, 3.0 mol) is added in 180 minutes while keeping the reaction temperature 120-140°C. After the correct weight of ethylene oxide is added, nitrogen is swept through the apparatus for 20-30 minutes as the sample is allowed to cool. The gold liquid product (323.0 g, 0.988 mol) is bottled under nitrogen.

Sulfation of Sasol C12,13 Alcohol Ethoxylate (E3)

Into a dried 2L 3 neck round bottom flask fitted with a gas inlet, dropping funnel, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added Sasol C12,13 Ethoxylate (E3) (261.6 g, 0.8 mol) and diethyl ether (300 ml). Chlorosulfonic acid (97.9 g, 0.84 mol) is slowly added to the stirred mixture while maintaining a reaction temperature of 5-15°C with an ice water bath. After the chlorosulfonic acid is added a slow nitrogen sweep and a vacuum (10-15 inches Hg) is begun to remove HCl. Also the reaction is warmed to 30-40°C with the addition of a warm water bath. After about 45 minutes the vacuum in increased to 25-30 inches Hg and maintained for an additional 45 minutes. The acidic reaction mixture is slowly poured into a vigorously stirred beaker of 25% sodium methoxide (190.1 g, 0.88 mol) and methanol (400ml) that is cooled in an ice water bath. After pH >12 is confirmed the solution is allowed to stir about 30 minutes then poured into a stainless pan. Most of the solvent is allowed to evaporate overnight in the fume hood. The next morning the sample is transferred to a glass dish and placed in a vacuum drying oven. The sample is allowed to dry all day and overnight at 40-60°C with 25-30 inches Hg vacuum. After bottling 304 g of yellow tacky solid, the cat
SO3 analysis shows the sample is about 95% active. The pH of the sample is about 10.1.

**Sulfation of Sasol C14,15 Alcohol**

Into a dried 500 ml 3 neck round bottom flask fitted with a gas inlet, dropping funnel, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added Sasol C14,15 Alcohol (87.2 g, 0.4 mol) and diethyl ether (150 ml). Chlorosulfonic acid (48.9 g, 0.42 mol) is slowly added to the stirred mixture while maintaining a reaction temperature of 5-15°C with an ice water bath. After the chlorosulfonic acid is added a slow nitrogen sweep and a vacuum (10-15 inches Hg) is begun to remove HCl. Also the reaction is warmed to 30-40°C with the addition of a warm water bath. After about 45 minutes the vacuum in increased to 25-30 inches Hg and maintained for an additional 45 minutes. The acidic reaction mixture is slowly poured into a vigorously stirred beaker of 25% sodium methoxide (95.0 g, 0.44 mol) and methanol (300 ml) that is cooled in an ice water bath. After pH >12 is confirmed the solution is allowed to stir about 30 minutes then poured into a stainless pan. Most of the solvent is allowed to evaporate overnight in the fume hood. The next morning the sample is transferred to a glass dish and placed in a vacuum drying oven. The sample is allowed to dry all day and overnight at 40-60°C with 25-30 inches Hg vacuum. After bottling 108g of yellow tacky solid, the cat SO3 analysis shows the sample is about 89% active. The pH of the sample is about 9.8.

**Ethoxylation of Sasol C14,15 Alcohol to E2.5**

Into a dried 1L 3 neck round bottom flask fitted with a gas inlet, mechanical stirrer, and a y-tube fitted with a thermometer and a gas outlet is added Sasol C14,15 Alcohol (218.0 g, 1.0 mol). For the purpose of removing trace amounts of moisture, the alcohol is sparged with nitrogen for about 30 minutes at 60-80°C. Continuing with a nitrogen sweep, sodium metal (1.2 g, 0.05 mol) is added as the catalyst and allowed to melt with stirring at 120-140°C. With vigorous stirring, ethylene oxide gas (110.0 g, 2.5 mol) is added in 140 minutes while keeping the reaction temperature 120-140°C. After the correct weight of ethylene oxide is added, nitrogen is swept through the apparatus for 20-30 minutes as the sample is allowed to cool. The amber liquid product (323.1 g, 0.985 mol) is bottled under nitrogen.

**Sulfation of Sasol C14,15 Alcohol Ethoxylate (E2.5)**

Into a dried 500 ml 3 neck round bottom flask fitted with a gas inlet, dropping funnel, mechanical stirrer, and a y-tube fitted with a thermometer and a gas
outlet is added Sasol C14,15 Ethoxylate (E2.5) (72.2 g, 0.22 mol) and diethyl ether (150 ml). Chlorosulfonic acid (26.8 g, 0.23 mol) is slowly added to the stirred mixture while maintaining a reaction temperature of 5-15°C with an ice water bath. After the chlorosulfonic acid is added a slow nitrogen sweep and a vacuum (10-15 inches Hg) is begun to remove HCl. Also the reaction is warmed to 30-40°C with the addition of a warm water bath. After about 45 minutes the vacuum in increased to 25-30 inches Hg and maintained for an additional 45 minutes. The acidic reaction mixture is slowly poured into a vigorously stirred beaker of 25% sodium methoxide (51.8 g, 0.24 mol) and methanol (300ml) that is cooled in an ice water bath. After pH >12 is confirmed the solution is allowed to stir about 30 minutes then poured into a stainless pan. Most of the solvent is allowed to evaporate overnight in the fume hood. The next morning the sample is transferred to a glass dish and placed in a vacuum drying oven. The sample is allowed to dry all day and overnight at 40-60°C with 25-30 inches Hg vacuum. After bottling 94 g of yellow tacky solid, the cat SO3 analysis shows the sample is about 91% active. The pH of the sample is about 10.3.

The following examples illustrate the preparation and performance advantages of the mid-chain branched surfactant containing non-aqueous liquid detergent compositions of the instant invention. Such examples, however, are not necessarily meant to limit or otherwise define the scope of the invention herein. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified. In the following Examples, the abbreviations for the various ingredients used for the compositions have the following meanings.

**ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAS</td>
<td>Sodium linear alkyl benzene sulfonate</td>
</tr>
<tr>
<td>MBAS_x</td>
<td>Mid-chain branched primary alkyl (average total carbons = x) sulfate</td>
</tr>
<tr>
<td>MBAE_xS_z</td>
<td>Mid-chain branched primary alkyl (average total carbons = z) ethoxylate (average EO = x) sulfate, sodium salt</td>
</tr>
<tr>
<td>MBAE_x</td>
<td>Mid-chain branched primary alkyl (average total = x) ethoxylate (average EO = 5)</td>
</tr>
<tr>
<td>Endolase</td>
<td>Endoglucanase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S</td>
</tr>
<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
</tr>
</tbody>
</table>
PG Propanediol
BPP Butoxy - propoxy - propanol
EtOH Ethanol
NaOH Solution of sodium hydroxide
NaTS Sodium toluene sulfonate
Citric acid Anhydrous citric acid
CxyFA \( C_{1x-1y} \) fatty acid
CxyEz A \( C_{1x-1y} \) branched primary alcohol condensed with an average of \( z \) moles of ethylene oxide
Carbonate Anhydrous sodium carbonate with a particle size between 200\( \mu \)m and 900\( \mu \)m
Citrate Tri-sodium citrate dihydrate of activity 86.4\% with a particle size distribution between 425\( \mu \)m and 850 \( \mu \)m
TFAA C16-18 alkyl N-methyl glucamide
LMFAA C12-14 alkyl N-methyl glucamide
APA C8-C10 amido propyl dimethyl amine
Fatty Acid (C12/14) C12-C14 fatty acid
Fatty Acid (TPK) Topped palm kernel fatty acid
Fatty Acid (RPS) Rapeseed fatty acid
Borax Na tetraborate decahydrate
PAA Polyacrylic Acid (\( mw = 4500 \))
PEG Polyethylene glycol (\( mw=4600 \))
MES Alkyl methyl ester sulfonate
SAS Secondary alkyl sulfate
NaPS Sodium paraffin sulfonate
C45AS Sodium \( C_{14-15} \) linear alkyl sulfate
CxyAS Sodium \( C_{1x-1y} \) alkyl sulfate (or other salt if specified)
CxyEzS Sodium \( C_{1x-1y} \) alkyl sulfate condensed with \( z \) moles of ethylene oxide (or other salt if specified)
CxyEz A \( C_{1x-1y} \) branched primary alcohol condensed with an average of \( z \) moles of ethylene oxide
AQA \( R_2N^+\text{(CH}_3\text{)}_x((\text{C}_2\text{H}_4\text{O})_y\text{H})_z \) with \( R_2 = \text{C}_8 - \text{C}_{18} \), \( x+z = 3 \), \( x = 0 \) to 3, \( z = 0 \) to 3, \( y = 1 \) to 15.
STPP Anhydrous sodium tripolyphosphate
Zeolite A Hydrated Sodium Aluminosilicate of formula
Na\textsubscript{12}(Al\textsubscript{10}Si\textsubscript{2}O\textsubscript{4})\textsubscript{12} 27H\textsubscript{2}O having a primary particle size in the range from 0.1 to 10 micrometers

NaSKS-6 Crystalline layered silicate of formula $\delta$-Na\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}

Carbonate Anhydrous sodium carbonate with a particle size between 200µm and 900µm

Bicarbonate Anhydrous sodium bicarbonate with a particle size distribution between 400µm and 1200µm

Silicate Amorphous Sodium Silicate (SiO\textsubscript{2}:Na\textsubscript{2}O; 2.0 ratio)

Sulfate Anhydrous sodium sulfate

PAE Ethoxylated (15-18) tetraethylene pentamine

PIE Ethoxylated polyethylene imine

PAEC Methyl quaternized ethoxylated dihexylene triamine

MA/AA Copolymer of 1:4 maleic/ acrylic acid, average molecular weight about 70,000.

CMC Sodium carboxymethyl cellulose

Protease Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase

Cellulase Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme

Amylase Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T

Lipase Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase

PB1 Anhydrous sodium perborate bleach of nominal formula NaBO\textsubscript{2}.H\textsubscript{2}O\textsubscript{2}

Percarbonate Sodium Percarbonate of nominal formula 2Na\textsubscript{2}CO\textsubscript{3}.3H\textsubscript{2}O\textsubscript{2}

NaDCC Sodium dichloroisocyanurate

NOBS Nonanoyoxybenzene sulfonate, sodium salt

TAED Tetraacetylethlenediamine

DTPMP Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under Trade name Dequest

2060 Photoactivated bleach Sulfonated Zinc Phthalocyanine bleach encapsulated in dextrin soluble polymer

Brightener 1 Disodium 4,4'-bis(2-sulphostyryl)biphenyl

Brightener 2 Disodium 4,4'-bis(4-anilino-6-morpholino)-1.3.5-
triazin-2-yl)amino) stilbene-2,2'-disulfonate.
HEDP 1,1-hydroxyethane diphosphonic acid
SRP 1 Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
SRP 2 sulfonated ethoxylated terephthalate polymer
SRP 3 methyl capped ethoxylated terephthalate polymer
Silicone antifoam Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
Isofol 16 Condea trademark for C16 (average) Guerbet alcohols
CaCl2 Calcium chloride
MgCl2 Magnesium chloride
DTPA Diethylene triamine pentaacetic acid

**EXAMPLE III**

**Preparation of LAS Powder for Use as a Structurant**

Sodium C12 linear alkyl benzene sulfonate (NaLAS) is processed into a powder containing two phases. One of these phases is soluble in the non-aqueous liquid detergent compositions herein and the other phase is insoluble. It is the insoluble fraction which serves to add structure and particle suspending capability to the non-aqueous phase of the compositions herein.

NaLAS powder is produced by taking a slurry of NaLAS in water (approximately 40-50% active) combined with dissolved sodium sulfate (3-15%) and hydrotrope, sodium sulfoisuccinate (1-3%). The hydrotrope and sulfate are used to improve the characteristics of the dry powder. A drum dryer is used to dry the slurry into a flake. When the NaLAS is dried with the sodium sulfate, two distinct phases are created within the flake. The insoluble phase creates a network structure of aggregate small particles (0.4-2 um) which allows the finished non-aqueous detergent product to stably suspend solids.

The NaLAS powder prepared according to this example has the following makeup shown in Table III.

**TABLE III**

**LAS Powder**

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaLAS</td>
<td>85%</td>
</tr>
<tr>
<td>Component</td>
<td>Percentage</td>
</tr>
<tr>
<td>--------------------</td>
<td>------------</td>
</tr>
<tr>
<td>Sulfate</td>
<td>11%</td>
</tr>
<tr>
<td>Sulfo succinate</td>
<td>2%</td>
</tr>
<tr>
<td>Water</td>
<td>2.5%</td>
</tr>
<tr>
<td>Unreacted, etc.</td>
<td>balance to 100%</td>
</tr>
<tr>
<td>% insoluble LAS</td>
<td>17%</td>
</tr>
<tr>
<td># of phase (via X-ray diffraction)</td>
<td>2</td>
</tr>
</tbody>
</table>
EXAMPLE IV

Non-aqueous based heavy duty liquid laundry detergent compositions (A to E) which comprise the mid-chain branched surfactants of the present invention are presented below.

TABLE IV

Non-Aqueous Liquid Detergent Composition with Bleach

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt % A</th>
<th>Wt % B</th>
<th>Wt % C</th>
<th>Wt % D</th>
<th>Wt % E</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAS, From Example I</td>
<td>16</td>
<td>13</td>
<td>8</td>
<td>8</td>
<td>2</td>
</tr>
<tr>
<td>Mid-branched Surfactant</td>
<td>22</td>
<td>25</td>
<td>28</td>
<td>30</td>
<td>34</td>
</tr>
<tr>
<td>BPP</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>Sodium citrate dihydrate</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Bleach activator</td>
<td>5.9</td>
<td>5.9</td>
<td>5.9</td>
<td>5.9</td>
<td>5.9</td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Maleic-acrylic copolymer</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Colored speckles</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>EDDS</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cellulase Prills</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Amylase Prills</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Ethoxylated diaminequat</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Sodium Perborate</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Optionals including: brightener, colorant, perfume, thickener, suds suppressor, colored speckles etc.</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>

The resulting Table IV compositions are stable, anhydrous heavy-duty liquid laundry detergents which provide excellent stain and soil removal performance when used in normal fabric laundering operations.
EXAMPLE V

A non-limiting example of bleach-containing nonaqueous liquid laundry detergent is prepared having the composition as set forth in Table V.

**TABLE V**

<table>
<thead>
<tr>
<th>Component</th>
<th>Wt. %</th>
<th>Range (% wt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Liquid Phase</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LAS</td>
<td>25.0</td>
<td>18-35</td>
</tr>
<tr>
<td>C₂₄ E5 or MBAE₁₄,₃</td>
<td>13.6</td>
<td>10-20</td>
</tr>
<tr>
<td>Hexylene glycol</td>
<td>27.3</td>
<td>20-30</td>
</tr>
<tr>
<td>Perfume</td>
<td>0.4</td>
<td>0-1.0</td>
</tr>
<tr>
<td>MBAE₂S₁₄,₄</td>
<td>2.3</td>
<td>1-3.0</td>
</tr>
<tr>
<td><strong>Solid Phase</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Protease</td>
<td>0.4</td>
<td>0-1.0</td>
</tr>
<tr>
<td>Citrate</td>
<td>4.3</td>
<td>3-6</td>
</tr>
<tr>
<td>PB1</td>
<td>3.4</td>
<td>2-7</td>
</tr>
<tr>
<td>NOBS</td>
<td>8.0</td>
<td>2-12</td>
</tr>
<tr>
<td>Carbonate</td>
<td>13.9</td>
<td>5-20</td>
</tr>
<tr>
<td>DTPA</td>
<td>0.9</td>
<td>0-1.5</td>
</tr>
<tr>
<td>Brightener 1</td>
<td>0.4</td>
<td>0-0.6</td>
</tr>
<tr>
<td>Silicone antifoam</td>
<td>0.1</td>
<td>0-0.3</td>
</tr>
<tr>
<td><strong>Minors</strong></td>
<td></td>
<td>Balance ------</td>
</tr>
</tbody>
</table>

The resulting composition is an anhydrous heavy duty liquid laundry detergent which provides excellent stain and soil removal performance when used in normal fabric laundering operations.
EXEMPLARY VI

Liquid detergent compositions are made according to the following.

**TABLE VI**

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂₅ AE3S</td>
<td>2</td>
<td>8</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>MBAS₁₄.₄</td>
<td>15</td>
<td>12</td>
<td>10</td>
<td>8</td>
</tr>
<tr>
<td>C₁₂-C₁₄ alkylimethyl amine oxide</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>C₂₅ AS</td>
<td>6</td>
<td>4</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>C₂₄ N-methyl glucamide</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>C₂₄ AE5</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>C₁₂-C₁₈ fatty acid</td>
<td>11</td>
<td>4</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Citric acid</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>DTPMP</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.5</td>
</tr>
<tr>
<td>MEA</td>
<td>8</td>
<td>5</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>NaOH</td>
<td>1</td>
<td>2.5</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>PG</td>
<td>14.5</td>
<td>13.1</td>
<td>10.0</td>
<td>8</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.8</td>
<td>4.7</td>
<td>5.4</td>
<td>1</td>
</tr>
<tr>
<td>Amylase (300KNU/g)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Lipase D₉₆/L (100KNU/g)</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Protease (35g/l)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Endolase</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Cellulase</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Terephthalate-based polymer</td>
<td>0.5</td>
<td>-</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Boric acid</td>
<td>2.4</td>
<td>2.8</td>
<td>2.8</td>
<td>2.4</td>
</tr>
<tr>
<td>Sodium xylene sulfonate</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-butyl-octanol</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Branched silicone</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Water &amp; minors</td>
<td>Up to 100%</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The above liquid detergent compositions (A-D) are found to be very efficient in the removal of a wide range of stains and soils from fabrics under various usage conditions.
EXAMPLE VII

The following compositions (E to J) are heavy duty liquid laundry detergent compositions according to the present invention.

<table>
<thead>
<tr>
<th>Example #:</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBAS_{14,4} or MBAE_{2}S_{14,4}</td>
<td>17</td>
<td>15</td>
<td>7.0</td>
<td>7.0</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>C35AE3S/C25AE3S</td>
<td>2.0</td>
<td>9.0</td>
<td>-</td>
<td>-</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>C25 AE2.5S</td>
<td>-</td>
<td>-</td>
<td>12.0</td>
<td>12.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C24 N-Me Glucamide</td>
<td>6.0</td>
<td>5.0</td>
<td>4.5</td>
<td>3.7</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>C35 E7</td>
<td>6.0</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C23 E9</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>1.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>C10 APA</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
<td>2.0</td>
<td>-</td>
<td>2.5</td>
</tr>
<tr>
<td>C24 Fatty Acid</td>
<td>7.5</td>
<td>1.1</td>
<td>2.0</td>
<td>4.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>C48 Fatty Acid</td>
<td>3.0</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>1.0</td>
<td>3.5</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Protease (34 g/#)</td>
<td>0.6</td>
<td>0.6</td>
<td>0.9</td>
<td>0.9</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Lipase</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Amylase (300KMU/g)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Cellulase</td>
<td>0.03</td>
<td>0.03</td>
<td>0.05</td>
<td>0.05</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Endolase</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Brightener 2</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Boric Acid</td>
<td>3.0</td>
<td>3.0</td>
<td>3.5</td>
<td>3.5</td>
<td>4.0</td>
<td>4.0</td>
</tr>
<tr>
<td>MEA</td>
<td>8.0</td>
<td>4.0</td>
<td>1.0</td>
<td>1.5</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>NaOH</td>
<td>1.0</td>
<td>4.0</td>
<td>3.0</td>
<td>2.5</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>PG</td>
<td>12.0</td>
<td>12.0</td>
<td>7.5</td>
<td>7.5</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.0</td>
<td>1.0</td>
<td>3.5</td>
<td>3.5</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Na TS</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Minors</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The Following Examples illustrate aqueous based liquid detergent compositions according to the present invention.
EXAMPLE VIII

Aqueous based heavy duty liquid laundry detergent compositions F to J which comprise the mid-chain branched surfactants of the present invention are presented below.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBAE1.8S14.4</td>
<td>10</td>
<td>12</td>
<td>14</td>
<td>16</td>
<td>20</td>
</tr>
<tr>
<td>Na C25AE1.8S</td>
<td>10</td>
<td>8</td>
<td>6</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>C23E9</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>LMFAA</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Citric acid builder</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Fatty acid builder</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>PAE</td>
<td>1</td>
<td>1</td>
<td>1.2</td>
<td>1.2</td>
<td>0.5</td>
</tr>
<tr>
<td>PG</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>4.5</td>
</tr>
<tr>
<td>EtOH</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Boric acid</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>2</td>
</tr>
<tr>
<td>Sodium Cumene Sulfonate</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>pH</td>
<td>8.0</td>
<td>8.0</td>
<td>8.0</td>
<td>8.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Enzymes, dyes, water</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
<td>balance</td>
</tr>
<tr>
<td></td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
</tr>
</tbody>
</table>
EXAMPLE IX

The following aqueous liquid laundry detergent compositions K to O are prepared in accord with the invention:

<table>
<thead>
<tr>
<th>TABLE IX</th>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBAE1.8S14.4 and or</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MBAS14.4</td>
<td>1 - 7</td>
<td>7 - 12</td>
<td>12 - 17</td>
<td>17 - 22</td>
<td>1 - 35</td>
</tr>
<tr>
<td>Any combination of:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C25 AEXS*Na (x = 1.8 - 2.5)</td>
<td>15 - 21</td>
<td>10 - 15</td>
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<td>0 - 5</td>
<td>0 - 25</td>
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<td>C25 AS (linear to high 2-alkyl)</td>
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<tr>
<td>C14-17 NaPS</td>
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<td></td>
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</tr>
<tr>
<td>C12-16 SAS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C18 1,4 disulfate</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>LAS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C12-16 MES</td>
<td></td>
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</tr>
<tr>
<td>LMFAA</td>
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<td>2.5</td>
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<td>0.06</td>
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<td>0.15</td>
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<td>0 - 0.6</td>
<td>0 - 2.5</td>
</tr>
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<td>1.2</td>
<td>1.2</td>
<td>0 - 2.5</td>
</tr>
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<td>0.3</td>
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<td>0.0013</td>
<td>0.0013</td>
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<td>Moisture/minors</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
<tr>
<td>Product pH (10% in DI water)</td>
<td>7.7</td>
<td>7.7</td>
<td>7.7</td>
<td>7.7</td>
<td>6 - 9.5</td>
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EXAMPLE X

The following aqueous liquid laundry detergent compositions P to T are prepared in accord with the invention:

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<tr>
<td>Ingredient</td>
<td>P</td>
<td>Q</td>
<td>R</td>
<td>S</td>
<td>T</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-------</td>
<td>-------</td>
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<td>-------</td>
<td>-------</td>
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<td>6.25</td>
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<td>19</td>
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<td></td>
</tr>
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<td>C12-16 SAS</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C18 1,4 disulfate</td>
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</tr>
<tr>
<td>LAS</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C12-16 MES</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>LMFAA</td>
<td>1 - 5.5</td>
<td>1 - 5.5</td>
<td>1 - 5.5</td>
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<td>1 - 5.5</td>
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<td>0 - 1.5</td>
<td>0 - 1.5</td>
<td>0 - 1.5</td>
<td>0 - 1.5</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Fatty Acid (TPK,C12/14)</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
<td>7.5</td>
</tr>
<tr>
<td>Fatty Acid (RPS)</td>
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<td>3.1</td>
<td>3.1</td>
<td>3.1</td>
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<td>1.5</td>
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<td>1.5</td>
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<td>0 - 2</td>
<td>0 - 2</td>
<td>0 - 2</td>
<td>0 - 2</td>
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<td>2 - 2.5</td>
<td>2 - 2.5</td>
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<td>0.3 -1</td>
<td>0.3 -1</td>
<td>0.3 -1</td>
<td>0.3 -1</td>
</tr>
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<td>0.05 - 0.3</td>
<td>0.05 - 0.3</td>
<td>0.05 - 0.3</td>
<td>0.05 - 0.3</td>
<td>0.05 - 0.3</td>
</tr>
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<td>0.05 - 0.5</td>
<td>0.05 - 0.5</td>
<td>0.05 - 0.5</td>
<td>0.05 - 0.5</td>
</tr>
<tr>
<td>Cellulase</td>
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<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
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<td>PIE</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
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<td>0 - 0.4</td>
<td>0 - 0.4</td>
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<td>0 - 2</td>
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<td>0.2 - 0.7</td>
<td>0.2 - 0.7</td>
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<td>SRP 3</td>
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<td>0.1 - 0.2</td>
<td>0.1 - 0.2</td>
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<tr>
<td>Brightener 1 or 2</td>
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<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
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<td>Silicone antifoam</td>
<td>0.2 - 0.25</td>
<td>0.2 - 0.25</td>
<td>0.2 - 0.25</td>
<td>0.2 - 0.25</td>
<td>0.2 - 0.25</td>
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<td>Isofol 16</td>
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<td>0 - 2</td>
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<td>Perfume</td>
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<td>0.5</td>
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<tr>
<td>Moisture/minors</td>
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<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
<tr>
<td>pH (10% in DI water)</td>
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<td>7.6</td>
<td>7.6</td>
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</table>

**EXAMPLE XI**

Aqueous based heavy duty liquid laundry detergent compositions which comprise the mid-chain branched surfactants of the present invention are presented below.

**TABLE XI**

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<th>Ingredient</th>
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<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<td>Silicone antifoam</td>
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<td>0.2 - 0.25</td>
<td>0.2 - 0.25</td>
<td>0.2 - 0.25</td>
<td>0.2 - 0.25</td>
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<tr>
<td>Isofol 16</td>
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<td>0 - 2</td>
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<td>0 - 2</td>
<td>0 - 2</td>
</tr>
<tr>
<td>Perfume</td>
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<td>0.5</td>
<td>0.5</td>
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<tr>
<td>Moisture/minors</td>
<td>Balance</td>
<td>Balance</td>
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<tr>
<td>pH (10% in DI water)</td>
<td>7.6</td>
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<tr>
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<td>7.0</td>
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<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
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</tbody>
</table>
WHAT IS CLAIMED IS:

1. A nonaqueous, liquid, heavy-duty detergent composition in the form of a stable suspension of solid, substantially insoluble particulate material dispersed throughout a structured, surfactant-containing liquid phase, wherein said composition is characterized by:

from 55% to 98.9% by weight of the composition of a structured, surfactant-containing liquid phase formed by combining:

i) from 1% to 80% by weight of said liquid phase of one or more nonaqueous organic diluents; and

ii) from 20% to 99% by weight of said liquid phase of a surfactant system characterized by surfactants selected from the group consisting of anionic, nonionic, cationic surfactants and combinations thereof;

wherein said surfactant system comprises at least 10%, by weight of a branched surfactant mixture, said branched surfactant mixture characterized by mid-chain branched and linear surfactant compounds, said linear compounds being greater than 25% and less than 70%, by weight of the branched surfactant mixture;

wherein the mid-chain branched surfactant compounds are of the formula:

\[ A^b - B \]

wherein:

\( A^b \) is a hydrophobic moiety having from 10 to 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from 9 to 17 carbon atoms, there being one or more \( C_1 - C_3 \) alkyl moieties branching from the longest chain, provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position \( \omega - 2 \) carbon, wherein \( \omega \) is the terminal carbon; and
B is a hydrophilic moiety selected from the group consisting of \( \text{OSO}_2^M \), \((\text{EO/PO})_m\text{OSO}_2^M\), \((\text{EO/PO})_m\text{OH}\) and mixtures thereof, wherein \(\text{EO/PO}\) are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, wherein \(m\) is at least 0.01 to 30 and \(M\) is hydrogen or a salt forming cation; provided that the average total number of carbon atoms in the \(A^b\) moiety in the branched surfactant mixture is within the range of greater than 12 to 14.5; and wherein the detergent composition further comprises from at least 0.1% by weight of the composition of a bleach activator selected from the group consisting of nonanoyloxybenzene sulfonate, amido-derived bleach activators of the formulae:

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

and mixtures thereof,

wherein \(R^1\) is an alkyl group containing from 6 to 12 carbon atoms, \(R^2\) is an alkyne containing from 1 to 6 carbon atoms, \(R^5\) is \(H\) or alkyl, aryl, or alkaryl containing from 1 to 10 carbon atoms, and \(L\) is a suitable leaving group.

2. The composition according to claim 1, wherein the branched surfactant mixture is made from an oxygenated product characterized by aldehydes or alcohols, wherein the oxygenated product is produced by subjecting an olefin-rich feedstock to carbon monoxide and hydrogen in the presence of a catalytically effective quantity of hydroformylation catalyst and under hydroformylation reaction conditions.

3. The composition according to claim 2, wherein the olefin-rich feedstock is obtained by subjecting a synthesis gas characterized by carbon monoxide (CO) and hydrogen (H\(_2\)) to Fischer-Tropsch reaction conditions in the presence of a Fischer-Tropsch catalyst selected from the group consisting of iron-based catalysts, cobalt-based catalysts and mixtures thereof.
4. The detergent composition according to claim 1, wherein the $\text{A}^\text{b}$ moiety of the mid-chain branched surfactant compound is a branched alkyl moiety having the formula:

$$\text{R} \quad \text{R}^1 \quad \text{R}^2$$

$$\text{CH}_3\text{CH}_2(\text{CH}_2)_w\text{CH}(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{CH}_2$$

wherein the total number of carbon atoms in the branched alkyl moiety of this formula, including the R, R$^1$, and R$^2$ branching, is from 12 to 17; R, R$^1$, and R$^2$ are each independently selected from hydrogen and C$_1$-C$_3$ alkyl, preferably methyl, provided R, R$^1$, and R$^2$ are not all hydrogen and, when z is 0, at least R or R$^1$ is not hydrogen; w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10 and $w + x + y + z$ is from 5 to 10.

5. The detergent composition according to claim 1, wherein the $\text{A}^\text{b}$ moiety of the mid-chain branched surfactant compound is a branched alkyl moiety having a formula selected from the group consisting of:

$$\text{CH}_3$$

$$\text{CH}_3(\text{CH}_2)_a\text{CH}(\text{CH}_2)_b\text{CH}_2,$$

(I)

$$\text{CH}_3$$

$$\text{CH}_3(\text{CH}_2)_d\text{CH}(\text{CH}_2)_e\text{CH}-\text{CH}_2,$$

(II)

and mixtures thereof;

wherein a, b, d, and e are integers, and a+b is from 8 to 13, d+e is from 6 to 11; and when $a + b = 8$, a is an integer from 2 to 7 and b is an integer from 1 to 6;
when $a + b = 9$, a is an integer from 2 to 8 and b is an integer from 1 to 7;
when $a + b = 10$, a is an integer from 2 to 9 and b is an integer from 1 to 8;
when $a + b = 11$, a is an integer from 2 to 10 and b is an integer from 1 to 9;
when $a + b = 12$, a is an integer from 2 to 11 and b is an integer from 1 to 10;
when $a + b = 13$, a is an integer from 2 to 12 and b is an integer from 1 to 11;
when \( d + e = 6 \), \( d \) is an integer from 2 to 5 and \( e \) is an integer from 1 to 4;
when \( d + e = 7 \), \( d \) is an integer from 2 to 6 and \( e \) is an integer from 1 to 5;
when \( d + e = 8 \), \( d \) is an integer from 2 to 7 and \( e \) is an integer from 1 to 6;
when \( d + e = 9 \), \( d \) is an integer from 2 to 8 and \( e \) is an integer from 1 to 7;
when \( d + e = 10 \), \( d \) is an integer from 2 to 9 and \( e \) is an integer from 1 to 8; and
when \( d + e = 11 \), \( d \) is an integer from 2 to 10 and \( e \) is an integer from 1 to 9.

6. An aqueous based heavy-duty liquid detergent composition characterized by:
A) from 5% to 70%, by weight of composition, of a surfactant system wherein said surfactant system comprises at least 10%, by weight of a branched surfactant mixture, said branched surfactant mixture characterized by mid-chain branched and linear surfactant compounds, said linear compounds being greater than 25% and less than 70%, by weight of the branched surfactant mixture;
wherein the mid-chain branched surfactant compounds are of the formula:

\[ A^b - B \]

wherein:

\( A^b \) is a hydrophobic moiety having from 10 to 18 total carbons divided between a longest chain and at least one short chain, the longest chain being in the range of from 9 to 17 carbon atoms, there being one or more \( C_1 \) - \( C_3 \) alkyl moieties branching from the longest chain, provided that at least one of the branching alkyl moieties is attached directly to a carbon of the longest linear carbon chain at a position within the range of position 3 carbon, counting from carbon #1 which is attached to the - B moiety, to position \( \omega - 2 \) carbon, wherein \( \omega \) is the terminal carbon; and

\( B \) is a hydrophilic moiety selected from the group consisting of \( \text{OSO}_3\text{M}, (\text{EO}/\text{PO})\text{mOSO}_3\text{M}, (\text{EO}/\text{PO})\text{mOH} \) and mixtures thereof, wherein \( \text{EO}/\text{PO} \) are alkoxy moieties selected from the group consisting of ethoxy, propoxy, and mixtures thereof, wherein \( m \) is at least 0.01 to 30 and \( M \) is hydrogen or a salt forming cation; provided that the average total number of carbon atoms in the \( A^b \) moiety in the branched surfactant mixture is within the range of greater than 12 to 14.5;
B) from 0.1 to 8% of a co-surfactant composition selected from the group consisting of alkyl polyhydroxy fatty acid amide, alkyl amidopropyl dimethyl amine and mixtures thereof; and
C) from 30% to 95%, of an aqueous liquid carrier.

7. The composition according to claim 22, wherein the branched surfactant mixture is made from an oxygenated product characterized by aldehydes or alcohols, wherein the oxygenated product is produced by subjecting an olefin-rich feedstock to carbon monoxide and hydrogen in the presence of a catalytically effective quantity of hydroformylation catalyst and under hydroformylation reaction conditions.

8. The composition according to claim 23, wherein the olefin-rich feedstock is obtained by subjecting a synthesis gas characterized by carbon monoxide (CO) and hydrogen (H₂) to Fischer-Tropsch reaction conditions in the presence of a Fischer-Tropsch catalyst selected from the group consisting of iron-based catalysts, cobalt-based catalysts and mixtures thereof.

9. The detergent composition according to claim 22, wherein the A² moiety of the mid-chain branched surfactant compound is a branched alkyl moiety having the formula:

\[
\text{CH}_3\text{CH}_2(\text{CH}_2)_w\text{CH}(\text{CH}_2)_x\text{CH}(\text{CH}_2)_y\text{CH}(\text{CH}_2)_z\text{CH}_2
\]

wherein the total number of carbon atoms in the branched alkyl moiety of this formula, including the R, R¹, and R² branching, is from 12 to 17; R, R¹, and R² are each independently selected from hydrogen and C₁-C₃ alkyl, preferably methyl, provided R, R¹, and R² are not all hydrogen and, when z is 0, at least R or R¹ is not hydrogen; w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10; w + x + y + z is from 5 to 10.
10. The detergent composition according to claim 22, wherein the $A^b$ moiety of the mid-chain branched surfactant compound is a branched alkyl moiety having a formula selected from the group consisting of:

\[
\begin{align*}
&\text{(I)} & \text{CH}_3 \\
& & \text{CH}_3 \text{(CH}_2)_a \text{CH (CH}_2)_b \text{CH}_2 \\
& & \text{CH}_3 \text{(CH}_2)_a \text{CH (CH}_2)_b \text{CH}_2 \\
& & \text{CH}_3 \text{(CH}_2)_a \text{CH (CH}_2)_b \text{CH}_2 \\
& & \text{CH}_3 \text{(CH}_2)_a \text{CH (CH}_2)_b \text{CH}_2 \\
& & \text{CH}_3 \text{(CH}_2)_a \text{CH (CH}_2)_b \text{CH}_2 \\
& & \text{CH}_3 \text{(CH}_2)_a \text{CH (CH}_2)_b \text{CH}_2 \\
& & \text{CH}_3 \text{(CH}_2)_a \text{CH (CH}_2)_b \text{CH}_2 \\
& & \text{CH}_3 \text{(CH}_2)_a \text{CH (CH}_2)_b \text{CH}_2 \\
& & \text{CH}_3 \text{(CH}_2)_a \text{CH (CH}_2)_b \text{CH}_2 \\
& & \text{CH}_3 \text{(CH}_2)_a \text{CH (CH}_2)_b \text{CH}_2 \\
\end{align*}
\]

and mixtures thereof,

wherein $a$, $b$, $d$, and $e$ are integers, and $a+b$ is from 8 to 13, $d+e$ is from 6 to 11; and when $a + b = 8$, $a$ is an integer from 2 to 7 and $b$ is an integer from 1 to 6; when $a + b = 9$, $a$ is an integer from 2 to 8 and $b$ is an integer from 1 to 7; when $a + b = 10$, $a$ is an integer from 2 to 9 and $b$ is an integer from 1 to 8; when $a + b = 11$, $a$ is an integer from 2 to 10 and $b$ is an integer from 1 to 9; when $a + b = 12$, $a$ is an integer from 2 to 11 and $b$ is an integer from 1 to 10; when $a + b = 13$, $a$ is an integer from 2 to 12 and $b$ is an integer from 1 to 11; when $d + e = 6$, $d$ is an integer from 2 to 5 and $e$ is an integer from 1 to 4; when $d + e = 7$, $d$ is an integer from 2 to 6 and $e$ is an integer from 1 to 5; when $d + e = 8$, $d$ is an integer from 2 to 7 and $e$ is an integer from 1 to 6; when $d + e = 9$, $d$ is an integer from 2 to 8 and $e$ is an integer from 1 to 7; when $d + e = 10$, $d$ is an integer from 2 to 9 and $e$ is an integer from 1 to 8; and when $d + e = 11$, $d$ is an integer from 2 to 10 and $e$ is an integer from 1 to 9.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER


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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>A, P</td>
<td>WO 97 38956 A (CONNOR DANIEL STEDMAN; PROCTER &amp; GAMBLE (US)) 23 October 1997  see page 2, line 31 - page 3, line 13; claims 1-8; example II</td>
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<td>A</td>
<td>WO 97 01521 A (SASTECH PTY LTD; SASOL CHEMICALS EUROP LTD (GB); BETTS MARK JUSTIN) 16 January 1997 cited in the application see example 13</td>
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X Further documents are listed in the continuation of box C.
X Patent family members are listed in annex.

"A" document defining the general state of the art which is not considered to be of particular relevance
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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"S" document member of the same patent family

Date of the actual completion of the international search

26 January 1999

Date of mailing of the international search report

19/02/1999

Name and mailing address of the ISA

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Authorized officer

Loiselet-Taisne, S

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<td>US 5 562 866 A (HU PATRICK C ET AL) 8 October 1996 see example 12</td>
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<td>WO 9700720 A</td>
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