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(54) **COMPOSITIONS DETERGENTES LIQUIDES NON AQUEUSES RENFERMANT DES TENSIOACTIFS RAMIFIES A CHAINE MOYENNE**

(54) **NON-AQUEOUS LIQUID DETERGENT COMPOSITIONS COMPRISING MID-CHAIN BRANCHED SURFACTANTS**

(57) L'invention concerne des compositions détergentes liquides non aqueuses de blanchissage à base d'une substance particulaire, ces compositions se présentant sous la forme d'une suspension d'une substance particulaire et renfermant essentiellement des tensioactifs ramifiés à chaîne moyenne, et de préférence un agent peroxyde de blanchiment et un adjuvant de détergence organique, dispersés dans une phase liquide idéalement structurée au moyen de tensioactifs supplémentaires. Lorsqu'elles sont utilisées, les compositions de cette invention permettent de nettoyer et de blanchir efficacement les tissus.

(57) Non-aqueous, particulate-containing liquid laundry detergent compositions which are in the form of a suspension of particulate material, essentially including mid-chain branched surfactants and preferably including a peroxygen bleaching agent and an organic detergent builder, dispersed in a liquid phase preferably structured with additional surfactants. Such compositions provide especially desirable cleaning and bleaching of fabrics laundered therewith.

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(54) Title: NON–AQUEOUS LIQUID DETERGENT COMPOSITIONS COMPRISING MID–CHAIN BRANCHED SURFACTANTS

(57) Abstract

Non–aqueous, particulate–containing liquid laundry detergent compositions which are in the form of a suspension of particulate material, essentially including mid–chain branched surfactants and preferably including a peroxygen bleaching agent and an organic detergent builder, dispersed in a liquid phase preferably structured with additional surfactants. Such compositions provide especially desirable cleaning and bleaching of fabrics laundered therewith.

NON-AQUEOUS LIQUID DETERGENT COMPOSITIONS COMPRISING MID-CHAIN BRANCHED SURFACTANTS

FIELD OF THE INVENTION

This invention relates to liquid laundry detergent products which are non-aqueous in nature and which are in the form of stable dispersions of particulate material and which include mid-chain branched surfactants and which preferably also include other materials such as bleaching agents and/or conventional detergent composition adjuvants.

BACKGROUND OF THE INVENTION

Liquid detergent products are often considered to be more convenient to use than are dry powdered or particulate detergent products. Liquid detergents have therefore found substantial favor with consumers. Such liquid detergent products are readily measurable, speedily dissolved in the wash water, capable of being easily applied in concentrated solutions or dispersions to soiled areas on garments to be laundered and are non-dusting. They also usually occupy less storage space than granular products. Additionally, liquid detergents may have incorporated in their formulations materials which could not withstand drying operations without deterioration, which operations are often employed in the manufacture of particulate or granular detergent products.

Although liquid detergents have a number of advantages over granular detergent products, they also inherently possess several disadvantages. In particular, detergent composition components which may be compatible with each other in granular products may tend to interact or react with each other in a liquid, and especially in an aqueous liquid, environment. Thus such components as enzymes, surfactants, perfumes, brighteners, solvents and especially bleaches and bleach activators can be especially difficult to incorporate into liquid detergent products which have an acceptable degree of chemical stability.

One approach for enhancing the chemical compatibility of detergent composition components in liquid detergent products has been to formulate non-aqueous (or anhydrous) liquid detergent compositions. In such non-aqueous products, at least some of the normally solid detergent composition components tend to remain insoluble in the liquid product and hence are less reactive with each other than if they had been dissolved in the liquid matrix. Non-aqueous liquid detergent

compositions, including those which contain reactive materials such as peroxygen bleaching agents, have been disclosed for example, in Hepworth et al., U.S. Patent 4,615,820, Issued October 17, 1986; Schultz et al., U.S. Patent 4,929,380, Issued May 29, 1990; Schultz et al., U.S. Patent 5,008,031, Issued April 16, 1991; Elder et al., EP-A-030,096, Published June 10, 1981; Hall et al., WO 92/09678, Published June 11, 1992 and Sanderson et al., EP-A-565,017, Published October 13, 1993.

Even though chemical compatibility of components may be enhanced in non-aqueous liquid detergent compositions, physical stability of such compositions may become a problem. This is because there is a tendency for such products to phase separate as dispersed insoluble solid particulate material drops from suspension and settles at the bottom of the container holding the liquid detergent product. As one consequence of this type of problem, there can also be difficulties associated with incorporating enough of the right types and amounts of surfactant materials into non-aqueous liquid detergent products. Surfactant materials must, of course, be selected such that they are suitable for imparting acceptable fabric cleaning performance to such compositions but utilization of such materials must not lead to an unacceptable degree of composition phase separation. Phase stabilizers such as thickeners or viscosity control agents can be added to such products to enhance the physical stability thereof. Such materials, however, can add cost and bulk to the product without contributing to the laundering/cleaning performance of such detergent compositions.

It is also possible to select surfactant systems for such liquid laundry detergent products which can actually impart a structure to the liquid phase of the product and thereby promote suspension of particulate components dispersed within such a structured liquid phase. An example of such a product with a structured surfactant system is found in van der Hoeven et al.; U.S. Patent 5,389,284; Issued February 14, 1995, which utilizes a structured surfactant system based on relatively high concentrations of alcohol alkoxylate nonionic surfactants and anionic defloculating agents. In products which employ a structured surfactant system, the structured liquid phase must be viscous enough to prevent settling and phase separation of the suspended particulate material, but not so viscous that the pourability and dispensability of the detergent product is adversely affected.

Thus, there is clearly a continuing need to identify and provide processes for preparing liquid, particulate-containing detergent compositions in the form of non-aqueous liquid products that have a high degree of chemical, e.g., bleach and enzyme, stability along with commercially acceptable phase stability, pourability and detergent composition laundering, cleaning or bleaching performance.

Accordingly, it is an object of the present invention to provide a process for preparing non-aqueous, particulate-containing liquid detergent products which have such especially desirable chemical and physical stability characteristics as well as outstanding pourability and fabric laundering/bleaching performance characteristics.

Given the foregoing, there is further a continuing need to formulate non-aqueous liquid products that provide an acceptable and desirable balance between cleaning performance and product stability. Accordingly, it is an object of the present invention to provide non-aqueous liquid detergent compositions which are especially stable and effective in hard water environments.

It has been found, that the mid-chain branched surfactants of the present invention provide improved low temperature stability of the finished product, less residual product remaining on the interior of the bottle, and improved rates of mixing of the product with water.

It has been found that certain selected surfactant systems which comprise the mid-chain branched surfactants defined below and other adjuvants can be made to provide non-aqueous liquid detergent compositions that achieve the foregoing objectives. The elements of these selected combinations of ingredients are described below.

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:

$$R^1CH(R^2)CH_2OSO_3X$$

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).

As noted hereinbefore, R.G. Laughlin in "The Aqueous Phase Behavior of Surfactants", Academic Press, N.Y. (1994) p. 347 describes the observation that as

branching moves away from the 2-alkyl position towards the center of the alkyl hydrophobe there is a lowering of Krafft temperatures. See also Finger et al., "Detergent alcohols - the effect of alcohol structure and molecular weight on surfactant properties", J. Amer. Oil Chemists' Society, Vol. 44, p. 525 (1967) and Technical Bulletin, Shell Chemical Co., SC: 364-80.

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 "Hydrophobic groups and their sources"; pp 28-29 "Alcohols" , pp 34-35 "Primary Alkyl Sulfates" and pp 35-36 "Secondary Alkyl Sulfates"); and literature on "higher" or "detergent" alcohols from which alkyl sulfates are typically made, including: CEH Marketing Research Report "Detergent Alcohols" by R.F. Modler et al., Chemical Economics Handbook, 1993, 609.5000 - 609.5002; Kirk Othmer's Encyclopedia of Chemical Technology, 4th Edition, Wiley, N.Y., 1991, "Alcohols, Higher Aliphatic" in Vol. 1, pp 865-913 and references therein.

SUMMARY OF THE INVENTION

The present invention provides non-aqueous liquid detergent compositions comprising a stable suspension of solid, substantially insoluble particulate material including mid-chain branched surfactants dispersed throughout a non-aqueous, surfactant-containing liquid phase.

Specifically, the present invention comprises 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. The detergent composition comprises 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 surfactant system is preferably substantially free of unreacted alcohol.

The surfactant system of the subject liquid detergent compositions comprises at least about 10%, preferably at least about 20%, more preferably at least about 30%, most preferably at least about 50%, by weight of a branched surfactant mixture, said branched surfactant mixture comprising mid-chain branched and linear surfactant compounds, said linear compounds comprising less than 25%, preferably less than about 15%, more preferably less than about 10% and most preferably less

than about 5%, by weight of the branched surfactant mixture and said mid-chain branched compounds being of the formula:

$$A^b - (EO/PO/BO)mOH$$

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 (EO/PO/BO)mOH 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 (EO/PO/BO)mOH moiety, to position ω - 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.

EO/PO/BO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, butoxy and mixtures thereof, and m is at least about 1 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 to about 14 and most preferably greater than about 12 to about 13.5. 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 0.01% to 50% by weight of the composition of particulate material which ranges in size from about 0.1 to 1500 microns, which is substantially insoluble in said 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 non-aqueous liquid detergent compositions of this invention comprise a surfactant-containing, preferably surfactant-structured liquid phase 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.)

Specifically, the present invention comprises 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. The detergent composition comprises 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.

As is discussed in greater detail below, the surfactant system is preferably substantially free of unreacted alcohol. Specifically, the surfactant system, including both the linear and branched surfactant components, should contain less than 3%, by weight, preferably less than 1%, by weight and most preferably less than 0.5%, by weight of unreacted alcohol.

The surfactant system of the subject liquid detergent compositions comprises at least about 10%, preferably at least about 20%, more preferably at least about 30%, most preferably at least about 50%, by weight of a branched surfactant mixture, said branched surfactant mixture comprising mid-chain branched and linear surfactant compounds, said linear compounds comprising less than 25%, preferably less than about 15%, more preferably less than about 10% and most preferably less than about 5%, by weight of the branched surfactant mixture and said mid-chain branched compounds being of the formula:

$$A^b - (EO/PO/BO)mOH$$

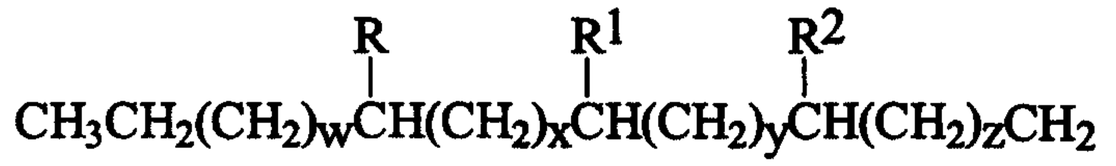
wherein:

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 (EO/PO/BO)mOH 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

(EO/PO/BO)mOH moiety, to position ω - 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.

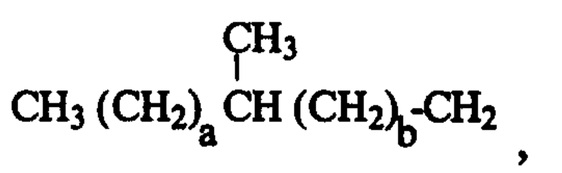
EO/PO/BO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, butoxy and mixtures thereof, and m is at least about 1 to about 30. The average total number of carbon atoms in the A^b moiety in the branched surfactant mixture defined above should be within the range of greater than 12 to about 14.5, preferably greater than about 12 to about 14 and most preferably greater than about 12 to about 13.5. 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.

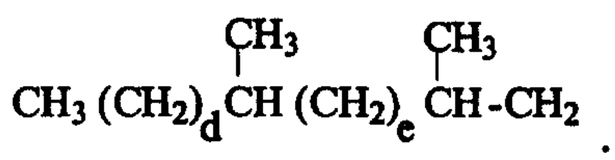
The A^b moiety of the mid-chain branched surfactant components of the present claims is preferably a branched alkyl moiety having the formula:



Wherein the total number of carbon atoms in the branched alkyl moiety, including the R, R^1, and R^2 branching, is from 10 to 17. R, R^1, and R^2 are each independently selected from hydrogen and C_1-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 A^b moiety of the mid-chain branched surfactant component is a branched alkyl moiety having the formula selected from the group consisting of:

(I) ,

(II) .

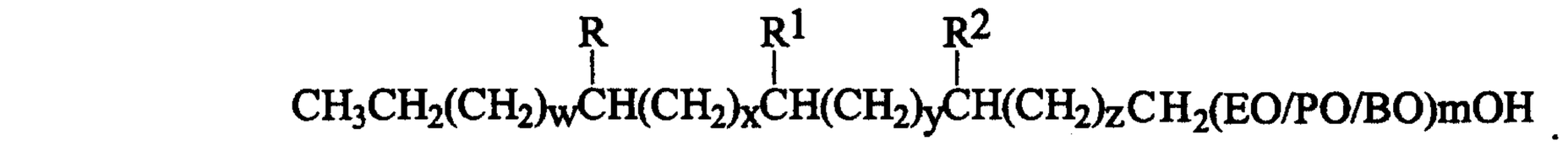
Wherein a, b, d, and e are integers, a+b is from 6 to about 13, d+e is from about 4 to about 11; and

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 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 10 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 to about 14 and most preferably greater than about 12 to about 13.5.

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, R^1 and/or R^2) 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, 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 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.

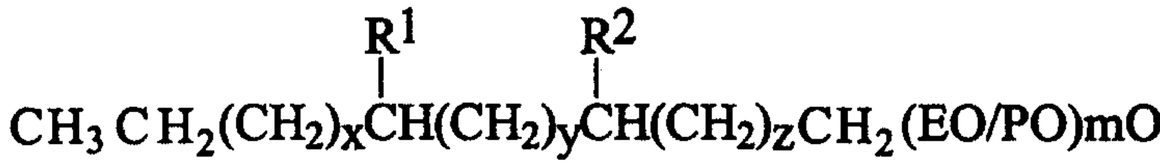
Further it is to be similarly recognized that non-alkoxylated mid-chain branched alcohol may comprise some amount of the present invention polyoxyalkylene-containing compositions. Such materials may be present as the result of incomplete alkoxylation of the alcohol used to prepare the polyoxyalkylene 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. As mentioned above, however, the surfactant system is preferably substantially free of unreacted alcohol. Specifically, the surfactant system, including both the linear and branched surfactant components, should contain less than 3%, by weight, preferably less than 1%, by weight and most preferably less than 0.5%, by weight of unreacted alcohol.

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/BO are alkoxy moieties, preferably selected from ethoxy, propoxy, butoxy and mixed ethoxy/propoxy/butoxy 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 $(EO/PO/BO)_m$ moiety may be either a distribution with average degree of alkoxylation (e.g., ethoxylation and/or propoxylation and/or butoxylation) corresponding to m, or it may be a single specific chain with alkoxylation (e.g., ethoxylation and/or propoxylation and/or butoxylation) of exactly the number of units corresponding to m.

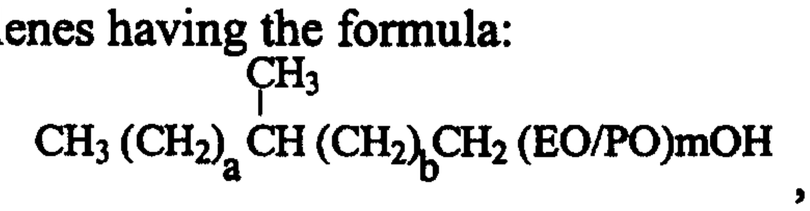
The preferred surfactant mixtures of the present invention have at least about 10%, more preferably at least about 20%, even more preferably at least about 30%, most preferably at least about 50%, by weight, of the mixture one or more mid-chain branched primary alkyl polyoxyalkylenes having the formula:



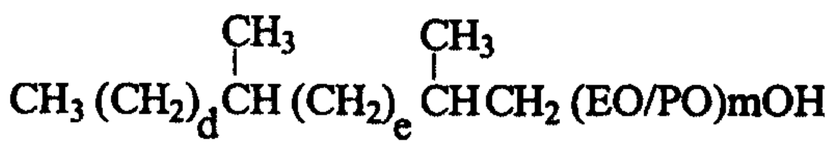
Wherein the total number of carbon atoms, including branching, is from 10 to 16, and the average total number of carbon atoms in the branched primary alkyl moieties is within the range of greater than 12 to about 14. R^1 and R^2 are each independently hydrogen or C_1-C_3 alkyl; x is from 0 to 10; y is from 0 to 10; z is from 0 to 10; and x + y + z is from 4 to 10. Provided R^1 and R^2 are not both hydrogen. EO/PO are alkoxy moieties selected from ethoxy, propoxy, and mixed ethoxy/propoxy 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 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 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) ,

(II) 

and mixtures thereof.

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

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;

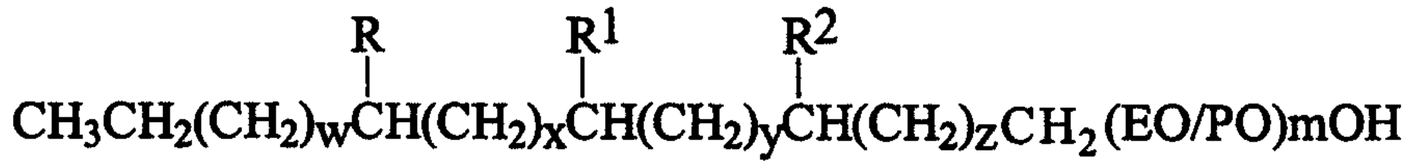
when d + e = 9, d is an integer from 2 to 8 and e is an integer from 1 to 7;

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/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.

Further, the present invention surfactant composition may comprise a mixture of branched primary alkyl polyoxyalkylenes having the formula:



Wherein the total number of carbon atoms per molecule, including branching, is from 10 to 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

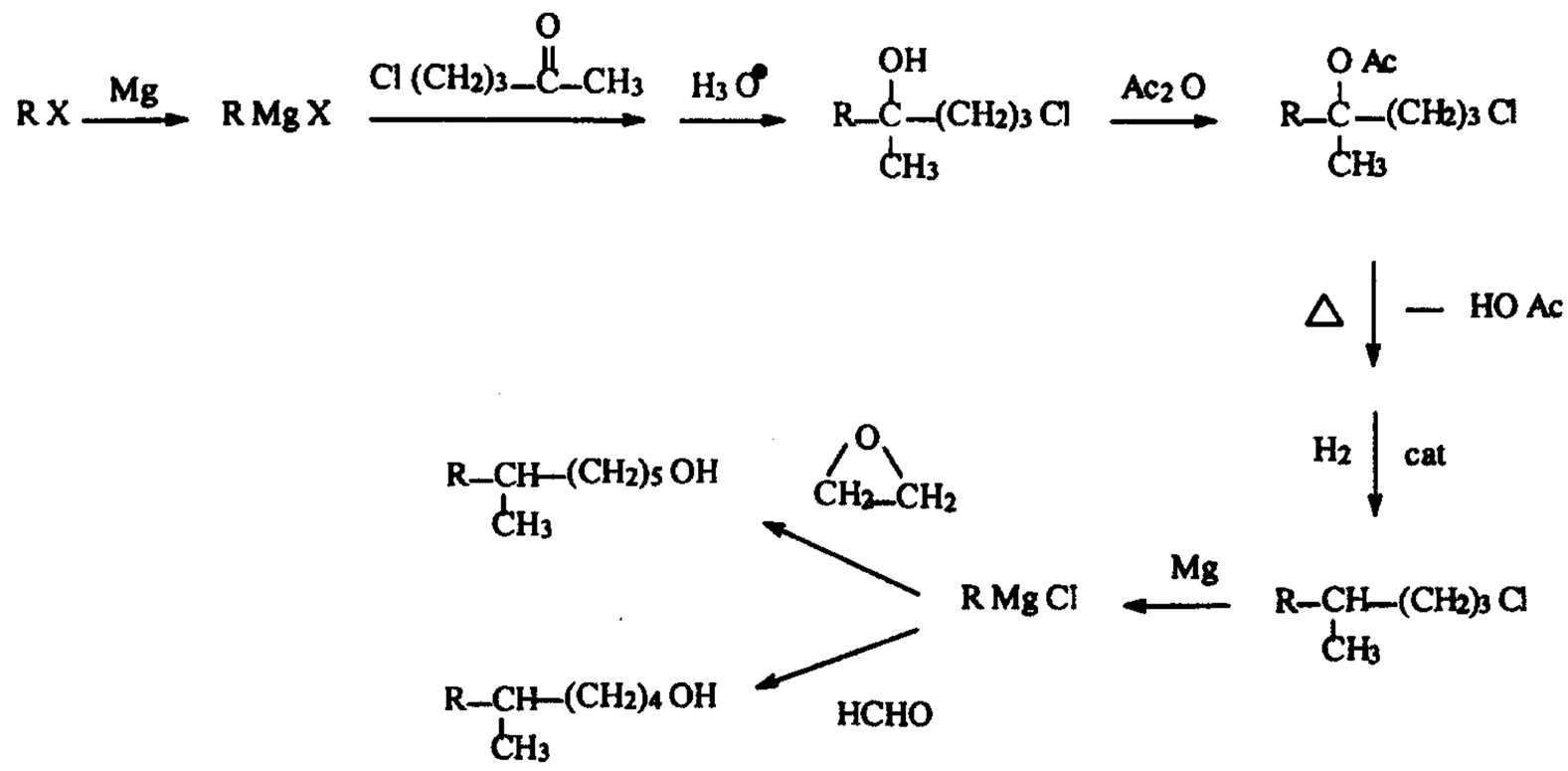
10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10; w + x + y + z is from 3 to 10. EO/PO are alkoxy moieties, preferably selected from ethoxy, propoxy, and mixed ethoxy/propoxy groups, wherein m is at least about 1, preferably within the range of from about 3 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 1 or greater to surfactants having z of 0 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 are 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 ethoxylation of from about 5 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 to prepare the mid-chain branched primary alkyl surfactants of the present invention.



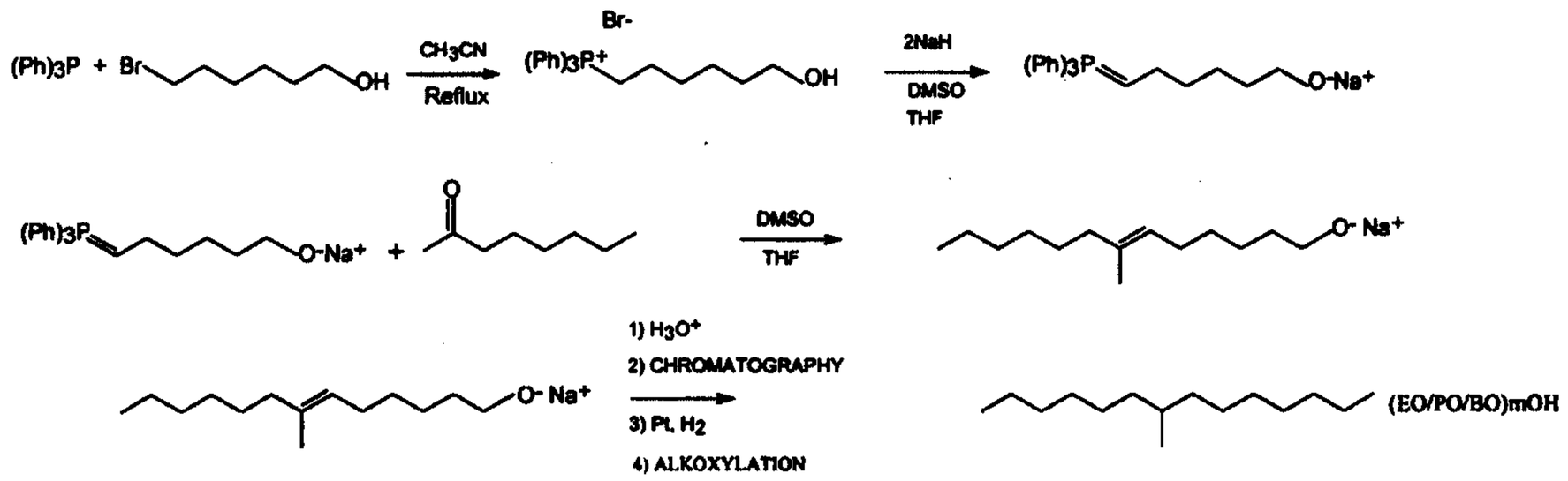
An alkyl halide is converted to a Grignard reagent and the Grignard is reacted with a haloketone. After conventional acid hydrolysis, acetylation and thermal elimination of acetic acid, an intermediate olefin is produced (not shown in the scheme) which is hydrogenated forthwith using any convenient hydrogenation 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 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 Nonmetallic Substances", M.S. Kharasch and O. Reinmuth, Prentice-Hall, N.Y., 1954; *J. Org. Chem.*, J. Cason and W. R. Winans, Vol. 15 (1950), pp 139-147; *J. Org Chem.*, J. Cason et al., Vol. 13 (1948), pp 239-248; *J. Org Chem.*, J. Cason et al., Vol. 14 (1949), pp 147-154; and *J. Org Chem.*, J. Cason et al., Vol. 15 (1950), pp 135- 138 all of which are incorporated herein by reference.

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 polyoxyalkylenes 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. Horiike 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 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. 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 C_1-C_3 branches, more preferably ethyl, most preferably methyl,

4) limit or eliminate gem dialkyl branching i.e. to avoid formation of quaternary carbon atoms.

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.

The process described herein above, with tridecene, gives the more preferred 5-methyl-tridecyl alcohol and therefore surfactants in higher yield than the less preferred 2,4-dimethyldodecyl materials. This mixture is desirable under the metes and bounds of the present invention in that each product comprises a total of 14 carbon atoms with linear alkyl chains having at least 12 carbon atoms.

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 "Bailey's Industrial Oil and Fat Products", Volume 2, Fourth Edition, edited by Daniel Swern, pp. 440-441.

SURFACTANT-CONTAINING LIQUID PHASE

The surfactant-containing, non-aqueous liquid phase of the present invention will generally comprise from about 49% to 99.95% by weight of the detergent compositions herein. More preferably, this liquid phase is surfactant-structured and will comprise from about 52% to 98.9% 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.

(A) 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 alkoxylated alcohols, ethylene oxide (EO)-propylene oxide (PO) block polymers, polyhydroxy fatty acid amides, alkylpolysaccharides, 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.

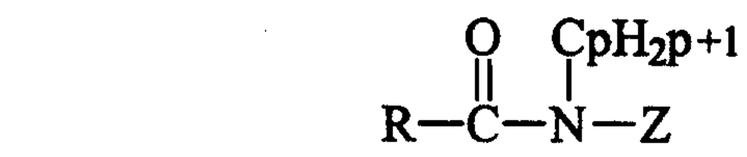
Other types of alcohol ethoxylates useful in the present compositions are higher molecular weight nonionics, such as Neodol 45-11, which are similar ethylene oxide condensation products of higher fatty alcohols, with the higher fatty alcohol being of 14-15 carbon atoms and the number of ethylene oxide 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 Davidson 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:



wherein R is a C_{9-17} alkyl or alkenyl, p is from 1 to 6, and Z is glycityl derived from a reduced sugar or alkoxylated derivative thereof. Such materials include the C_{12}-C_{18} N-methyl glucamides. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucityl oleamide. Processes for making polyhydroxy fatty acid, amides are know 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 peroxygen 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 C_4-C_8 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 C_4-C_8 branched or straight chain alkylene glycols. Materials of this type include hexylene glycol (4-methyl-2,4-pentanediol), 1,6-hexanediol, 1,3-butylene 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- C_2-C_3 alkylene glycol mono C_2-C_6 alkyl ethers. The specific examples of such compounds include diethylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, dipropolyene glycol monoethyl ether, and dipropylene 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: R^1-C(O)-OCH_3 wherein R^1 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 alkoxylate 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.

(B) 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 polyalkxylate 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

$$ROSO_3^-M^+$$

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_{10-14} 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:

$$CH_3(CH_2)_n(CHOSO_3^-M^+)\,(CH_2)_mCH_3$$

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, peroxygen 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

$$R^2\text{-}O\text{-}(C_mH_{2m}O)_n\text{-}SO_3M$$

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 peroxygen 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 bi-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.

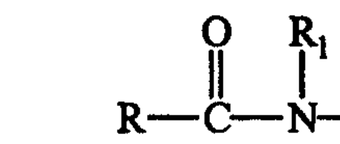
The anionic surfactant-containing powder that results after drying can comprise from about 45% to 94%, more preferably from about 60% to 94%, by weight of the powder of alkyl benzene sulfonic acid salts. Such concentrations are generally sufficient to provide from about 0.5% to 60%, more preferably from 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.

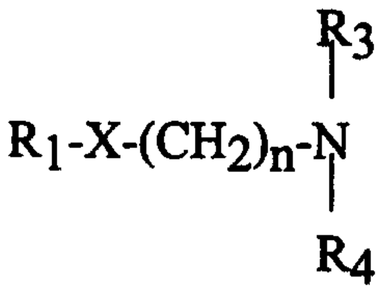
A structured, surfactant-containing liquid phase of the preferred detergent compositions herein can be prepared by combining the non-aqueous organic diluents hereinbefore described with the anionic surfactant-containing powder as hereinbefore described. Such combination results in the formation of a 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:

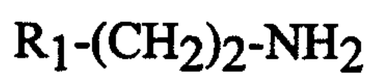


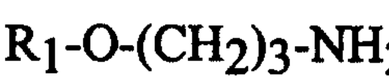
wherein R is a C_{9-17} alkyl or alkenyl, R_1 is a methyl group and Z is glycityl derived from a reduced sugar or alkoxylated derivative thereof. Examples are N-methyl N-1-deoxyglucityl cocoamide and N-methyl N-1-deoxyglucityl oleamide. Processes for making polyhydroxy fatty acid amides are known and 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.

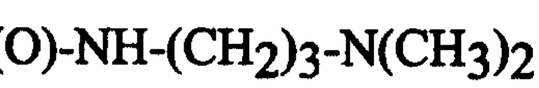
Preferred surfactants for use in the detergent compositions described herein are amine based surfactants of the general formula:

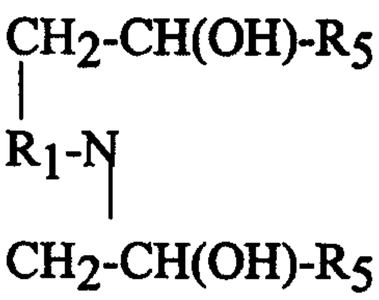


wherein R_1 is a C_6-C_{12} alkyl group; n is from about 2 to about 4, X is a bridging group which is selected from NH, CONH, COO, or O or X can be absent; and R_3 and R_4 are individually selected from H, C_1-C_4 alkyl, or (CH_2-CH_2-O(R_5)) wherein R_5 is H or methyl. Especially preferred amines based surfactants include the following:



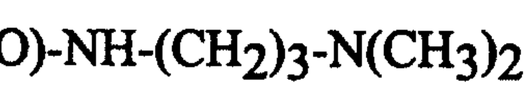






wherein R_1 is a C_6-C_{12} alkyl group and R_5 is H or CH_3. Particularly preferred amines for use in the surfactants defined above include those selected from the group consisting of octyl amine, hexyl amine, decyl amine, dodecyl amine, C_8-C_{12} bis(hydroxyethyl)amine, C_8-C_{12} bis(hydroxyisopropyl)amine, 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:



wherein R_1 is C_8-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 0.1% 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:

(A) 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 monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, Hartman, Issued November 20, 1984; 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 peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used. 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.

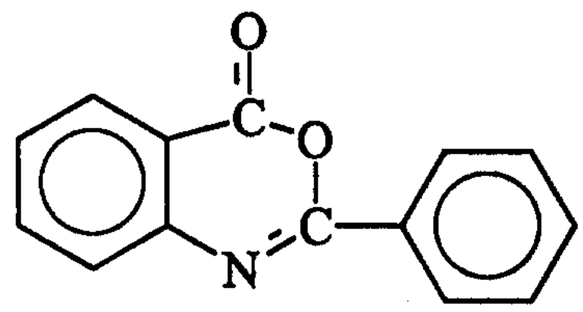
Other useful amido-derived bleach activators are those of the formulae:

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

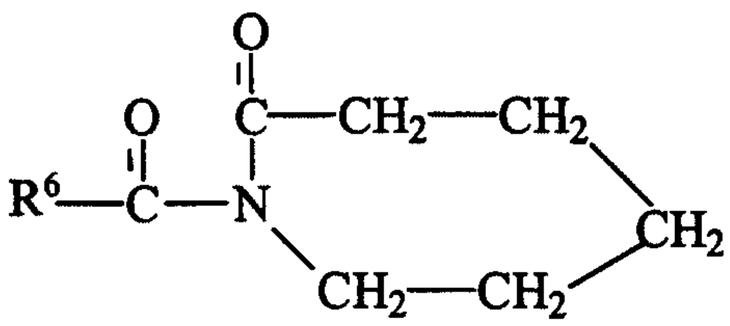
wherein R^1 is an alkyl group containing from about 6 to about 12 carbon atoms, R^2 is an alkylene containing from 1 to about 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from about 1 to about 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is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

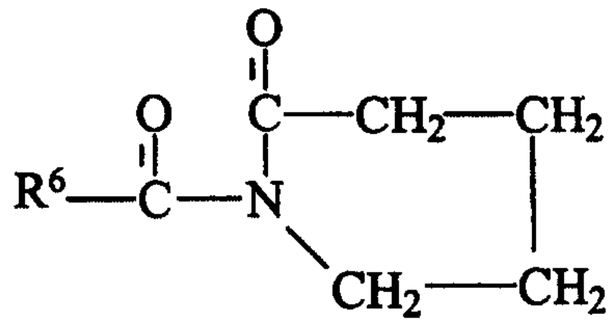
Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl) oxybenzenesulfonate, (6-decanamido-caproyl)oxybenzenesulfonate and mixtures thereof as described in the hereinbefore referenced U.S. Patent 4,634,551. Such mixtures are characterized herein as (6-C_8-C_{10} 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:



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





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 peroxygen bleaching agents are used as all or part of the particulate material, they will generally comprise from about 1% to 30% by weight of the composition. More preferably, peroxygen bleaching agent will comprise from about 1% to 20% by weight of the composition. Most preferably, peroxygen 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.

(B) 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 alkanehydroxy 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.

(C) 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 peroxygen 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/carrier 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.

OTHER OPTIONAL COMPOSITION COMPONENTS

In addition to the composition liquid and solid phase components as hereinbefore described, the detergent compositions herein 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:

(a) 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.

(b) 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.

(c) 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 peroxygen 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, triethylenetetraaminehexacetates, 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 ethylenediaminetetrakis (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-ethyldiphosphonic 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.

(d) 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.

(e) <u>Optional Clay Soil Removal/Anti-redeposition Agents</u>

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 Gosselink, 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, 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 anti-redeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

(f) 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.

(g) 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 $Mn^{IV}_2(u\text{-}O)_3$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2$-$(PF_6)_2$, $Mn^{III}_2(u\text{-}O)_1(u\text{-}OAc)_2$(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2(ClO_4)_2$, $Mn^{IV}_4(u\text{-}O)_6$(1,4,7-triazacyclononane)$_4(ClO_4)_4$, $Mn^{III}Mn^{IV}_4(u\text{-}O)_1(u\text{-}OAc)_2$-(1,4,7-trimethyl-1,4,7-triazacyclononane)$_2(ClO_4)_3$, Mn^{IV}(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 $[Co(NH_3)_5OAc]$ T_y, wherein "OAc" represents an acetate moiety and "T_y" is an anion, and especially cobalt pentaamine acetate chloride, $[Co(NH_3)_5OAc]Cl_2$; as well as $[Co(NH_3)_5OAc](OAc)_2$; $[Co(NH_3)_5OAc](PF_6)_2$; $[Co(NH_3)_5OAc](SO_4)$; $[Co(NH_3)_5OAc](BF_4)_2$; and $[Co(NH_3)_5OAc](NO_3)_2$ (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 4,810,410, to Diakun et al, issued March 7,1989, J. Chem. Ed. (1989), 66 (12), 1043-45; The Synthesis and Characterization of Inorganic Compounds, W.L. Jolly (Prentice-Hall; 1970), pp. 461-3; Inorg. Chem., 18, 1497-1502 (1979); Inorg. Chem., 21, 2881-2885 (1982); Inorg. Chem., 18, 2023-2025 (1979); Inorg. Synthesis, 173-176 (1960); and Journal of Physical Chemistry, 56, 22-25 (1952).

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.

(h) Optional Brighteners, Suds Suppressors, Dyes and/or Perfumes

The detergent compositions herein may also optionally contain conventional brighteners, suds suppressors, dyes and/or perfume materials. Such brighteners, suds 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 suds suppressors, dyes and/or perfumes will typically comprise from about 0.0001% to 2% by weight of the compositions herein.

(i) 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.

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 Carrimed CSL2 Rheometer at a shear rate of 20 s^{-1}.

COMPOSITION PREPARATION AND USE

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 peroxygen bleaching agent can be added to the composition, again while the mixture is maintained under shear agitation. By adding the peroxygen 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 peroxygen 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 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.

EXAMPLE I

Preparation of 7-methyltridecyl ethoxylated (E2)

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 140C 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).

Alkoxylation 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-methyltridecyl ethoxylate (average of 2 ethoxylates per molecule) product is then collected.

EXAMPLE II

Preparation of mid-chain branched C12,13 and C14,15 alcohol ethoxylates from experimental clathrated Sasol alcohol samples

Experimental test mid-branched alcohol samples were derived by urea clathration of C12,13 and C14,15 detergent range alcohol samples from Sasol.

Alcohol ethoxylates were prepared from the experimental alcohols. The urea clathration was used to separate the mid-chain branched alcohols from the high levels (35-45% by weight) of conventional linear alcohols present in Sasol's alcohol samples. A 10:1 to 20:1 molar ratio of urea to alcohol was used in the separation. Urea clathration is described in Advanced Organic Chemistry by J. March, 4th ed., Wiley and Sons, 1992, pp. 87-88 and by Takemoto; Sonoda, in Atwood; Davies; MacNicol treatise titled *Inclusion Compounds*, vol. 2, pp. 47-67. The original Sasol alcohol samples had been prepared by hydroformylation of alpha olefins produced by Fischer Tropsch process as described by patents WO 97/01521 and according to the Sasol R&D technical product bulletin published October 1, 1996 entitled SASOL DETERGENT ALCOHOLS. The clathration procedure reduced the linear content from 35-45%, depending on the sample, down to about 5% by weight, leaving C12,13 and C14,15 alcohols that comprised about 95% branched alcohols. Of the branched alcohols, about 70% were mid-chain branched alcohols according to the present invention and the other 30% were alcohols branched at the 2-carbon position, counting from the oxygen in the alcohol.

Urea Clathration of Sasol C12,13 Alcohol

Into a dry 12 L 3 neck round bottom flask fitted with a mechanical stirrer is added Sasol C12,13 Alcohol (399.8 g , 2.05 mol) and urea (2398.8 g , 39.98 mol) and methanol (7 L). The reagents are allowed to stir at room temperature for about 20 hours. During this time, the urea forms a complex with the linear components of the Sasol alcohol but not with the branched components. After about 20 hours the suspension is filtered through a medium fritted funnel. Vacuum evaporation of the methanol followed by a hexane wash of the urea and vacuum evaporation of the hexane gives 189 g of almost colorless liquid. The GC analysis shows that the recovered alcohol is 5.4% linear and 94.6% branched. Of the branched alcohols, 67.4% are mid-chain branched and 32.6% are branched at the 2-carbon position counting from the oxygen in the alcohol.

Ethoxylation of Sasol C12,13 Clathrated Alcohol to E5

Into a dried 500 ml 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 Clathrated Alcohol (134.4 g , 0.7 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 (0.8 g , 0.04 mol) is added as the catalyst and allowed to melt with stirring at 120-140°C. With vigorous

stirring, ethylene oxide gas (154 g , 3.5 mol) is added in 60 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 (285 g , 0.69 mol) is bottled under nitrogen.

Urea Clathration of Sasol C14,15 Alcohol

Into a dry 12 L 3 neck round bottom flask fitted with a mechanical stirrer is added Sasol C14,15 Alcohol (414.0 g , 1.90 mol) and urea (2220.0 g , 37.0 mol) and methanol (3.5 L). The reagents are allowed to stir at room temperature for about 48 hours. During this time, the urea forms a complex with the linear components of the Sasol alcohol but not with the branched components. After about 48 hours the suspension is filtered through a medium fritted funnel. Vacuum evaporation of the methanol followed by a hexane wash of the urea and vacuum evaporation of the hexane gives 220 g of almost colorless liquid. The GC analysis shows that the recovered alcohol is 2.9% linear and 97.1% branched. Of the branched alcohols, 70.4% are mid-chain branched and 29.6% are branched at the 2-carbon position counting from the oxygen in the alcohol.

Ethoxylation of Sasol C14,15 Clathrated Alcohol to E7

Into a dried 500 ml 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 Clathrated Alcohol (76.3 g , 0.35 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 (0.4 g , 0.02 mol) is added as the catalyst and allowed to melt with stirring at 120-140°C. With vigorous stirring, ethylene oxide gas (37.7 g , 2.45 mol) is added in 35 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 (179.9 g , 0.34 mol) is bottled under nitrogen.

EXAMPLE III

Synthesis of sodium 7-methyldodecyl ethoxylated (E5)

Synthesis of 7- methyldodecene-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, prepared as described previously) 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-heptanone (125.4g, 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 at 140C and 1mm Hg.

Hydrogenation of 7- methyldodecene-1-ol

Into a 3L rocking autoclave liner is added 7-methyldodecene-1-ol (100.6g, 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.

Alkoxylation of 7-methyldodecanol

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 7-methyldodecanol. 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 five 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-methyldodecyl ethoxylate (average of 5 ethoxylates per molecule) product is then collected.

EXAMPLE IV

Preparation of mid-chain branched C13 alcohol ethoxylate from experimental Shell Research alcohol samples

Shell Research experimental test C13 alcohol samples are used to make alcohol ethoxylates. These experimental alcohols are ethoxylated according to the following procedures. The experimental alcohols are made from C12 alpha olefins in this case. The C12 alpha olefins are skeletally rearranged to produce branched chain olefins. The skeletal rearrangement produces a limited number of branches, preferably mid-chain. The rearrangement produces C1-C3 branches, more preferably ethyl, most preferably methyl. The branched chain olefin mixture is subjected to catalytic hydroformylation to produce the desired branched chain alcohol mixture.

Ethoxylation of Shell C13 Experimental Alcohol to E9

Into a dried 250 ml 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 Shell C13 Experimental Alcohol (50.0 g , 0.25 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 (0.3 g , 0.01 mol) is added as the catalyst and allowed to melt with stirring at 120-140°C. With vigorous stirring, ethylene oxide gas (99.0 g , 2.25 mol) is added in 35 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 yellow liquid product (143 g , 0.24 mol) is bottled under nitrogen.

The following analytical method for characterizing branching in the present invention surfactant compositions is useful: Separation and Identification of Components in Fatty Alcohols (prior to alkoxylation or after hydrolysis of alcohol sulfate for analytical purposes). The position and length of branching found in the precursor fatty alcohol materials is determined by GC/MS techniques [see: D. J. Harvey, Biomed, Environ. Mass Spectrom (1989). 18(9), 719-23; D. J. Harvey, J. M. Tiffany, J. Chromatogr. (1984), 301(1), 173-87; K. A. Karlsson, B. E. Samuelsson, G. O. Steen, Chem. Phys. Lipids (1973), 11(1), 17-38].

EXAMPLE V

Preparation of LAS Powder for Use as a Structurant

Sodium C_{12} 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 sulfosuccinate (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 I.

TABLE V

LAS Powder

Component	Wt. %
NaLAS	85%
Sulfate	11%
Sulfosuccinate	2%
Water	2.5%
Unreacted, etc.	balance to 100%
% insoluble LAS	17%
# of phase (via X-ray diffraction)	2

EXAMPLE VI

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

TABLE VI

Non-Aqueous Liquid Detergent Composition with Bleach

Component	Wt % A	Wt % B	Wt % C	Wt % D	Wt % E
LAS, From Example I	16	13	8	8	2
$C_{12-14}E0=5$ alcohol ethoxylate	21	20	18	10	4
Branched Alcohol Ethoxylate surfactant	1	5	10	20	30
BPP	19	19	19	19	19
Sodium citrate dihydrate	3	3	3	3	3
Bleach activator	5.9	5.9	5.9	5.9	5.9
Sodium carbonate	9	9	9	9	9
Maleic-acrylic copolymer	3	3	3	3	3
Colored speckles	0.4	0.4	0.4	0.4	0.4
EDDS	1	1	1	1	1
Cellulase Prills	0.1	0.1	0.1	0.1	0.1
Amylase Prills	0.4	0.4	0.4	0.4	0.4
Ethoxylated diamine quat	1.3	1.3	1.3	1.3	1.3
Sodium Perborate	15	15	15	15	15
Optionals including: brightener, colorant, perfume, thickener, suds suppresor, colored speckles etc.	balance	balance	balance	balance	balance
	100%	100%	100%	100%	100%

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

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:

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 characterized by less than 25% by weight of the branched surfactant mixture and said mid-chain branched compounds being of the formula:

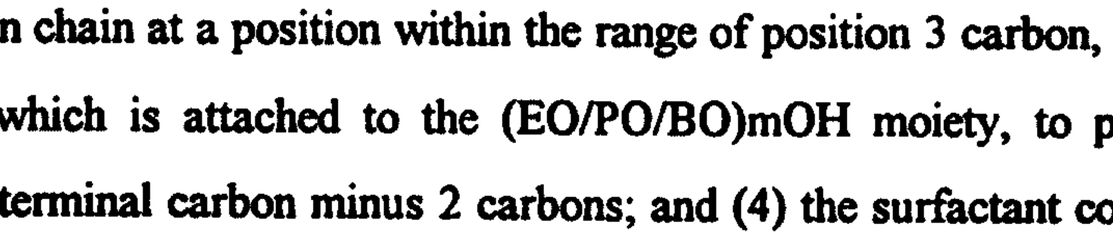
$$A^b - (EO/PO/BO)mOH$$

wherein:

A^b is a hydrophobic C9 to C18, total carbons in the moiety, mid-chain branched alkyl moiety having: (1) a longest linear carbon chain attached to the (EO/PO/BO)mOH 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 (EO/PO/BO)mOH moiety, to position ω - 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 14.5; and

EO/PO/BO are alkoxy moieties selected from the group consisting of ethoxy, propoxy, butoxy and mixtures thereof, and m is at least 1 to 30.

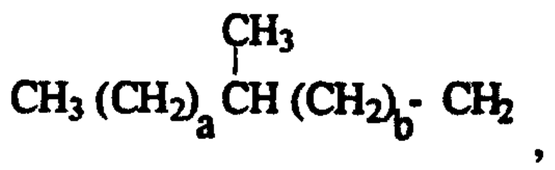
2. The detergent composition according to claim 1, wherein the A^b moiety of the mid-chain branched surfactant compound is a branched alkyl moiety having the formula:

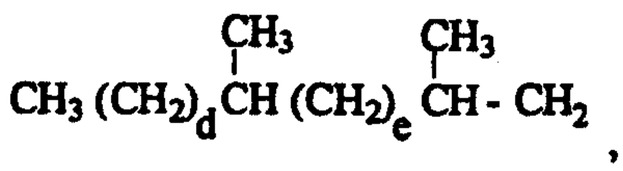


wherein w is an integer from 0 to 10; x is an integer from 0 to 10; y is an integer from 0 to 10; z is an integer from 0 to 10; and w + x + y + z is from 3 to 10; further, the total number of carbon atoms in the branched alkyl moiety, including the R, R^1, and R^2 branching, is from

10 to 17; R, R^1, and R^2 are each independently selected from hydrogen and C_1-C_3 alkyl, provided that R, R^1, and R^2 are not all hydrogen; and further provided that when z is 0, at least R or R^1 is not hydrogen.

3. The detergent composition according to claim 1, 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:

(I) 

(II) 

and mixtures thereof; wherein a, b, d, and e are integers, a+b is from 6 to 13, d+e is from 4 to 11; and

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.

4. The detergent composition according to claim 1, wherein the detergent composition further comprises 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.

5. The detergent composition according to claim 1, wherein the detergent composition further comprises from 0.1 to 8% of an alkyl polyhydroxy fatty acid amide.

6. The detergent composition according to claim 1, wherein said particulate material comprises from 0.01% to 50% by weight of the composition, said particulate material ranging in size from 0.1 to 1500 microns, and is selected from the group consisting of peroxygen bleaching agents, bleach activators, colored speckles, organic detergent builders, inorganic alkalinity sources and mixtures thereof.

7. The detergent composition according to claim 1, wherein said surfactant system is characterized by at least 20%, preferably at least 50%, by weight of the branched surfactant mixture.

8. The detergent composition according to claim 1, wherein the A^b hydrophobic moiety has from 10 to 17, preferably from 11 to 15 total carbons.

9. The detergent composition according to claim 1, wherein 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.

10. The detergent composition according to claim 2, wherein when R^2 is a C_1-C_3 alkyl the molar ratio of surfactants having z equal to 0 to surfactants having z equal to 1 or greater is at least 1:1 preferably at least 1:10.