(54) Title: CO-SULFATION OF ETHOXYLATED ALCOHOLS AND UNSATURATED FATTY ALCOHOLS

(57) Abstract

The present invention is directed to a process for co-sulfating alkyl ethoxylated alcohols and unsaturated fatty alcohols to prepare a mixed product system which can be neutralized to form a mixed surfactant system. This process comprises sulfating together both an unsaturated alcohol of the formula R-OH, wherein R is a C₃-C₂₂ alkenyl group, and an alkyl ethoxylated alcohol of the formula R¹(OCH₂CH₂)ₙOH, wherein R¹ is a C₆-C₂₀ alkyl group and n is an integer from 1 to 10, inclusive. The mole ratio of unsaturated alcohol plus alkyl ethoxylated alcohol to sulfating agent in the process of the present invention ranges from about 1:1 to about 5:1. The final product resulting from the process of the present invention is a mixed product system comprising an unsaturated fatty acid sulfate of the formula R-OSO₂H, wherein R is as hereinbefore defined, and an alkyl ethoxylated acid sulfate of the formula R¹(OCH₂CH₂)ₙOSO₂H, wherein R¹ and n are as hereinbefore defined. This mixed product system can be neutralized to form a mixed surfactant system comprising the neutralized salts of said acid sulfates.
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CO-SULFATION OF ETHOXYLATED ALCOHOLS AND UNSATURATED FATTY ALCOHOLS

TECHNICAL FIELD

The present invention relates to a process for co-sulfating alkyl ethoxylated alcohols and unsaturated fatty alcohols. In particular, it relates to a process in which an alkyl ethoxylated alcohol and an unsaturated fatty alcohol are sulfated together to form a mixed product system containing an alkyl ethoxylated acid sulfate and an unsaturated fatty acid sulfate. This mixed product system can be neutralized to form a mixed surfactant system.

BACKGROUND OF THE INVENTION

The neutralized sulfate salts of ethoxylated alcohols and unsaturated fatty alcohols are excellent surfactants and are widely utilized in heavy duty detergents, light duty liquids, shampoos and other cleaning products. Certain types of unsaturated fatty sulfates, such as sodium oleyl sulfate, are especially preferred surfactants due to their solubility, foaming, detergency and mildness properties. Additionally, mixtures of such sulfate salts of ethoxylated alcohols and unsaturated fatty alcohols exhibit excellent detergent properties.

The sulfation of unsaturated alcohols, however, is complicated by the reaction of sulfating agents, such as SO₃, H₂SO₄ and ClSO₃H, at the double bond of the unsaturated alcohol reactant. Thus, sulfation reactions for unsaturated alcohols using such common sulfating agents usually result in low quality products due to by-products caused by side reactions. Furthermore, even in the cases wherein an unsaturated alcohol can be cleanly sulfated to obtain a pure product, the process generally requires reagents which are expensive or difficult to work with or reaction conditions which make the process unsuitable for industrial scale-up. Therefore, it would be desirable to develop a process for preparing unsaturated acid sulfates in which conventional industrial sulfating agents may be used and in which
the resulting sulfation product is substantially free of by-products resulting from side reactions.

Processes for sulfating unsaturated fatty alcohols are known in the art. U.S. Patent 2,079,347, issued May 4, 1937, to Hailwood, discloses a process for preparing unsaturated sulfate esters wherein unsaturated long-chain alcohols, or mixtures thereof, are treated with the addition product of sulfur trioxide and an amine. In the disclosed process the unsaturated long-chain alcohols are converted into their sulfuric esters, or salts thereof, without attack on their unsaturated linkages.

U.S. Patent 2,099,214, issued November 16, 1937, to McAllister, discloses a process for sulfating unsaturated alcohols wherein said alcohols are reacted with a reagent consisting of the addition product of sulfur trioxide and dioxane. Chlorosulfonic acid may be substituted for sulfur trioxide in preparing the addition product reactant.

U.S. Patent 2,060,254, issued November 10, 1936, to Siebenburger, discloses a process for reacting unsaturated fatty alcohols with the addition compound of sulfur trioxide and a liquid organic base, in the presence of excess organic base, to form sulfuric acid esters of said alcohols. The sulfuric acid esters are prepared in a condition free from other sulfonation products, such as are formed by replacement of a hydrogen atom by an SO3H group or by addition of a sulfuric acid residue at an unsaturated linkage.

U.S. Patent 2,075,914, issued April 6, 1937, to Snoddy et al., discloses a process for sulfating unsaturated alcohols with reagents prepared by (a) reacting sulfur trioxide with a metal chloride, or (b) reacting chlorosulfonic acid with a metal chloride or a metal sulfate.

Processes for sulfating ethoxylated compounds are also known in the art. U.S. Patent 4,464,292, issued August 7, 1984, to Lengyel, discloses a process for the preparation of mixed ethoxylated alcohol/ethoxy sulfate surfactants wherein an initial
mixture containing an ethoxylated alcohol and either an alkyl alcohol or an alkylaryl alcohol is partially sulfated, preferably effecting a 50 to 80% conversion to form the corresponding sulfates of the initial reactants.

U.S. Patent 3,687,999, issued August 29, 1972, to Kapur et al., discloses a process for sulfating ethoxylated long chain aliphatic alcohols or ethoxylated alkylphenols in the presence of a small or minor amount of borohydride.

U.S. Patent 3,565,939, issued February 23, 1971, to Beiser, discloses the preparation of sulfuric acid esters of ethoxylated alcohols by sulfation of said ethoxylated alcohols with sulfation agents such as H₂SO₄, SO₃, and chlorosulfonic acid.

The co-sulfation process of the present invention produces a reaction product mixture containing an unsaturated fatty acid sulfate and an alkyl ethoxylated acid sulfate, which mixture may be neutralized to form a mixed surfactant system containing the salts of said acid sulfates. Compositions containing ethoxylated sulfates in admixture with other ingredients as well as compositions containing unsaturated fatty alcohol sulfates in admixture with other ingredients are known in the art as well.

U.S. Patent 3,676,374, issued July 11, 1972, to Zaki et al., discloses a liquid detergent composition comprising an alkane sulfonate, an alpha-olefin sulfonate, or mixtures thereof; an ethoxylated alcohol or an alkyl phenol sulfate thereof; and an enzyme.

U.S. Patent 4,671,895, issued June 9, 1987, to Erilli et al., discloses a liquid detergent composition based on paraffin sulfonate; ethoxylated higher alcohol sulfate; nonionic surfactant; and a small amount of an alcohol sulfate.

U.S. Patent 3,979,340, issued September 7, 1976, to Klisch et al., discloses liquid detergent compositions containing a mixture of an olefin sulfonate; an alkyl ethoxamer sulfate salt; and an alkanolamide foam booster.

U.S. Patent 3,852,221, issued December 3, 1974, to Bentley, discloses a liquid detergent composition containing an olefin sulfonate; an alcohol ether sulfate; a substituted fatty acid
amide component; a sulfonated hydrotrope; a monohydric water-
miscible alcohol; and water.

U.S. Patent 4,102,826, issued July 25, 1978, to Renaud,
discloses a liquid detergent which contains a C14 and/or C15
paraffin monosulfonate, most preferably with a supplementary
anionic detergent such as a sulfated ethoxylate of a higher fatty
alcohol, and a higher fatty acid lower monoalkanolamide, in an
aqueous medium.

U.S. Patent 4,052,342, issued October 4, 1977, to Fernley et
al., discloses detergent compositions containing low crystalline
fraction secondary alkyl sulfates derived from C10-C18 olefins and
alcohol ethoxy sulfates and/or alcohol ethoxylates.

U.S. Patent 4,412,945, issued November 1, 1983, to Takahashi
et al., discloses a high concentration surfactant slurry
containing at least 50 wt. % of a higher alcohol ethoxylate
sulfate salt and a polyoxyethylene alkyl ether having an average
molecular weight of about 4,000 to 10,000 and an alkyl group of
8-16 carbon atoms.

None of the above referenced reactions, however, disclose a
cosulfation process wherein an unsaturated fatty alcohol and an
alkyl ethoxylated alcohol are sulfated together to provide a mixed
product system containing an alkyl ethoxylated acid sulfate and an
unsaturated fatty acid sulfate. It is therefore an object of the
present invention to provide such a process.

It is another object of the present invention to provide such
a co-sulfation process wherein conventional industrial sulfating
agents may be used and in which the reaction conditions are not
prohibitive to industrial scale-up.

These objects are realized by the present invention.

SUMMARY OF THE INVENTION

The present invention is directed to a process for preparing
a mixed product system which can be neutralized to form a mixed
surfactant system, said process comprising reacting a mixture of
an unsaturated fatty alcohol of the formula R-OH, wherein R is a
straight- or branched-chain C8-C22 alkenyl group, and an alkyl
ethoxylated alcohol of the formula R^1(OCH₂CH₂)_nOH, wherein R^1 is a C₈-C₂₀ alkyl group and n is an integer from 1 to 10, inclusive, with a sulfating agent, wherein the mole ratio of unsaturated fatty alcohol plus alkyl ethoxylated alcohol to sulfating agent ranges from about 1:1 to about 5:1, to form a mixed product system comprising an unsaturated fatty acid sulfate of the formula R-OΣO₃H and an alkyl ethoxylated acid sulfate of the formula R^1(OCH₂CH₂)_nOSO₃H.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the present invention, a co-sulfation process is described herein comprising sulfating a mixture of an unsaturated fatty alcohol and an alkyl ethoxylated alcohol with a sulfating agent to form a mixed product system containing an unsaturated fatty acid sulfate and an alkyl ethoxylated acid sulfate. This mixed product system may be neutralized to form a mixed surfactant system containing the neutralized salts of said acid sulfates.

In the co-sulfation process of the present invention, an unsaturated fatty alcohol reactant of the formula R-OH, wherein R is a straight- or branched-chain C₆-C₂₂ alkenyl group, preferably a C₁₅-C₂₁ straight-chain alkenyl group, most preferably an oleyl group, is sulfated together with an alkyl ethoxylated alcohol of the formula R^1(OCH₂CH₂)_nOH, wherein R^1 is a C₈-C₂₀ alkyl group, preferably a C₁₀-C₁₆ alkyl group, most preferably a C₁₀ alkyl group, and n is an integer from 1 to 10, inclusive, preferably from 3 to 8, inclusive, most preferably about 5. It is important to note that the R group of the unsaturated fatty alcohol reactant is not an aromatic compound, nor does it contain any pendent aromatic groups.

Any monounsaturated or polyunsaturated fatty alcohol may be sulfated in the co-sulfation process of the present invention. Examples of unsaturated fatty alcohol compounds useful as reactants in the process of the present invention include, but are not limited to, oleyl alcohol, cis-11-hexadecen-1-ol, 3,7,11,15-tetra-methyl-2-hexadecen-1-ol, cis-7-tetradecen-1-ol, and elaidyl alcohol, with oleyl alcohol being most preferred.
Although any alkyl ethoxylated alcohol may be sulfated in the co-sulfation process of the present invention, it is necessary that there be at least one ethoxy group in the alkyl ethoxylated alcohol molecule for each mole of sulfating agent. Examples of alkyl ethoxylated alcohol compounds useful as reactants in the process of the present invention include, but are not limited to, CH₃(CH₂)₁₁(OCH₂CH₂)₃OH, CH₃(CH₂)₁₅(OCH₂CH₂)₄OH, CH₃(CH₂)₉(OCH₂CH₂)₅OH, CH₃(CH₂)₁₇(OCH₂CH₂)₂OH and CH₃(CH₂)₁₃(OCH₂CH₂)₇OH, with the alkyl ethoxylated alcohol compound of the formula CH₃(CH₂)₉(OCH₂CH₂)₅OH being most preferred.

Numerous sulfating agents known to those skilled in the art can be used to sulfate the alkyl ethoxylated alcohol and unsaturated fatty alcohol reactants of the present invention. Examples of specific agents believed to be useful herein include sulfuric acid, sulfur trioxide, chlorosulfonic acid, sodium methoxyethyl sulfate, sodium methoxyethoxy ethyl sulfate, oleum, pyridine-SO₃, and sulfamic acid. Preferred sulfating agents include sulfuric acid, chlorosulfonic acid and pyridine-SO₃, with sulfuric acid being most preferred.

The mole ratio of unsaturated fatty alcohol reactant plus alkyl ethoxylated alcohol reactant to sulfating agent ranges from about 1:1 to about 5:1, preferably from about 1:1 to about 3:1, most preferably at a mole ratio of about 1:1.

The reaction mixture of the present invention typically comprises from about 10% to about 35% by weight, more typically from about 15% to about 25% by weight, most typically about 22% by weight of unsaturated fatty alcohol reactant; from about 15% to about 50% by weight, more typically from about 25% to about 35% by weight, most typically about 31% by weight of alkyl ethoxylated alcohol reactant; and from about 10% to about 30% by weight, more typically from about 15% to about 20% by weight, most typically about 17% by weight of sulfating agent.

Although not necessarily preferred, a solvent may be included when preparing the reaction mixture. When the co-sulfation reaction is carried out in the presence of a solvent, the solvent
will typically comprise from about 10% to about 40% by weight, more typically from about 25% to about 35% by weight, most typically about 29% by weight of the reaction mixture. Solvents useful herein include ethers and other organic compounds. Examples of ether compounds useful as solvents in the present invention include dioxane, THF, diethyl ether, and other ethers. Examples of other organic compounds useful as solvents in the present invention include methylene chloride and hexane. The most preferred of these solvents is diethyl ether. It is important to note that alcohols cannot be used as solvents in the process of the present invention.

The co-sulfation reaction described above is carried out at temperatures typically ranging from about 0°C to about 80°C, more typically at temperatures ranging from about 20°C to about 60°C.

The co-sulfation reaction of the present invention is carried out for a period of time typically ranging from about 2 hours to about 8 hours, more typically from about 3 hours to about 6 hours, even more typically from about 3.5 hours to about 4.5 hours.

The co-sulfation reaction of the present invention will typically, although not necessarily, be carried out under a vacuum ranging from about 0.01 to about 0.1 mm Hg, more typically from about 0.04 mm Hg to about 0.06 mm Hg. The vacuum acts to remove water produced during sulfation reactions involving the preferred H₂SO₄ sulfating agent, together with any solvents utilized in the reaction, and thus maximizes product yield. An aspirator vacuum may also be used in the process of the present invention. This aspirator vacuum acts to remove certain products which may result from the co-sulfation reaction of the present invention (e.g., HCl which is produced when chlorosulfonic acid is used as a sulfating agent). The aspirator vacuum may also act to remove any solvent utilized in the reaction.

The mixed product system resulting from the co-sulfation process of the present invention typically comprises from about 20% to about 35% by weight, most typically about 35% by weight of an unsaturated fatty acid sulfate of the formula R-OSO₃H, wherein R is as hereinbefore defined; from about 25% to about 45% by
weight, most typically about 45% by weight of an alkyl ethoxylated acid sulfate of the formula R¹(OCH₂CH₂)ₙOSO₃H, wherein R¹ and n are as hereinbefore defined; from 0% to about 30% by weight, typically from 0% to about 10% by weight, most typically 0% by weight of solvent; and less than 40% by weight, more typically less than 30% by weight, most typically about 20% by weight of the initial reactants and reaction by-products. The mixed product system resulting from the process of the present invention will typically not contain any solvent because any solvent present will be evacuated by the vacuum under which the reaction is typically carried out.

As will be appreciated by one skilled in the art, the particular reaction conditions of the process of the present invention will be dependent upon the particular reactants and sulfating agents being utilized, and will also be interdependent upon each other.

In the process of the present invention, sulfation of the unsaturated fatty alcohol reactant occurs primarily at the hydroxyl group. Typically, about 90%, more typically about 95%, most typically in excess of 99% of the initial unsaturated alcohol reactant is sulfated at its hydroxyl group. While not intending to be bound by theory, it is believed that the presence of the alkyl ethoxylated alcohol co-reactant exerts a moderating effect on the unsaturated fatty alcohol sulfation reaction, thus beneficially inhibiting sulfonation side reactions and reactions at the double bond of the unsaturated alcohol. An additional benefit associated with the presence of the ethoxylated alcohol reactant and its acid sulfate product is that substantially no isomerization of the unsaturated fatty acid sulfate product to the elaidyl compound occurs. A further benefit of the present invention is that the mixed product system resulting from the instant co-sulfation process may be used upon neutralization in most product applications without further processing.

In the most preferred embodiment of the present invention, equimolar quantities of oleyl alcohol and CH₃(CH₂)₉(OCH₂CH₂)₅OH
are sulfated together. An equivalent amount of sulfuric acid sulfating agent is used to sulfate these alcohol reactants in the presence of an ether solvent, thus forming a mixed product system containing oleyl acid sulfate and CH₃(CH₂)₉(OCH₂CH₂)₅OSO₃H. The co-sulfation reactions of this most preferred embodiment of the present invention are carried out at a temperature ranging from about 40°C to about 50°C, for a period of about 4 hours, and under a vacuum of about 0.05 mm Hg. 
These co-reactions proceed as follows:

\[
\text{oleyl-OH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{oleyl-OSO}_3\text{H} + \text{H}_2\text{O}
\]

\[
\text{CH}_3(\text{CH}_2)_9(\text{OCH}_2\text{CH}_2)_5\text{OH} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{CH}_3(\text{CH}_2)_9(\text{OCH}_2\text{CH}_2)_5\text{OSO}_3\text{H} + \text{H}_2\text{O}
\]

The products of the co-sulfation process of this invention tend to be unstable and therefore should be neutralized by methods known to one skilled in the art to form salts of the prepared acid sulfates. Examples of neutralizing agents useful in forming such salts include those containing alkali metal or amine groups. Such neutralized salts are useful as surfactants.

The neutralized mixed product system of the process of the present invention may be used in laundry detergent compositions, as described herein.

**DETERGENT COMPOSITIONS**

Laundry care compositions may be prepared containing the neutralized product of the process of the present invention. Such compositions are especially suitable for textile laundering operations. Both solid and liquid detergent compositions can be prepared using the neutralized reaction product of this invention. Such composition typically contain from about 1% by weight to about 40% by weight of the neutralized product of this invention.

**Optional Detergent Components**

Laundry care compositions prepared using the neutralized product of the process of the present invention can also contain conventional detergent components and adjuvants at their art-established levels.
Detergents Surfactants

The surfactant component can comprise as little as about 1% of the laundry care compositions herein, but preferably the compositions will contain from about 5% to about 40%, more preferably from about 10% to about 30%, of surfactant.

Combinations of anionic (preferably linear alkyl benzene sulfonates) and nonionic (preferably alkyl polyethoxylated alcohols) surfactants are preferred for optimum combined cleaning and textile softening performance, but other classes of surfactants, such as semi-polar, ampholytic, zwitterionic, and cationic may be used. Mixtures of these surfactants can also be used.

A. Nonionic Detergent Surfactants

Suitable nonionic detergent surfactants are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, at column 13, line 14 through column 16, line 6, incorporated herein by reference. Classes of useful nonionic surfactants include:

1. The polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, the ethylene oxide being present in an amount equal to from about 5 to about 25 moles of ethylene oxide per mole of alkyl phenol. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of phenol; dodecyl phenol condensed with about 12 moles of ethylene oxide per mole of phenol; dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol; and dioisoctyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol. Commercially available non-ionic surfactants of this type include Igepal™ CO-630, marketed by the GAF Corporation; and Triton™ X-45, X-114, X-100, and X-102, all marketed by the Rohm & Haas Company.

2. The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl
chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Particularly preferred are the condensation products of alcohols having an alkyl group containing from about 10 to about 20 carbon atoms with from about 4 to about 10 moles of ethylene oxide per mole of alcohol. Examples of such ethoxylated alcohols include the condensation product of myristyl alcohol with about 10 moles of ethylene oxide per mole of alcohol; and the condensation product of coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from 10 to 14 carbon atoms) with about 9 moles of ethylene oxide. Examples of commercially available nonionic surfactants of this type include Tergitol™ 15-S-9 (the condensation product of C_{11}-C_{15} linear alcohol with 9 moles ethylene oxide), Tergitol™ 24-L-6 NMM (the condensation product of C_{12}-C_{14} primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; Neodol™ 45-9 (the condensation product of C_{14}-C_{15} linear alcohol with 9 moles of ethylene oxide), Neodol™ 23-6.5 (the condensation product of C_{12}-C_{13} linear alcohol with 6.5 moles of ethylene oxide), Neodol™ 45-7 (the condensation product of C_{14}-C_{15} linear alcohol with 7 moles of ethylene oxide), Neodol™ 45-4 (the condensation product of C_{14}-C_{15} linear alcohol with 4 moles of ethylene oxide), marketed by Shell Chemical Company, and Kyro™ EOB (the condensation product of C_{13}-C_{15} alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company.

3. The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds has a molecular weight of from about 1500 to about 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation
product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially-available Pluronic™ surfactants, marketed by Wyandotte Chemical Corporation.

4. The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic™ compounds, marketed by Wyandotte Chemical Corporation.

5. Semi-polar nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms.

Preferred semi-polar nonionic detergent surfactants are the amine oxide surfactants having the formula

\[ \text{R}^2(\text{OR}^3)_{x}\text{N(\text{R}^4)}_2 \]

wherein R² is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms;
R^3 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^4 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^4 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

Preferred amine oxide surfactants are C_{10-18} alkyl dimethyl amine oxides and C_{8-12} alkoxy ethyl dihydroxy ethyl amine oxides.

6. Alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g., a polyglycoside, hydrophilic group containing from about 1.5 to about 10, preferably from about 1.5 to about 3, most preferably from about 1.6 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties. (Optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside.) The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6-positions on the preceding saccharide units.

Optionally, and less desirably, there can be a polyalkyleneoxide chain joining the hydrophobic moiety and the polysaccharide moiety. The preferred alkyleneoxide is ethylene oxide. Typical hydrophobic groups include alkyl groups, either saturated or unsaturated, branched or unbranched containing from about 8 to about 18, preferably from about 10 to about 16, carbon atoms. Preferably, the alkyl group is a straight chain saturated alkyl group. The alkyl group can contain up to about 3 hydroxy groups and/or the polyalkyleneoxide chain can contain up to about 10, preferably less than 5, alkyleneoxide moieties. Suitable alkyl polysaccharides are octyl, nonyldecyl, undecylododecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl, di-,
tri-, tetra-, penta-, and hexaglucosides, galactosides, lactosides, glucose, fructosides, fructose and/or galactoses. Suitable mixtures include coconut alkyl, di-, tri-, tetra-, and pentaglucosides and tallow alkyl tetra-, penta-, and hexaglucosides.

The preferred alkylpolyglycosides have the formula
$$R^5O(C_nH_{2n}O)_t(glycosyl)_x$$

wherein $R^5$ is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; $n$ is 2 or 3, preferably 2; $t$ is from 0 to about 10, preferably 0; and $x$ is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2- position.

7. Fatty acid amide surfactants having the formula:
$$\text{R}^6 - \text{C} - \text{N}(\text{R}^7)_2$$

wherein $\text{R}^6$ is an alkyl group containing from about 7 to about 21 (preferably from about 9 to about 17) carbon atoms and each $\text{R}^7$ is selected from the group consisting of hydrogen, C$_1$-C$_4$ alkyl, C$_1$-C$_4$ hydroxyalkyl, and -(C$_2$H$_4$O)$_x$H where $x$ varies from about 1 to about 3.

Preferred amides are C$_8$-C$_{20}$ ammonia amides, monoethanolamides, diethanolamides, and isopropanolamides.

B. Anionic Detergent Surfactants

Anionic detergent surfactants suitable for use in laundry care compositions containing the neutralized product of the present invention are generally disclosed in U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, at column
23, line 58 through column 29, line 23 and in U.S. Patent 4,294,710, Hardy et al., issued October 13, 1981, both of which are incorporated herein by reference. Classes of useful anionic surfactants include:

1. Ordinary alkali metal soaps, such as the sodium, potassium, ammonium and alkylammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms, preferably from about 10 to about 20 carbon atoms. Preferred alkali metal soaps are sodium laurate, sodium stearate, sodium oleate and potassium palmitate.

2. Water-soluble salts, preferably the alkali metal, ammonium and alkylammonium salts, of organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 10 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.)

Examples of this group of anionic surfactants are the sodium and potassium alkylbenzene sulfonates in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in U.S. Patent 2,220,099, Guenther et al., issued November 5, 1940, and U.S. Patent 2,477,383, Lewis, issued December 26, 1946. Especially useful are linear straight chain alkylbenzene sulfonates in which the average number of carbon atoms in the alkyl group is from about 11 to about 13, abbreviated as C₁₁₋₁₃ LAS.

Other anionic surfactants include sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 carbon atoms.

Also included are water-soluble salts of esters of alpha-
sulfonated fatty acids containing from about 6 to about 20 carbon atoms in the fatty acid group and from about 1 to about 10 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from about 2 to about 9 carbon atoms in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl sulfates (AS) containing from about 10 to about 20 carbon atoms in the alkyl group; sulfates such as those of the formula R^8O(C_2H_4O)_mSO_3M, wherein R^8 is a C_{10}-C_{16} alkyl (preferred) or hydroxyalkyl group, m is from about 0.5 to about 4, and M is a compatible cation water-soluble salts of olefin sulfonates containing from about 12 to about 24 carbon atoms; and betaalkyloxy alkane sulfonates containing from about 1 to about 3 carbon atoms in the alkyl group and from about 8 to about 20 carbon atoms in the alkane moiety. Useful alkylether sulfates are described in detail in U.S. Patent 4,807,219, to Hughes, issued March 26, 1985, which is incorporated herein by reference. The above surfactant preferably represent from about 8% to about 18%, by weight (on an acid basis) of the composition, more preferably from about 9% to about 14%.

Preferred alkyletheroxylated sulfate surfactants of the above formula are those wherein the R^8 substituent is a C_{12}-C_{15} alkyl group and m is from about 1.5 to about 3. Examples of such materials are C_{12}-C_{15} alkyl polyethoxylate (2.25) sulfate (C_{12}-15E_{2.25}S); C_{14}-15E_{2.25}S; C_{12}-13E_{1.5}S; C_{14}-15E_{3}S; and mixtures thereof.

Particularly preferred surfactants for use in liquid detergent composition are linear C_{11} to C_{13} alkyl benzene sulfonates, alkyl sulfates, and alkyletheroxylated sulfates (anionic) and C_{12} to C_{13} alkyl polyethoxylated alcohols (nonionic) and mixtures thereof. Liquid detergent compositions which contain alkyl and/or alkyletheroxylated sulfates as detergent surfactants preferably comprise no more than about 5% of such detergent surfactants, and the anionic compound of the ion-pair complex is most preferably a C_{11}-C_{13} LAS or benzene sulfonate. Particularly preferred surfactants for use in granular detergents are the
linear C_{11}-C_{13} alkyl benzene sulfonates and the C_{8}-C_{18} alkyl sulfates and mixtures thereof. Most preferred are mixtures of these two anionic surfactants in a weight ratio of linear alkyl benzene sulfonate to alkyl sulfate is from about 0.5:1 to about 3:1 and more preferably from about 0.5:1 to about 2:1.

3. Anionic phosphate surfactants.
4. N-alkyl substituted succinamates.

C. Ampholytic Surfactants

Ampholytic surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 18 carbon atoms and at least one of the aliphatic substituents contains an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate. See U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, column 19, line 38 through column 22, line 48, incorporated herein by reference, for examples of ampholytic surfactants useful herein.

D. Zwitterionic Surfactants

Zwitterionic surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent 3,929,678, Laughlin et al., issued December 30, 1975, column 19, line 38 through column 22, line 48, incorporated herein by reference, for examples of zwitterionic surfactants useful herein.

E. Cationic Surfactants

Cationic surfactants are also useful in laundry care compositions containing the neutralized product of the process of the present invention. Cationic surfactants comprise a wide variety of compounds characterized by one or more organic hydrophobic groups in the cation and generally by a quaternary nitrogen associated with an acid radical. Nitrogen ring compounds are also considered quaternary nitrogen compounds. Suitable
anions are halides, methyl sulfate and hydroxide. Tertiary amines can have characteristics similar to cationic surfactants at washing solutions pH values less than about 8.5.

Suitable cationic surfactants include the quaternary ammonium surfactants having the formula:

$$[R^9(OR^{10})_y][R^{11}(OR^{10})_y]_2R^{12}N^+X^-$$

wherein $R^9$ is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain; each $R^{10}$ is independently selected from the group consisting of $-\text{CH}_2\text{CH}_2-, -\text{CH}_2\text{CH(CH}_3)-, -\text{CH}_2\text{CH(CH}_2\text{OH})-, -\text{CH}_2\text{CH}_2\text{CH}_2-$; each $R^{11}$ is independently selected from the group consisting of $\text{C}_1-\text{C}_4$ alkyl, $\text{C}_1-\text{C}_4$ hydroxyalkyl, benzyl, ring structures formed by joining the two $R^{11}$ groups, $-\text{CH}_2\text{CHOHCHOHCO}_3\text{CHOHCH}_2\text{OH}$ wherein $R^{13}$ is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when $y$ is not 0; $R^{12}$ is the same as $R^{11}$ or is an alkyl chain wherein the total number of carbon atoms of $R^9$ plus $R^{12}$ is not more than about 18; each $y$ is from 0 to about 10 and the sum of the $y$ values is from 0 to about 15; and $X$ is any compatible anion.

Preferred examples of the above compounds are the alkyl quaternary ammonium surfactants, especially the mono-long chain alkyl surfactants described in the above formula when $R^{12}$ is selected from the same groups as $R^{11}$. The most preferred quaternary ammonium surfactants are the chloride, bromide and methylsulfate $C_8-C_{16}$ alkyl trimethylammonium salts, $C_8-C_{16}$ alkyl di(hydroxyethyl)methylammonium salts, the $C_8-C_{16}$ alkyl hydroxyethylidimethylammonium salts, and $C_8-C_{16}$ alkylxypropyltrimethylammonium salts. Of the above, decyl trimethylammonium methylsulfate, lauryl trimethylammonium chloride, myristyl trimethylammonium bromide and coconut trimethylammonium chloride and methylsulfate are particularly preferred.

A more complete disclosure of these and other cationic surfactants useful herein can be found in U.S. Patent 4,228,044, Cambre, issued October 14, 1980, incorporated herein by reference.

Detergent Builders

Laundry care compositions containing the neutralized product
of the process of the present invention can also contain inorganic and/or organic detergent builders to assist in mineral hardness control. These builders comprise from 0% to about 80% by weight of the compositions. Liquid formulations preferably comprise from about 5% to about 50%, more preferably about 5% to about 30%, by weight of detergent builder. Granular formulations preferably comprise from about 10% to about 80%, more preferably from about 24% to about 80% by weight of the detergent builder.

Useful water-soluble organic builders for granular and liquid compositions include the various alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates and polyhydroxysulfonates. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citrate. The citrate (preferably in the form of an alkali metal or alkanolammonium salt) is generally added to the composition as citric acid, but can be added in the form of a fully neutralized salt.

Highly preferred polycarboxylate builders are disclosed in U.S. Patent 3,308,067, Diehl, issued March 7, 1967, incorporated herein by reference. Such materials include the water-soluble salts of homo- and copolymers of aliphatic carboxylic acids such as maleic acid, itaconic acid, mesaconic acid, fumaric acid, aconitic acid, citraconic acid and methylene malonic acid.


A class of useful phosphorus-free detergent builder materials have been found to be ether polycarboxylates. A number of ether polycarboxylates have been disclosed for use as detergent builders. Examples of useful ether polycarboxylates include oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972, both of which are incorporated herein by reference.
A specific type of ether polycarboxylates useful as builders in the present invention are those having the general formula:

\[
\begin{array}{c}
\text{A-CH} \quad \text{CH} \quad \text{O} \quad \text{CH} \quad \text{CH}-B \\
\text{COOX} \quad \text{COOX} \quad \text{COOX} \quad \text{COOX}
\end{array}
\]

wherein A is H or OH; B is H or \(-\text{CH-CH}_2\); and

\[
\begin{array}{c}
\text{COOX} \quad \text{COOX}
\end{array}
\]

X is H or a salt-forming cation. For example, if in the above general formula A and B are both H, then the compound is oxydi-succinic acid and its water-soluble salts. If A is OH and B is H, then the compound is tartrate monosuccinic acid (TMS) and its water-soluble salts. If A is H and B is

\[
\begin{array}{c}
\text{O-CH} \quad \text{CH}_2, \\
\text{COOX} \quad \text{COOX},
\end{array}
\]

then the compound is tartrate disuccinic acid (TDS) and its water-soluble salts. Mixtures of these builders are especially preferred for use herein. Particularly preferred are mixtures of TMS and TDS in a weight ratio of TMS to TDS of from about 97:3 to about 20:80. These builders are disclosed in U.S. Patent 4,663,071, issued to Bush et al., on May 5, 1987.

Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903, all of which are incorporated herein by reference.

Other useful detergency builders include the ether hydroxy-polycarboxylates represented by the structure:
wherein M is hydrogen or a cation wherein the resultant salt is water-soluble, preferably an alkali metal, ammonium or substituted ammonium cation, n is from about 2 to about 15 (preferably n is from about 2 to about 10, more preferably n averages from about 2 to about 4) and each R14 is the same or different and selected from hydrogen, C1-4 alkyl or C1-4 substituted alkyl (preferably R14 is hydrogen).

Also suitable in such laundry care compositions are the 3,3-dicarboxy-4-oxa-1,6-hexanedicarboxylic acids and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986, incorporated herein by reference. Other useful builders include the C5-C20 alkyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenyloxysuccinic acid.

Useful builders also include sodium and potassium carboxymethylxymalonic acid, carboxymethylxysuccinate, cis-cyclohexanehexacarboxylate, cis-cyclopentanetetracarboxylate phloroglucinol trisulfonate, water-soluble polyacrylates (having molecular weights of from about 2,000 to about 200,000, for example), and the copolymers of maleic anhydride with vinyl methyl ether or ethylene.

Other suitable polycarboxylates are the polyacetal carboxylates disclosed in U.S. Patent 4,144,226, Crutchfield et al., issued March 13, 1979, incorporated herein by reference. These polyacetal carboxylates can be prepared by bringing together, under polymerization conditions, an ester of glyoxyllic acid and a polymerization initiator. The resulting polyacetal carboxylate ester is then attached to chemically stable end groups to stabilize the polyacetal carboxylate against rapid
depolymerization in alkaline solution, converted to the corresponding salt, and added to a surfactant.

Especially useful builders include alkyl succinates of the general formula R^{15}\text{-CH(COOH)CH}_2(COOH)\text{i.e., derivatives of succinic acid, wherein } R^{15} \text{ is hydrocarbon, e.g., C}_{10}-C_{20} \text{ alkyl or alkenyl, preferably C}_{12}-C_{16} \text{ or wherein } R^{15} \text{ may be substituted with hydroxyl, sulfo, sulfoxy or sulfone substituents, all as described in the above-mentioned patents.}

The succinate builders are preferably used in the form of their water-soluble salts, including the sodium, potassium, ammonium and alkanoammonium salts.

Specific examples of succinate builders include: lauryl succinate, myristyl succinate, palmityl succinate, 2-dodecenyl succinate (preferred), 2-pentadecenyl succinate, and the like.

Other useful detergency builders include the C_{10}-C_{18} alkyl monocarboxylic (fatty) acids and salts thereof. These fatty acids can be derived from animal and vegetable fats and oils, such as tallow, coconut oil and palm oil. Suitable saturated fatty acids can also be synthetically prepared (e.g., via the oxidation of petroleum or by hydrogenation of carbon monoxide via the Fisher-Tropsch process). Particularly preferred C_{10}-C_{18} alkyl monocarboxylic acids are saturated coconut fatty acids, palm kernel fatty acids, and mixtures thereof.

**Chelating Agents**

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

Amino carboxylates useful as optional chelating agents in compositions of the invention have one or more, preferably at
least two, units of the substructure

\[
\begin{align*}
\text{N} - (\text{CH}_2)^x - \text{COOM}, \\
\text{N} - (\text{CH}_2)^x - \text{PO}_3\text{M}_2,
\end{align*}
\]

wherein M is hydrogen, alkali metal, ammonium or substituted ammonium (e.g. ethanolamine) and x is from 1 to about 3, preferably 1. Preferably, these amino carboxylates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms. Operable amine carboxylates include ethylenediaminetetraacetates, N-hydroxyethylethylene diaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, diethylenetriaminepentaacetates, and ethanol diglycines, alkali metal, ammonium, and substituted ammonium salts thereof and mixtures thereof.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions. Compounds with one or more, preferably at least two, units of the substructure

\[
\begin{align*}
\text{N} - (\text{CH}_2)^x - \text{PO}_3\text{M}_2,
\end{align*}
\]

wherein M is hydrogen, alkali metal, ammonium or substituted ammonium and x is from 1 to about 3, preferably 1, are useful and include ethylenediaminetetrakis (methylene phosphonates), nitrilotris (methylene phosphonates) and diethylenetriaminepentakis (methylene phosphonates). Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms. Alkylene groups can be shared by substructures.
Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. These materials comprise compounds having the general formula

![Chemical Structure](image)

wherein at least one $R^{16}$ is -SO$_3$H or -COOH or soluble salts thereof and mixtures thereof. U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al., incorporated herein by reference, discloses polyfunctionally-substituted aromatic chelating and sequestering agents. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes and 1,2-dihydroxy-3,5-disulfobenzene or other disulfonated catechols in particular.

Alkaline detergent compositions can contain these materials in the form of alkali metal, ammonium or substituted ammonium (e.g. mono- or triethanolamine) salts.

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

**Soil Release Agent**

Polymeric soil release agents useful in the present invention include cellulosic derivatives such as hydroxyether cellulosic polymers, copolymeric blocks of ethylene terephthalate and polyethylene oxide or polypropylene oxide terephthalate, and cationic guar gums, and the like.

The cellulosic dérivatives that are functional as soil release agents are commercially available and include hydroxyethers of cellulose such as Methocel® (Dow) and cationic
cellulose ether derivatives such as Polymer JR-124®, JR-400®, and JR-30M® (Union Carbide). See also U.S. Patent 3,928,213 to Temple et al., issued December 23, 1975, which is incorporated by reference.

Other effective soil release agents are cationic guar gums such as Jaguar Plau® (Stein Hall) and Gendrive 458® (General Mills).

Preferred cellulosic soil release agents for use herein are selected from the group consisting of methyl cellulose; hydroxypropyl methylcellulose; hydroxybutyl methylcellulose; or a mixture thereof, said cellulosic polymer having a viscosity in aqueous solution at 20°C of 15 to 75,000 centipoise.

A more preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. More specifically, these polymers are comprised of repeating units of ethylene terephthalate and PEO terephthalate in a mole ratio of ethylene terephthalate units to PEO terephthalate units of from about 25:75 to about 35:65, said PEO terephthalate units containing polyethylene oxide having molecular weights of from about 300 to about 2000. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976, which is incorporated by reference. See also U.S. Patent 3,893,929 to Basadur issued July 8, 1975 (incorporated by reference) which discloses similar copolymers. Surprisingly, it has been found that these polymeric soil release agents balance the distribution of the fabric care agent of the present invention against a broad range of synthetic fabrics such as polyesters, nylons, poly cottons and acrylics. This more uniform distribution of the fabric care agent can result in improved fabric care qualities.

Another preferred polymeric soil release agent is a crystallizable polyester with repeat units of ethylene terephthalate units containing 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxy-
ethylene glycol of average molecular weight 300-5,000, and the mole ratio of ethylene terephthalate units to polyoxyethylene terephthalate units in the crystallizable polymeric compound is between 2:1 and 6:1. Examples of this polymer include the commercially available material Zelcon® 5126 (from Dupont) and Milease® T (from ICI).

The foregoing polymers and methods of their preparation are more fully described in European Patent Application 185,417, Gosselin, published June 25, 1986, which is incorporated herein by reference.

If utilized, these soil release agents will generally comprise from about 0.01% to about 5.0% by weight of the detergent compositions herein, more preferably soil release agents will comprise from about 0.2% to about 3.0% by weight of such compositions.

Enzymes

Enzymes are a preferred optional ingredient and are incorporated in an amount of from about 0.025% to about 2%, preferably from about 0.05% to about 1.5% of the total composition. Preferred proteolytic enzymes should provide a proteolytic activity of at least about 5 Anson units (about 1,000,000 Delft units) per liter, preferably from about 15 to about 70 Anson units per liter, most preferably from about 20 to about 40 Anson units per liter. A proteolytic activity of from about 0.01 to about 0.05 Anson units per gram of product is desirable. Other enzymes, including amylolytic enzymes, are also desirably included in the present compositions.

Suitable proteolytic enzymes include the many species known to be adapted for use in detergent compositions. Commercial enzyme preparations such as Savinase™ and Alcalase™ sold by Novo Industries and Maxatase™ sold by Gist-Brocades, Delft, The Netherlands, are suitable. Other preferred enzyme compositions include those commercially available under the tradenames SP-72 (Esperase™) manufactured and sold by Novo Industries, A/S, Copenhagen, Denmark and AZ-Protease™ manufactured and sold by Gist-Brocades, Delft, The Netherlands.
Suitable amylases include Rapidase™ sold by Gist-Brocades and Termamyl™ sold by Novo Industries.

A more complete disclosure of suitable enzymes can be found in U.S. Patent No. 4,101,457, Place et al., issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both incorporated herein by reference.

**Other Optional Detergent Ingredients**

Other optional ingredients which can be included in detergent compositions using the neutralized product of the present invention, in their conventional art-established levels for use (generally from 0 to about 20%), include solvents, hydroterpnes, solubilizing agents, suds suppressors, processing aids, soil-suspending agents, corrosion inhibitors, dyes, fillers, optical brighteners, germicides, pH adjusting agents (monoethanolamine, sodium carbonate, sodium hydroxide, etc.), enzyme-stabilizing agents, bleaches, bleach activators, clay fabric softeners, perfumes, and the like.

**Product Formulations**

1. Liquid Compositions

Liquid detergent compositions containing the neutralized product of the process of the present invention can contain water and other solvents. Small quantities of low molecular weight primary or secondary alcohols, exemplified by methanol, ethanol, propanol, and isopropanol, are suitable solvents. Liquid compositions may comprise the neutralized product of the process of the present invention as the only fabric care agent, or this agent may be combined with other fabric care agents. The active components of the liquid composition may primarily be fabric conditioning agents, may include detergent ingredients such as those disclosed herein, and may include other cleaning, conditioning, or other ingredients not specifically listed herein.

With liquid detergent compositions it is preferred to include monohydric alcohols for solubilizing the surfactant, but polyols containing from about 2 to about 6 carbon atoms and from about 2 to about 6 hydroxy groups can be used and can provide improved enzyme stability (if enzymes are included in the composition).
Examples of polyols include propylene glycol, ethylene glycol, glycerine and 1,2-propanediol. Propylene glycol is a particularly preferred alcohol.

Other optional components of these liquid conditioning compositions of this type are conventional in nature, and generally comprise from about 0.1% to about 20% by weight of the composition. Such optional components for fabric conditioners include, but are not limited to, colorants, perfumes, bacterial inhibitors, optical brighteners, opacifiers, viscosity modifiers, fabric absorbency boosters, emulsifiers, stabilizers, shrinkage controllers, spotting agents, germicides, fungicides, anti-corrosion agents and the like.

The ratios of water and other solvents in the compositions will be determined in part by the resulting state of the fabric care agent. At ambient temperatures, the fabric care agent must be substantially insoluble in the product, and within the particle size specifications heretofore discussed. This will place restrictions upon the selection of solvents and solvent levels in the compositions.

The liquid fabric conditioning compositions of the present invention can be prepared by conventional methods.

2. Granular Compositions

Granular detergent compositions may comprise the neutralized product of the process of the present invention as the only fabric conditioning agent, or this agent may be combined with other fabric conditioning agents. The active components of the granular composition may primarily be fabric conditioning agents, may include detergent ingredients such as those disclosed herein, and may include cleaning, conditioning, or other ingredients not specifically listed herein.

Granular detergent compositions embodying the present invention can be formed by conventional techniques, i.e., by slurrying the individual components (with the exception of the ion-pair complex) in water and then atomizing and spray-drying the resultant mixture, or by pan or drum agglomeration of the ingredients.
In a laundry method aspect of the invention, typical laundry wash water solutions comprise from about 0.1% to about 2% by weight of the detergent compositions of the invention. Fabrics to be laundered are agitated in these solutions to effect cleaning, stain removal, and fabric care benefits.

The conditioning agents of the invention are particularly suitable for laundry use, but are also suitable as a hair conditioning component in shampoos and hair conditioning compositions.

The foregoing description fully describes the nature of the present invention. The following examples are presented for the purpose of illustrating the invention. The scope of the invention is to be determined by the claims, which follow the examples.

All parts, percentages and ratios herein are by weight unless otherwise specified.

**EXAMPLE I**

A mixed product system containing an unsaturated fatty acid sulfate compound and an alkyl ethoxylated acid sulfate is prepared as follows: A mixture of 2.05 g of 96.4% sulfuric acid and 5 ml diethyl ether is cooled with an ice bath to 0°C while adding 3.78 g of CH$_3$(CH$_2$)$_g$(OCH$_2$CH$_2$)$_5$OH and 2.68 g of oleyl alcohol. The ice bath is then removed and the ether is evaporated under aspirator vacuum. The reaction is next heated to a temperature of 40-50°C for a period of 4 hours while under a vacuum of 0.05 mm Hg. The mixed product system contains oleyl-OSO$_3$H, CH$_3$(CH$_2$)$_g$(OCH$_2$CH$_2$)$_5$OSO$_3$H and starting material, with no discernible contamination due to reaction side-products.

**EXAMPLE II**

A process identical to that in Example I above, except the acid sulfate compounds contained in the mixed product system are treated further by being taken up in 50 ml ethanol and neutralized with 25 ml 1N NaOH. The final neutralized composition of this further treatment is a mixed surfactant system containing oleyl-OSO$_3$Na, CH$_3$(CH$_2$)$_g$(OCH$_2$CH$_2$)$_5$OSO$_3$Na and starting material, with no discernible contamination due to reaction side-products.
EXAMPLE III

A mixed product system containing an unsaturated fatty acid sulfate compound and an alkyl ethoxylated acid sulfate is prepared as follows: A mixture of 2.05 g of 96.4% sulfuric acid and 5 ml diethyl ether is cooled with an ice bath to 0°C while adding 3.78 g of CH₃(CH₂)₉(OCH₂CH₂)₅OH and 2.40 g of cis-11-hexadecen-1-ol. The ice bath is then removed and the ether is evaporated under aspirator vacuum. The reaction is next heated to a temperature of 500°C for a period of 4 hours while under a vacuum of 0.05 mm Hg. The mixed product system contains CH₃(CH₂)₃CH=CH(CH₂)₁₀SO₃H, CH₃(CH₂)₉(OCH₂CH₂)₅OSO₃H and starting material, with no discernible contamination due to reaction side-products.

EXAMPLE IV

A process identical to that in Example III above, except the acid sulfate compounds contained in the mixed product system are treated further by being taken up in 50 ml ethanol and neutralized with IN NaOH. The final neutralized composition of this further treatment is a mixed surfactant system containing CH₃(CH₂)₃CH=CH(CH₂)₁₀SO₃Na, CH₃(CH₂)₉(OCH₂CH₂)₅SO₃Na and starting material, with no discernible contamination due to reaction side-products.

EXAMPLE V

A mixed product system containing an unsaturated fatty acid sulfate compound and an alkyl ethoxylated acid sulfate is prepared as follows: A mixture of 3.78 g of CH₃(CH₂)₉(OCH₂CH₂)₅OH and 2.96 g of 3,7,11,15-tetramethyl-2-hexadecen-1-ol in 25 ml diethyl ether is cooled with an ice bath to 0°C while 2.33 g of chlorosulfonic acid is added dropwise. The ice bath is removed and the reaction stirred at ambient temperature for 2 hours. The ether is evaporated under aspirator vacuum. The mixed product system contains CH₃[CH(CH₃)(CH₂)₃]C(CH₃)=CHCH₂SO₃H, CH₃(CH₂)₉(OCH₂CH₂)₅OSO₃H and starting material, with no discernible contamination due to products resulting from side reactions with the 3,7,11,15-tetramethyl-2-hexadecen-1-ol reactant. Note that HCl will be one product resulting from the co-sulfation reactions between the particular reactants of this example. Substantially all of this HCl will be removed by the aspirator vacuum.
EXAMPLE VI

A process identical to that in Example V above, except the acid sulfate compounds contained in the mixed product system are treated further by being taken up in 50 ml ethanol and neutralized with 1N NaOH. The final neutralized composition of this further treatment is a mixed surfactant system containing \( \text{CH}_3[\text{CH}(\text{CH}_3)(\text{CH}_2)_3\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OSO}_3\text{Na} \), \( \text{CH}_3(\text{CH}_2)_9(\text{OCH}_2\text{CH}_2)_5\text{OSO}_3\text{Na} \) and starting material, with no discernible contamination due to reaction side-products. Sodium chloride may result from this neutralization step. The sodium chloride may be removed by methods known to those skilled in the art.

EXAMPLE VII

A mixed product system containing an unsaturated fatty acid sulfate compound and an alkyl ethoxylated acid sulfate is prepared as follows: A mixture of 3.78 g of \( \text{CH}_3(\text{CH}_2)_9(\text{OCH}_2\text{CH}_2)_5\text{OH} \) and 2.12 g of cis-7-tetradecen-1-ol in 25 ml diethyl ether is stirred at 0°C while adding 3.18 g of pyridine·\text{SO}_3. The reaction is stirred 1 hr. at ambient temperature and then the ether is evaporated under aspirator vacuum. The mixed product system contains \( \text{CH}_3(\text{CH}_2)_9\text{CH}=\text{CH(\text{CH}_2)_6\text{OSO}_3\text{H·pyridine}}, \)
\( \text{CH}_3(\text{CH}_2)_9(\text{OCH}_2\text{CH}_2)_5\text{OSO}_3\text{H·pyridine} \) and starting material, with no discernible contamination due to products resulting from side reactions with the cis-7-tetradecen-1-ol reactant.

EXAMPLE VIII

A process identical to that in Example VII above, except the acid sulfate compounds contained in the mixed product system are treated further by being taken up in 50 ml ethanol and neutralized with 1N NaOH. The final neutralized composition of this further treatment is a mixed surfactant system containing \( \text{CH}_3(\text{CH}_2)_9\text{CH}=\text{CH(\text{CH}_2)_6\text{OSO}_3\text{Na}}, \) \( \text{CH}_3(\text{CH}_2)_9(\text{OCH}_2\text{CH}_2)_5\text{OSO}_3\text{Na}, \) \( \text{H}_2\text{O}, \) pyridine and starting material, with no discernible contamination due to reaction side-products. The sulfate salts resulting from this neutralization step may be isolated from the pyridine and \( \text{H}_2\text{O} \) by methods known to those skilled in the art: e.g., crystallization from the pyridine.
1. A process comprising reacting a mixture of an unsaturated fatty alcohol of the formula R-OH, wherein R is an oleyl group, and an alkyl ethoxylated alcohol of the formula R\(^1\)(OCH\(_2\)CH\(_2\))\(_n\)OH, wherein R\(^1\) is a straight- or branched-chain C\(_{10}\) alkyl group, and n is an integer from 3 to 8, inclusive, with a sulfuri acid, wherein the mole ratio of unsaturated alcohol plus alkyl ethoxylated alcohol to sulfuri acid ranges from 1:1 to 3:1, to form a mixed product system comprising an unsaturated fatty acid sulfate of the formula R-OSO\(_3\)H and an alkyl ethoxylated acid sulfate of the formula R\(^1\)(OCH\(_2\)CH\(_2\))\(_n\)OSO\(_3\)H.

2. A process according to Claim 1 wherein n is 5.

3. A process according to Claim 2 wherein the mole ratio of unsaturated fatty alcohol reactant plus alkyl ethoxylated alcohol reactant to sulfating agent is 1:1.

4. A process according to Claim 3 wherein the reaction is carried out for a period of time ranging from 2 hours to 8 hours, preferably from 3 hours to 6 hours.

5. A process according to Claim 3 wherein the reaction between the unsaturated alcohol and the ether sulfate is carried out for a period of time ranging from 3.5 to 4.5 hours.

6. A process according to Claim 4 or 5 wherein the reaction is carried out at a temperature ranging from 0\(^\circ\)C to about 80\(^\circ\)C, preferably from 20\(^\circ\)C to 60\(^\circ\)C, more preferably from 40\(^\circ\)C to 50\(^\circ\)C.

7. A process according to Claim 5 or 6 wherein the reaction is carried out under a vacuum ranging from 0.01mmHg to 0.1mmHg, preferably from 0.04mmHg to 0.06mmHg.
8. A process according to Claim 3 wherein the mixed product system comprises from 20% to 35%, preferably 35% by weight of the unsaturated fatty acid sulfate compound of the formula R-OSO$_3$H and from 25% to 45%, preferably 45% by weight of the alkyl ethoxylated acid compound of the formula R'(OCH$_2$CH$_2$)$_n$OSO$_3$H.
INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER
According to International Patent Classification (IPC) or to both National Classification and IPC
IPC(5): C07C 305/10, 305/14
US CL.: 558/34, 558/36

II. FIELDS SEARCHED

Minimum Documentation Searched

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<th>Classification System</th>
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<td>US</td>
<td>558/34, 558/36</td>
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III. DOCUMENTS CONSIDERED TO BE RELEVANT

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<tr>
<th>Category</th>
<th>Citation of Document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to Claim No.</th>
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<tbody>
<tr>
<td>X</td>
<td>US, A, 4,464,292 (LENGYEL) 07 August 1984 See column 15.</td>
<td>1-8</td>
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<tr>
<td>X</td>
<td>US, A, 2,044,919 (SCHRAUTH) 23 June 1936 See column 2.</td>
<td>1-8</td>
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<td>X</td>
<td>N Chemical Abstracts, volume 75, No. 1, published 05 July 1971 (Columbus, Ohio, USA) The abstract no. 5154m, (DOMINIK NOWAK et al.), Sulfating of Unsaturated Aliphatic Alcohols by Gaseous Sulfur Trioxide, Przem. Chem., 1971, 50(4), 222-5.</td>
<td>1-8</td>
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* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
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  "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
  "Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search: 24 MAY 1991

Date of Mailing of this International Search Report: 25 JUN 1991

International Searching Authority: RO/US

Signature of Authorized Officer: NICKY CHAN