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(54) Title: ENHANCED OIL RECOVERY SYSTEMS AND CONSUMER PRODUCTS CONTAINING SECONDARY ALCOHOL DERIVATIVES

(57) Abstract: One embodiment of this invention is a composition and method of treating a hydrocarbon containing formation, comprising: (a) providing a composition to at least a portion of the hydrocarbon containing formation, wherein the composition comprises a secondary alcohol derivative; and (b) allowing the composition to interact with hydrocarbons in the hydrocarbon containing formation. Another embodiment is a composition produced from a hydrocarbon containing formation, comprising hydrocarbons from a hydrocarbon containing formation and a secondary alcohol derivative. Another embodiment is a personal care composition for topical application to the skin or hair comprising (a) a secondary alcohol derivative; and (b) a cosmetically-acceptable vehicle. Another embodiment is a personal care composition for topical application to the skin comprising (a) a secondary alcohol alkoxycarboxylate, preferably, ethoxycarboxylate, or alkoxysulfate, preferably, ethoxysulfate component; (b) at least one sunscreen; and (c) a cosmetically acceptable vehicle. Another embodiment is a shampoo composition for topical application to the skin or hair comprising (a) a secondary alcohol derivative; (b) at least one co-surfactant, and (c) water.

WO 2008/079855 A2

ENHANCED OIL RECOVERY SYSTEMS AND CONSUMER PRODUCTS CONTAINING SECONDARY ALCOHOL DERIVATIVES

Field of the Invention

The present invention relates to secondary alcohol derivatives and to new surfactant systems, including enhanced oil recovery systems, comprising one or more of these compounds and to consumer products comprising said compounds or surfactant systems, including personal cleansing products.

Background of the Invention

Hydrocarbons may be recovered from hydrocarbon containing formations by penetrating the formation with one or more wells. Hydrocarbons may flow to the surface through the wells. Conditions (e.g., permeability, hydrocarbon concentration, porosity, temperature, pressure) of the hydrocarbon containing formation may affect the economic viability of hydrocarbon production from the hydrocarbon containing formation. A hydrocarbon containing formation may have natural energy (e.g., gas, water) to aid in mobilizing hydrocarbons to the surface of the hydrocarbon containing formation. Natural energy may be in the form of water. Water may exert pressure to mobilize hydrocarbons to one or more production wells. Gas may be present in the hydrocarbon containing formation at sufficient pressures to mobilize hydrocarbons to one or more production wells. The natural energy source may become depleted over time. Supplemental recovery processes may be used to continue recovery of hydrocarbons from the hydrocarbon containing formation. Examples of supplemental processes include waterflooding, polymer flooding, alkali flooding, thermal processes, solution flooding or combinations thereof.

Compositions and methods for enhanced hydrocarbons recovery are described in U.S. Patent No. 3,943,160 to Farmer et al., entitled "Heat-Stable Calcium-Compatible Waterflood

Surfactant;” U.S. Patent No. 3,946,812 to Gale et al., entitled “Use Of Materials As Waterflood Additives;” U.S. Patent No. 4,077,471 to Shupe et al., entitled “Surfactant Oil Recovery Process Usable In High Temperature, High Salinity Formations;” U.S. Patent No. 4,216,079 to Newcombe, entitled “Emulsion Breaking With Surfactant Recovery;” U.S. Patent No. 5,318,709 to Wuest et al., entitled “Process for the Production of Surfactant Mixtures Based On Ether Sulfonated And Their Use;” U.S. Patent No. 5,723,423 to Van Slyke, entitled “Solvent Soaps and Methods Employing Same;” U.S. Patent No. 6,022,834 to Hsu et al., entitled “Alkaline Surfactant Polymer Flooding Composition and Process;” U.S. Patent No. 6,269,881 to Chou et al., entitled “Oil Recovery Method For Waxy Crude Oil Using Alkylaryl Sulfonate Surfactants Derived From Alpha-Olefins and the Alpha-Olefin Compositions” and by Wellington, et al. in “Low Surfactant Concentration Enhanced Waterflooding,” Society of Petroleum Engineers, 1995; all of which are incorporated by reference herein.

The developer and formulator of surfactants for personal cleansing detergents must consider a wide variety of possibilities with limited (sometimes inconsistent) information, and then strive to provide overall improvements in one or more of a whole array of criteria, including performance in the presence of free calcium, in complex mixtures of surfactants and polymers, formulation changes including silicone conditioners, enzyme, various changes in consumer habits and practices, and the need for biodegradability. Furthermore, personal cleansing detergents should also employ materials that enhance product phase stability at low temperatures. Lack of phase stability can lead to unacceptable rheological and aesthetic properties as well as to performance issues. Such low temperatures can be encountered in warehouses, in the consumer's garage, in the consumer's automobile, during street vending, on a cold bathroom window sill, and the like.

Further, personal cleansing compositions should employ materials that enhance the dissolution, or rate of product mixing, with water. Further, personal cleansing detergents should employ materials that enhance the tolerance of the system to hardness, especially to avoid the precipitation of the calcium salts of anionic surfactants. Precipitation of the calcium salts of anionic surfactants is known to cause suppression of suds, irritation to the skin, and can lead to an undesirable hair feel. The lack of tolerance to low temperature and hardness prevents widespread use of personal cleansing products in which sodium alkyl sulfate is the only anionic surfactant. The development of improved surfactants for use in personal cleansing compositions is clearly a complex challenge.

Summary of the Invention

The present invention encompasses improvements in enhanced oil recovery (EOR). The present invention also encompasses improvements in consumer products, especially personal care products, made possible though innovation in secondary alcohols and their derivatives. Consumer products ranging from personal care products to laundry detergents, cosmetics and paper products, into which the materials can be formulated, are encompassed.

Secondary alcohol derivatives are used in these applications to prove improved properties and performance. Secondary alcohol derivatives may include secondary alcohol alkoxylates (SAA), including the ethoxylates (SAE), secondary alcohol alkoxysulfates (SAAS), including the ethoxysulfates (SAES), and secondary alcohol alkoxycarboxylates (SAAC), including the ethoxycarboxylates (SAEC).

One embodiment of this invention is a composition and method of treating a hydrocarbon containing formation, comprising: (a) providing a composition to at least a portion of the hydrocarbon containing formation, wherein the composition comprises a secondary alcohol derivative (which, for example, may be selected from secondary alcohol alkoxylates, secondary alcohol alkoxysulfates, secondary alcohol alkoxycarboxylates, and mixtures of any of these components; wherein ethoxylates are preferred); and (b) allowing the composition to interact with hydrocarbons in the hydrocarbon containing formation. In another embodiment, the invention is a composition produced from a hydrocarbon containing formation, comprising hydrocarbons from a hydrocarbon containing formation and a secondary alcohol derivative (which, for example, may be selected from secondary alcohol ethoxylates, secondary alcohol ethoxysulfates, secondary alcohol ethoxycarboxylates, and mixtures of any of these components). The composition may comprise from 0.01 %wt to 30 %wt of the secondary alcohol derivative, from 1 %wt to 99 %wt of the hydrocarbons and from 1 %wt to 99 %wt of other components such as brine.

Another embodiment of this invention is a personal care composition for topical application to the skin or hair comprising (a) a secondary alcohol derivative (which, for example, may be selected from secondary alcohol alkoxylates, secondary alcohol alkoxysulfates, secondary alcohol alkoxycarboxylates, and mixtures of any of these components; wherein ethoxylates are preferred); and (b) a cosmetically-acceptable vehicle. The personal care compositions may comprise from 0.1 %wt to 30 %wt of the secondary alcohol derivative, from 50 %wt to 99 %wt of the cosmetically-acceptable vehicle.

Another embodiment is a personal care composition for topical application to the skin comprising (a) a secondary alcohol derivative (which, for example, may be selected from secondary alcohol alkoxylates, secondary alcohol alkoxysulfates, secondary alcohol alkoxycarboxylates, and mixtures of any of these components; wherein ethoxylates are preferred); (b) at least one sunscreen; and (c) a cosmetically acceptable vehicle. The sunscreen-containing compositions may comprise from 0.1 %wt to 30 %wt of the secondary alcohol derivative, from 50 %wt to 99 %wt of the cosmetically-acceptable vehicle and from 0.1 %wt to 20 %wt of the sunscreen.

Still another embodiment is a shampoo composition for topical application to the skin or hair comprising (a) a secondary alcohol derivative (which, for example, may be selected from secondary alcohol alkoxylates, secondary alcohol alkoxysulfates, secondary alcohol alkoxycarboxylates, and mixtures of any of these components; wherein ethoxylates are preferred); (b) water, (c) at least one co-surfactant, and optionally other ingredients such as dye, fragrance, conditioning agents, etc. The shampoo composition may comprise from 0.1 wt to 40%wt of the secondary alcohol derivative.

Detailed Description of the Invention

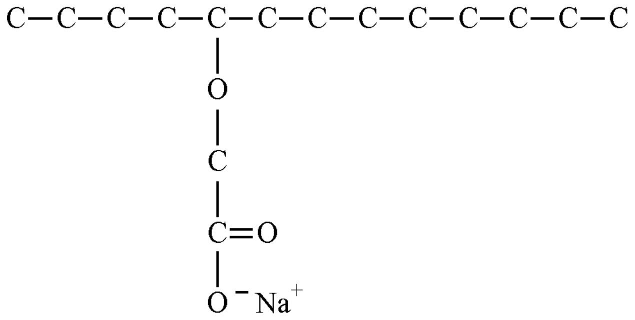
The secondary alcohol derivatives described herein are highly preferred for the purpose of consumer cleaning products such as laundry detergents, enhanced oil recovery (EOR) systems and personal care compositions of the invention.

Secondary alcohols and processes for making them have been well known for many years. They may be made by subjecting a straight chain paraffin to liquid phase oxidation thereby forming a random secondary alcohol. One such process is described in Chemical Engineering Progress, vol. 64, No. 7, pp. 61-66 and another in Hydrocarbon Processing, January 1978, pp. 145-151.

Secondary alcohol alkoxylates (SAA) are also well known. They may be made from olefins and alkylene glycols by sulfating the olefins with sulfuric acid to yield monoalkyl sulfuric acids and reacting these acids and the glycols. They can also be made by subjecting a straight chain paraffin to liquid phase oxidation thereby forming a random secondary alcohol and adding an alkylene oxide such as ethylene oxide to the secondary alcohol using a Lewis acid catalyst to obtain a low alkylene oxide adduct. Such processes are described in U.S. Patent Nos. 4,317,938, 6,017,875, 6,346,509, and 6,255,275, all of which are herein incorporated by reference in their entirety. SAE may be made by other processes such as those described in U.S. Patent Nos. 4,360,698, 4,762,952, 6,417,408, and 6,734,327, all of which are herein incorporated by reference in their entirety.

Secondary alcohol alkoxysulfates (SAAS) may be made by reacting a secondary alcohol (SA) or a secondary alcohol alkoxylate (i.e., SAE) with sulfur trioxide or chlorosulfonic acid. Such processes are described in U.S. Patent Nos. 3,919,125, 4,261,917, 4,954,646, and 6,346,509, all of which are herein incorporated by reference in their entirety.

SAEC refers to secondary alcohol ethoxycarboxylates. They are one example of the secondary alcohol alkoxycarboxylates (SAAC) of this invention. They have a carboxylate moiety instead of a sulfate moiety. They have the following general structure for a one-mole SAE starting material converted, for example, by Shell's TEMPO oxidation process:



SAEC has about the same surfactant properties as SAES but have the advantage of being more stable at low pH and high temperatures.

SAAC may be made by first alkoxylating a secondary alcohol as described above to make SAA and oxidizing the SAA with oxygen or air in the presence of an oxidation catalyst such as one formed from a stable free radical nitroxide such as a NO_x-generating compound followed by neutralization of the acid with sodium hydroxide. The reaction may be carried out in the presence of the TEMPO catalyst system which comprises a NO_x-generating compound and, optionally, anoxidant and/or a solvent. The NO_x-generating compound is able to produce a stable free radical nitroxide (a free radical nitroxide that can be prepared by conventional chemical methods and will exist long enough to be used in a subsequent chemical reaction or examined in a static system by normal methods of spectroscopy; and the term "stable free radical" includes the precursor to a stable free radical from which the stable free radical may be produced in-situ). The stable free radical initiators are precursors to catalysts, i.e., oxoammonium salts, which are active for the oxidation of SAA to SAAC. These catalysts may be generated *in situ* by the oxidation of a stable free radical nitroxide to an oxoammonium salt with an oxygen-containing oxidant. The stable free radical nitroxide may be obtained by the oxidation of secondary amines or hydroxylamines. Typical stable free radical nitroxide which may be used include desribed in U.S. Patent Nos. 5,166,423, 5,239,116, 5,250,727, 5,256,819, 5,352,824, and 5,495,045, which are herein incorporated by reference in their entirety.

The process of making SAAC is typically conducted under mild conditions, with good results being obtained using a temperature in the range of from 0 to 100°C, preferably 20 to 70°C, and most preferably, 40 to 60°C. Reaction pressures are not critical although higher pressures may result in increased reaction rates. Pressures in the range of from atmospheric pressure up to 1 MPa can be employed with good results. See U.S. Patent Nos. 5,166,423, 5,239,116, 5,250,727, 5,256,819, 5,352,824, and 5,495,045, which are herein incorporated by reference in their entirety, for more detailed applicable process information.

In one embodiment, the nitroxide may be selected from the group consisting of 2,2,6,6-tetramethyl-piperidine-1-oxyl, 4-hydroxy-2, 2,6,6-tetramethyl-piperidine-1-oxyl, 2,2,6,6-tetramethylpiperidine-1-oxyl-4-sulfate, 4-alkoxy-2,2,6,6-tetramethyl-piperidine-1-oxyl, and mixtures thereof, with 2,2,6,6-tetramethyl-piperidine-1-oxyl, 2,2,6,6-tetramethyl-piperidine-1-oxyl-4-sulfate, and 4-alkoxy-2,2,6,6-tetramethylpiperidine-1-oxyl being particularly preferred. The NO_x -generating compound in the present process may typically be selected from the group consisting of an alkali metal nitrosodisulfonate, nitric acid and mixtures thereof, with nitric acid being preferred. However, any compound which serves to generate NO_x during the course of the reaction and which does not interfere with the reaction would be suitable.

In another embodiment, an oxidant is also added as a reactant. In general, when catalytic amounts of the NO_x -generating compound are used, the addition of an oxidant is preferred, whereas when stoichiometric amounts of the NO_x -generating compound are used, an oxidant is not needed. The oxidants suitable for use in the instant invention are those compounds which are capable, in the presence of nitric acid, of oxidizing the stable free radical nitroxide to the oxoammonium salt. Suitable oxidants include oxygen-containing gases such as pure oxygen and oxygen in air. Whereas pure oxygen can is preferred to accomplish the desired conversion, the oxygen can also be diluted with an inert gas such as nitrogen, helium, argon, or other similar gas. While air can be used as the oxidant, the reaction rate is much slower.

The reaction may be carried out in the presence of a solvent. When the molecular weight is such that the alkoxyalkanol reactant is a solid or a viscous liquid, a solvent in which the solid or highly viscous alkoxyalkanol reactant is soluble must be added. Suitable solvents are thus those in which the alkoxyalkanol reactant is soluble and those which do not interfere with the reaction. Suitable solvents include dichloromethane, triglyme, tertiary butyl alcohol, acetonitrile, carbon tetrachloride, monoglyme, diglyme, tertiary amyl alcohol and the like, and mixtures thereof. In one embodiment, the solvent is selected from the group consisting of dichloromethane, acetonitrile, tertiary butyl alcohol and mixtures thereof. The weight ratio of solvent to alkoxyalkanol reactant is typically in the range of from 1:1 to 1:100, and preferably in the range of from 1:1 to 1:5.

The amounts and concentrations of the reactants utilized in the process of making SAAC can vary within wide ranges. The amount of stable free radical nitroxide is typically in the range of from 1 mole percent to 500 mole percent, preferably from 2 mole percent to 20 mole percent, basis the number of moles starting alkoxyalkanol. Generally, the amount of nitric acid used is in the range of from 5 mole percent to 1,000 mole percent, basis the number of moles of alkoxyalkanol.

Other methods for making the secondary alcohol alkoxycarboxylates include reaction with chloroacetic acid or a sodium salt thereof followed by neutralization with sodium hydroxide and platinum-based oxidation.

The invention also encompasses mixtures of the foregoing composition(s) of matter with known materials, i.e., builders, solvents, fragrances, dyes, soil antiredeposit agents, conditioning aids, etc.

Certain very valuable mixtures of the invention are further illustrated by: a composition wherein the composition of matter includes: one or more SAE; and one or more SAES or SAEC. Also encompassed by way of mixtures is a composition comprising (i) at least 1% of the secondary alcohol derivatives; and (iii) at least 1% of conventional ingredients for the desired product.

Enhanced Oil Recovery Compositions

As used herein the term enhanced oil recovery composition refers to a composition which includes at least one of the secondary alcohol derivatives of the present invention as a surfactant and other commonly used EOR components such as, for example, sodium carbonate as a source of alkalinity, and reservoir brine which is used to dissolve the secondary alcohol derivative.

Hydrocarbons may be recovered from hydrocarbon containing formations by penetrating the formation with one or more wells. Hydrocarbons may flow to the surface through the wells. Conditions (e.g., permeability, hydrocarbon concentration, porosity, temperature, pressure) of the hydrocarbon containing formation may affect the economic viability of hydrocarbon production from the hydrocarbon containing formation. A hydrocarbon containing formation may have natural energy (e.g., gas, water) to aid in mobilizing hydrocarbons to the surface of the hydrocarbon containing formation. Natural energy may be in the form of water. Water may exert pressure to mobilize hydrocarbons to one or more production wells. Gas may be present in the hydrocarbon containing formation at sufficient pressures to mobilize hydrocarbons to one or more production wells. The natural energy source may become depleted over time. Supplemental recovery processes may be used to continue recovery of hydrocarbons from the hydrocarbon containing formation. Examples of supplemental processes include waterflooding, polymer flooding, alkali flooding, thermal processes, solution flooding or combinations thereof.

In an embodiment, hydrocarbons may be produced from a hydrocarbon containing formation by a method that includes treating at least a portion of the hydrocarbon containing formation with a hydrocarbon recovery composition. In certain embodiments, at least a portion of the hydrocarbon containing formation may be oil wet. In some embodiments, at least a portion of the hydrocarbon formation may include low salinity water. In other embodiments, at least a portion of the hydrocarbon containing formation may exhibit an average temperature of less than 50°C. Fluids, substances or combinations thereof may be added to at least a portion of the hydrocarbon containing formation to aid in mobilizing hydrocarbons to one or more production wells in certain embodiments.

In one embodiment, a hydrocarbon recovery composition may include a secondary alcohol derivative such as SAA, SAAS, and SAAC. In certain embodiments, an anionic surfactant used in the EOR composition may be SAES and/or SAEC. In some embodiments, a nonionic additive may be SAE.

Hydrocarbons may be produced from hydrocarbon formations through wells penetrating a hydrocarbon containing formation. "Hydrocarbons" are generally defined as molecules formed primarily of carbon and hydrogen atoms. Hydrocarbons may also include other elements, such as, but not limited to, halogens, metallic elements, nitrogen, oxygen and/or sulfur. Hydrocarbons derived from a hydrocarbon formation may include, but are not limited to, kerogen, bitumen, pyrobitumen, asphaltenes, oils or combinations thereof. Hydrocarbons may be located within or adjacent to mineral matrices within the earth. Matrices may include, but are not limited to, sedimentary rock, sands, silicilytes, carbonates, diatomites and other porous media.

A "formation" includes one or more hydrocarbon containing layers, one or more non-hydrocarbon layers, an overburden and/or an underburden. An "overburden" and/or an "underburden" includes one or more different types of impermeable materials. For example, overburden/underburden may include rock, shale, mudstone, or wet/tight carbonate (i.e., an impermeable carbonate without hydrocarbons). For example, an underburden may contain shale or mudstone. In some cases, the overburden/underburden may be somewhat permeable. For example, an underburden may be composed of a permeable mineral such as sandstone or limestone. In some embodiments, at least a portion of a hydrocarbon containing formation may exist at less than 1000 feet below the earth's surface.

Properties of a hydrocarbon containing formation may affect how hydrocarbons flow through an underburden/overburden to one or more production wells. Properties include, but are not limited to, porosity, permeability, pore size distribution, surface area, salinity or temperature of formation. Overburden/underburden properties in combination with hydrocarbon properties, such as, capillary pressure (static) characteristics and relative permeability (flow) characteristics may effect mobilization of hydrocarbons through the hydrocarbon containing formation.

Permeability of a hydrocarbon containing formation may vary depending on the formation composition. A relatively permeable formation may include heavy hydrocarbons entrained in, for example, sand or carbonate. "Relatively permeable," as used herein, refers to formations or portions thereof, that have an average permeability of 10 millidarcy or more. "Relatively low permeability" as used herein, refers to formations or portions thereof that have an average permeability of less than 10 millidarcy. One darcy is equal to about 0.99 square micrometers. An impermeable portion of a formation generally has a permeability of less than 0.1 millidarcy, preferably less than 0.01. In some cases, a portion or all of a hydrocarbon portion of a relatively permeable formation may include predominantly heavy hydrocarbons and/or tar with no supporting mineral grain framework and only floating (or no) mineral matter (e.g., asphalt lakes).

Fluids (e.g., gas, water, hydrocarbons or combinations thereof) of different densities may exist in a hydrocarbon containing formation. A mixture of fluids in the hydrocarbon containing formation may form layers between an underburden and an overburden according to fluid density. Gas may form a top layer, hydrocarbons may form a middle layer and water may form a bottom layer in the hydrocarbon containing formation. The fluids may be present in the hydrocarbon containing formation in various amounts. Interactions between the fluids in the formation may create interfaces or boundaries between the fluids. Interfaces or boundaries between the fluids and the formation may be created through interactions between the fluids and the formation. Typically, gases do not form boundaries with other fluids in a hydrocarbon containing formation. In an embodiment, a first boundary may form between a water layer and underburden. A second boundary may form between a water layer and a hydrocarbon layer. A third boundary may form between hydrocarbons of different densities in a hydrocarbon containing formation. Multiple fluids with multiple boundaries may be present in a hydrocarbon containing formation, in some embodiments. It should be understood, that many combinations of boundaries between fluids and between fluids and the overburden/underburden may be present in a hydrocarbon containing formation.

Production of fluids may perturb the interaction between fluids and between fluids and the overburden/underburden. As fluids are removed from the hydrocarbon containing formation, the different fluid layers may mix and form mixed fluid layers. The mixed fluids may have different interactions at the fluid boundaries. Depending on the interactions at the boundaries of the mixed fluids, production of hydrocarbons may become difficult. Quantification of the interactions (e.g., energy level) at the interface of the fluids and/or fluids and overburden/underburden may be useful to predict mobilization of hydrocarbons through the hydrocarbon containing formation.

Quantification of energy required for interactions (e.g., mixing) between fluids within a formation at an interface may be difficult to measure. Quantification of energy levels at an interface between fluids may be determined by generally known techniques (e.g., spinning drop tensiometer). Interaction energy requirements at an interface may be referred to as interfacial tension. "Interfacial tension" as used herein, refers to a surface free energy that exists between two or more fluids that exhibit a boundary. A high interfacial tension value (e.g., greater than 10 dynes/cm) may indicate the inability of one fluid to mix with a second fluid to form a fluid emulsion. As used herein, an "emulsion" refers to a dispersion of one immiscible fluid into a second fluid by addition of a composition that reduces the interfacial tension between the fluids to achieve stability. The inability of the fluids to mix may be due to high surface interaction energy between the two fluids. Low interfacial tension values (e.g., less than 1 dyne/cm) may indicate less surface interaction between the two immiscible fluids. Less surface interaction energy between two immiscible fluids may result in the mixing of the two fluids to form an emulsion. Fluids with low interfacial tension values may be mobilized to a well bore due to reduced capillary forces and subsequently produced from a hydrocarbon containing formation.

Fluids in a hydrocarbon containing formation may wet (e.g., adhere to an overburden/underburden or spread onto an overburden/underburden in a hydrocarbon containing formation). As used herein, "wettability" refers to the preference of a fluid to spread on or adhere to a solid surface in a formation in the presence of other fluids. Methods to determine wettability of a hydrocarbon formation are described by Craig, Jr. in "The Reservoir Engineering Aspects of Waterflooding", 1971 Monograph Volume 3, Society of Petroleum Engineers. In an embodiment, hydrocarbons may adhere to sandstone in the presence of gas or water. An overburden/underburden that is substantially coated by hydrocarbons may be referred to as "oil wet." An overburden/underburden may be oil wet due to the presence of polar and/or heavy hydrocarbons (e.g., asphaltenes) in the hydrocarbon containing formation. Formation composition (e.g., silica, carbonate or clay) may determine the amount of adsorption of hydrocarbons on the surface of an overburden/underburden. In some embodiments, a porous and/or permeable formation may allow hydrocarbons to more easily wet the overburden/underburden. A substantially oil wet overburden/underburden may inhibit hydrocarbon production from the hydrocarbon containing formation. In certain embodiments, an oil wet portion of a hydrocarbon containing formation may be located at less than 1000 feet below the earth's surface. For example, oil wet formations may be located in Canada, China, Wyoming, Oklahoma and Louisiana.

A hydrocarbon formation may include water. Water may interact with the surface of the underburden. As used herein, "water-wet " refers to the formation of a coat of water on the surface of the overburden/underburden. A water-wet overburden/underburden may enhance hydrocarbon production from the formation by preventing hydrocarbons from wetting the overburden/underburden. In certain embodiments, a water-wet portion of a hydrocarbon containing formation may include minor amounts of polar and/or heavy hydrocarbons.

Water in a hydrocarbon containing formation may contain minerals (e.g., minerals containing barium, calcium, or magnesium) and mineral salts (e.g., sodium chloride, potassium chloride, magnesium chloride). Water salinity and/or water hardness of water in a formation may affect recovery of hydrocarbons in a hydrocarbon containing formation. As used herein "salinity" refers to an amount of dissolved solids in water. "Water hardness," as used herein, refers to a concentration of divalent ions (e.g., calcium, magnesium) in the water. Water salinity and hardness may be determined by generally known methods (e.g., conductivity, titration). As used herein, "high salinity water" refers to water that has greater than 30,000 ppm total dissolved solids based on sodium chloride. As water salinity increases in a hydrocarbon containing formation, interfacial tensions between hydrocarbons and water may be increased and the fluids may become more difficult to produce.

Low salinity water in a hydrocarbon containing formation may enhance hydrocarbon production from a hydrocarbon containing formation. Hydrocarbons and low salinity water may form a well dispersed emulsion due to a low interfacial tension between the low salinity water and the hydrocarbons. Production of a flowable emulsion (e.g., hydrocarbons/water mixture) from a hydrocarbon containing formation may be more economically viable to a producer. As used herein, "low salinity water" refers to water salinity in a hydrocarbon containing formation that is less than 20,000 parts per million (ppm) total dissolved solids based on sodium chloride. In some embodiments, hydrocarbon-containing formations may include water with a salinity of less than 13,000 ppm. In certain embodiments, hydrocarbon-containing formations may include water with a salinity ranging from 3,000 ppm to 10,000 ppm. In other embodiments, salinity of the water in hydrocarbon containing formations may range from 5,000 ppm to 8,000 ppm.

A hydrocarbon containing formation may be selected for treatment based on factors such as, but not limited to, thickness of hydrocarbon containing layers within the formation, assessed liquid production content, location of the formation, salinity content of the formation, temperature of the formation, and depth of hydrocarbon containing layers. Initially, natural formation pressure and temperature may be sufficient to cause hydrocarbons to flow into well bores and out to the surface. Temperatures in a hydrocarbon containing formation may range from 25°C to 300°C. A hydrocarbon formation of a depth less than 1000 feet below the earth's surface may exhibit a temperature less than 50°C. In some embodiments, a hydrocarbon formation temperature of a depth less than 1000 feet below the earth's surface may be less than 40°C. In other embodiments, a hydrocarbon formation of a depth less than 1000 feet below the earth's surface temperature may be less than 30°C. As hydrocarbons are produced from a hydrocarbon containing formation, pressures and/or temperatures within the formation may decline. Various forms of artificial lift (e.g., pumps, gas injection) and/or heating may be employed to continue to produce hydrocarbons from the hydrocarbon containing formation. Production of desired hydrocarbons from the hydrocarbon containing formation may become uneconomical as hydrocarbons are depleted from the formation.

Mobilization of residual hydrocarbons retained in a hydrocarbon containing formation may be difficult due to viscosity of the hydrocarbons and capillary effects of fluids in pores of the hydrocarbon containing formation. As used herein "capillary forces" refers to attractive forces between fluids and at least a portion of the hydrocarbon containing formation. In an embodiment, capillary forces may be overcome by increasing the pressures within a hydrocarbon containing formation. In other embodiments, capillary forces may be overcome by reducing the interfacial tension between fluids in a hydrocarbon containing formation. The ability to reduce the capillary forces in a hydrocarbon containing formation may depend on a number of factors, including, but not limited to, the temperature of the hydrocarbon containing formation, the salinity of water in the hydrocarbon containing formation, and the composition of the hydrocarbons in the hydrocarbon containing formation.

As production rates decrease, additional methods may be employed to make a hydrocarbon containing formation more economically viable. Methods may include adding sources of water (e.g., brine, steam), gases, polymers, monomers or any combinations thereof to the hydrocarbon formation to increase mobilization of hydrocarbons.

In an embodiment, a hydrocarbon containing formation may be treated with a flood of water. A waterflood may include injecting water into a portion of a hydrocarbon containing formation through injections wells. Flooding of at least a portion of the formation may water wet a portion of the hydrocarbon containing formation. The water-wet portion of the hydrocarbon containing formation may be pressurized by known methods and a water/hydrocarbon mixture may be collected using one or more production wells. The water layer, however, may not mix with the hydrocarbon layer efficiently. Poor mixing efficiency may be due to a high interfacial tension between the water and hydrocarbons.

Production from a hydrocarbon containing formation may be enhanced by treating the hydrocarbon containing formation with a polymer and/or monomer that may mobilize hydrocarbons to one or more production wells. The polymer and/or monomer may reduce the mobility of the water phase in pores of the hydrocarbon containing formation. The reduction of water mobility may allow the hydrocarbons to be more easily mobilized through the hydrocarbon containing formation. Polymers include, but are not limited to, polyacrylamides, partially hydrolyzed polyacrylamide, polyacrylates, ethylenic copolymers, biopolymers, carboxymethylcellulose, polyvinyl alcohol, polystyrene sulfonates, polyvinylpyrrolidone, AMPS (2-acrylamide-2-methyl propane sulfonate) or combinations thereof. Examples of ethylenic copolymers include copolymers of acrylic acid and acrylamide, acrylic acid and lauryl acrylate, lauryl acrylate and acrylamide. Examples of biopolymers include xanthan gum and guar gum. In some embodiments, polymers may be crosslinked in situ in a hydrocarbon containing formation. In other embodiments, polymers may be generated in situ in a hydrocarbon containing formation. Polymers and polymer preparations for use in oil recovery are described in U.S. Patent No. 6,427,268 to Zhang et al., entitled "Method For Making Hydrophobically Associative Polymers, Methods of Use and Compositions;" U.S. Patent No. 6,439,308 to Wang, entitled "Foam Drive Method;" U.S. Patent No. 5,654,261 to Smith, entitled, "Permeability Modifying Composition For Use In Oil Recovery;" U.S. Patent No. 5,284,206 to Surles et al., entitled "Formation Treating;" U.S. Patent 5,199,490 to Surles et al., entitled "Formation Treating" and U.S. Patent No. 5,103,909 to Morgenthaler et al., entitled "Profile Control In Enhanced Oil Recovery," all of which are incorporated by reference herein.

In an embodiment, addition of an additive may increase the solubility of a hydrocarbon recovery composition in a hydrocarbon phase. Alternatively, addition of an additive may increase solubility of the hydrocarbon recovery composition in a water phase. As used herein, a molecule soluble in a hydrocarbon phase may be referred to as "lipophilic." A molecule soluble in a water phase, as used herein, may be referred to as "hydrophilic." The effectiveness of the additive may be measured by combining the additive with a hydrocarbon and water mixture and determining if an emulsion is formed. The effectiveness of the additive to form an emulsion may be reported as a hydrophile-lipophile balance (HLB) number. Typically, HLB numbers range between 1 and 40. A high HLB number may indicate that a hydrocarbon-in-water emulsion is formed. A low HLB number may indicate that a water-in-hydrocarbon emulsion is formed. As used herein, a "nonionic additive" refers to an additive that exhibits a hydrophile-lipophile balance (HLB) number of less than 10.

In an embodiment, a hydrocarbon recovery composition may be provided to the hydrocarbon containing formation. In an embodiment, a composition may include one or more nonionic additives (e.g., alcohols, ethoxylated alcohols, nonionic surfactants and /or sugar based esters) and one or more anionic surfactants (e.g., sulfates, sulfonates, ethoxylated sulfates, and/or phosphates). The remainder of the composition may include, but is not limited to, water, low molecular weight alcohols, organic solvents, alkyl sulfonates, aryl sulfonates, brine or combinations thereof. Low molecular weight alcohols include, but are not limited to, methanol, ethanol, propanol, isopropyl alcohol, tert-butyl alcohol, sec-butyl alcohol, butyl alcohol, tert-amyl alcohol or combinations thereof. Organic solvents include, but are not limited to, methyl ethyl ketone, acetone, lower alkyl cellosolves, lower alkyl carbitols or combinations thereof.

The secondary alcohol derivatives of the present invention may be used in the EOR compositions of this invention. SAA may be included as a nonionic surfactant in the EOR composition. SAAS and/or SAAC may be included as an anionic surfactant. These secondary alcohol derivatives may comprise from 0.01 %wt to 30 %wt of the total EOR composition, preferably from 0.01 %wt to 20 %wt, most preferably from 0.01 %wt to 10 %wt.

A hydrocarbon recovery composition may be prepared by combining (e.g., mixing) a nonionic additive (e.g., an SAA or long chain secondary alcohol salt nonionic additive) with an appropriate amount of an anionic additive (e.g., an SAAS, or SAAC anionic surfactant). Combining of the nonionic additive with the anionic additive may be performed at temperatures less than 50°C. In certain embodiments, mixing temperatures may be less than 25°C.

In an embodiment, an EOR composition may include a secondary alcohol of this invention in combination with one or more sugar-based surfactants. Sugar-based surfactants include surfactants composed of a long chain aliphatic ester. In one embodiment, a sugar-based surfactant is composed of a long chain aliphatic portion coupled to the carbonyl group of the ester and a sugar-coupled to the oxygen portion of the ester. Sugar-based surfactants include, but are not limited to, sorbitan monolaurate, sorbitan monplamitate, sorbitan monostearate, sorbitan monooleate, sorbitan sesquioleate, sorbitan trioleate, polyoxyethylene (20) sorbitan monolaurate, polyoxyethylene (20) sorbitan monopalmitate, polyoxyethylene (20) sorbitan monostearate, polyoxyethylene (20) sorbitan monooleate, polyoxyethylene (20) sorbitan trioleate or combinations thereof. Other sugar based surfactants include sugar based ethers and sugar based ethoxylated ethers. The compositions may be prepared by combining the aliphatic anionic surfactant with one or more sugar based surfactants at a temperature of less than 50°C.

A hydrocarbon recovery composition may interact with hydrocarbons in at least a portion of the hydrocarbon containing formation. Interaction with the hydrocarbons may reduce an interfacial tension of the hydrocarbons with one or more fluids in the hydrocarbon containing formation. In other embodiments, a hydrocarbon recovery composition may reduce the interfacial tension between the hydrocarbons and an overburden/underburden of a hydrocarbon containing formation. Reduction of the interfacial tension may allow at least a portion of the hydrocarbons to mobilize through the hydrocarbon containing formation.

The ability of a hydrocarbon recovery composition to reduce the interfacial tension of a mixture of hydrocarbons and fluids may be evaluated using known techniques. In an embodiment, an interfacial tension value for a mixture of hydrocarbons and water may be determined using a spinning drop tensiometer. An amount of the hydrocarbon recovery composition may be added to the hydrocarbon/water mixture and an interfacial tension value for the resulting fluid may be determined. A low interfacial tension value (e.g., less than 1 dyne/cm) may indicate that the composition reduced at least a portion of the surface energy between the hydrocarbons and water. Reduction of surface energy may indicate that at least a portion of the hydrocarbon/water mixture may mobilize through at least a portion of a hydrocarbon containing formation.

In an embodiment, a hydrocarbon recovery composition may be added to a hydrocarbon/water mixture and the interfacial tension value may be determined. An ultralow interfacial tension value (e.g., less than 0.1 dyne/cm) may indicate that the hydrocarbon recovery composition lowered at least a portion of the surface tension between the hydrocarbons and water such that at least a portion of the hydrocarbons may mobilize through at least a portion of the hydrocarbon containing formation. At least a portion of the hydrocarbons may mobilize more easily through at least a portion of the hydrocarbon containing formation at an ultra low interfacial tension than hydrocarbons that have been treated with a composition that results in an interfacial tension value greater than 0.1 dynes/cm for the fluids in the formation. Addition of a hydrocarbon recovery composition to fluids in a hydrocarbon containing formation that results in an ultra-low interfacial tension value may increase the efficiency at which hydrocarbons may be produced. A hydrocarbon recovery composition concentration in the hydrocarbon containing formation may be minimized to minimize cost of use during production.

A hydrocarbon recovery composition may be provided to the formation in an amount based on hydrocarbons present in a hydrocarbon containing formation. The amount of hydrocarbon recovery composition, however, may be too small to be accurately delivered to the hydrocarbon containing formation using known delivery techniques (e.g., pumps). To facilitate delivery of small amounts of the hydrocarbon recovery composition to the hydrocarbon containing formation, the hydrocarbon recovery composition may be combined with water and/or brine to produce an injectable fluid. An amount of a hydrocarbon recovery composition injected into hydrocarbon containing formation may be less than 0.5 wt.% of the total weight of the injectable fluid. In certain embodiments, an amount of a hydrocarbon recovery composition provided to a hydrocarbon containing formation may be less than 0.3 wt.% of the total weight of injectable fluid. In some embodiments, an amount of a hydrocarbon recovery composition provided to a hydrocarbon containing formation may be less than 0.1 wt.% of the total weight of injectable fluid. In other embodiments, an amount of a hydrocarbon recovery composition provided to a hydrocarbon containing formation may be less than 0.05 wt.% of the total weight of injectable fluid.

In an embodiment, a hydrocarbon recovery composition may interact with at least a portion of hydrocarbons and at least a portion of one or more other fluids in the formation to reduce at least a portion of the interfacial tension between the hydrocarbons and one or more fluids. Reduction of the interfacial tension may allow at least a portion of the hydrocarbons to form an emulsion with at least a portion of one or more fluids in the formation. An interfacial tension value between the hydrocarbons and one or more fluids may be altered by the hydrocarbon recovery composition to a value of less than 0.1 dyne/cm. In some embodiments, an interfacial tension value between the hydrocarbons and other fluids in a formation may be reduced by the hydrocarbon recovery composition to be less than 0.05 dyne/cm. An interfacial tension value between hydrocarbons and other fluids in a formation may be lowered by the hydrocarbon recovery composition to less than 0.001 dyne/cm, in other embodiments.

In certain embodiments, a hydrocarbon containing formation may be pretreated with a hydrocarbon removal fluid. A hydrocarbon removal fluid may be composed of water, steam, brine, gas, liquid polymers, foam polymers, monomers or mixtures thereof. A hydrocarbon removal fluid may be used to treat a formation before a hydrocarbon recovery composition is provided to the formation. A hydrocarbon containing formation may be less than 1000 feet below the earth's surface, in some embodiments. A hydrocarbon removal fluid may be heated before injection into a hydrocarbon containing formation, in certain embodiments. A hydrocarbon removal fluid may reduce a viscosity of at least a portion of the hydrocarbons within the formation. Reduction of the viscosity of at least a portion of the hydrocarbons in the formation may enhance mobilization of at least a portion of the hydrocarbons to a production well. After at least a portion of the hydrocarbons in hydrocarbon containing formation have been mobilized, repeated injection of the same or different hydrocarbon removal fluids may become less effective in mobilizing hydrocarbons through the hydrocarbon containing formation. Low efficiency of mobilization may be due to hydrocarbon removal fluids creating more permeable zones in hydrocarbon containing formation. Hydrocarbon removal fluids may pass through the permeable zones in the hydrocarbon containing formation and not interact with and mobilize the remaining hydrocarbons. Consequently, displacement of heavier hydrocarbons adsorbed to the underburden may be reduced over time. Eventually, the formation may be considered low producing or economically undesirable to produce hydrocarbons.

In certain embodiments, injection of a hydrocarbon recovery composition after treating the hydrocarbon containing formation with a hydrocarbon removal fluid may enhance mobilization of heavier hydrocarbons absorbed to underburden. The hydrocarbon recovery composition may interact with the hydrocarbons to reduce an interfacial tension between the hydrocarbons and the underburden. Reduction of the interfacial tension may be such that hydrocarbons are mobilized to and produced from the production well. Produced hydrocarbons from production well may include, in some embodiments, at least a portion of the components of the hydrocarbon recovery composition, the hydrocarbon removal fluid injected into the well for pretreatment, methane, carbon dioxide, ammonia, or combinations thereof. Adding the hydrocarbon recovery composition to at least a portion of a low producing hydrocarbon containing formation may extend the production life of the hydrocarbon containing formation. Hydrocarbon production from the hydrocarbon containing formation may be increased by greater than 50% after the hydrocarbon recovery composition has been added to hydrocarbon containing formation. Increased hydrocarbon production may increase the economic viability of the hydrocarbon containing formation.

In some embodiments, a hydrocarbon recovery composition may be added to a portion of hydrocarbon containing formation that may have an average temperature of less than 50°C. To facilitate delivery of an amount of the hydrocarbon recovery composition to the hydrocarbon containing formation, the hydrocarbon composition may be combined with water or brine to produce an injectable fluid. Less than 0.5 wt% of the hydrocarbon recovery composition, based on the total weight of injectable fluid, may be injected into hydrocarbon containing formation through the injection well. In certain embodiments, the concentration of the hydrocarbon recovery composition injected through the injection well may be less than 0.3 wt.%, based on the total weight of injectable fluid. In some embodiments, the concentration of the hydrocarbon recovery composition may be less than 0.1 wt.% based on the total weight of injectable fluid. In other embodiments, the concentration of the hydrocarbon recovery composition may be less than 0.05 wt.% based on the total weight of injectable fluid.

Interaction of the hydrocarbon recovery composition with at least a portion of hydrocarbons in the formation may reduce at least a portion of an interfacial tension between the hydrocarbons and the underburden. Reduction of at least a portion of the interfacial tension may mobilize at least a portion of hydrocarbons through the hydrocarbon containing formation. Mobilization of at least a portion of hydrocarbons, however, may not be at an economically viable rate. In one embodiment, polymers may be injected into the hydrocarbon formation through the injection well, after treatment of the formation with a hydrocarbon recovery composition, to increase mobilization of at least a portion of the hydrocarbons through the formation. Suitable polymers include, but are not limited to, CIBA® ALCOFLOOD®, manufactured by Ciba Specialty Additives (Tarrytown, New York), Tramfloc® manufactured by Tramfloc Inc. (Temple, Arizona), and HE® polymers manufactured by Chevron Phillips Chemical Co. (The Woodlands, Texas). Interaction between the hydrocarbons, the hydrocarbon recovery composition and the polymer may increase mobilization of at least a portion of the hydrocarbons remaining in the formation to the production well.

In some embodiments, a hydrocarbon recovery composition may be added to a portion of the hydrocarbon containing formation that has an average temperature of less than 50°C. In some embodiments, a hydrocarbon recovery composition may be combined with at least a portion of a hydrocarbon removal fluid (e.g. water, polymer solutions) to produce an injectable fluid. Less than 0.5 wt% of the hydrocarbon recovery composition, based on the total weight of injectable fluid, may be injected into the hydrocarbon containing formation through the injection well. In certain embodiments, a concentration of the hydrocarbon recovery composition injected through the injection well may be less than 0.3 wt.%, based on the total weight of injectable fluid. In some embodiments, less than 0.1 wt.% of the hydrocarbon recovery composition, based on the total weight of injectable fluid, may be injected through the injection well into the hydrocarbon containing formation. In other embodiments, less than 0.05 wt.% of the hydrocarbon recovery composition, based on the total weight of injectable fluid, may be injected through the injection well into the hydrocarbon containing formation. Interaction of the hydrocarbon recovery composition with hydrocarbons in the formation may reduce at least a portion of an interfacial tension between the hydrocarbons and the underburden. Reduction of at least a portion of the interfacial tension may mobilize at least a portion of hydrocarbons to a selected section of the hydrocarbon containing formation to form a hydrocarbon pool. At least a portion of the hydrocarbons may be produced from the hydrocarbon pool in the selected section of the hydrocarbon containing formation.

In other embodiments, mobilization of at least a portion of hydrocarbons to the selected section may not be at an economically viable rate. Polymers may be injected into the hydrocarbon formation to increase mobilization of at least a portion of the hydrocarbons through the formation. Interaction between at least a portion of the hydrocarbons, the hydrocarbon recovery composition and the polymers may increase mobilization of at least a portion of the hydrocarbons to the production well.

In some embodiments, a hydrocarbon recovery composition may include an inorganic salt (e.g. sodium carbonate (Na_2CO_3), sodium chloride (NaCl), or calcium chloride ($CaCl_2$)). The addition of the inorganic salt may help the hydrocarbon recovery composition disperse throughout a hydrocarbon/water mixture. The enhanced dispersion of the hydrocarbon recovery composition may decrease the interactions between the hydrocarbon and water interface. The decreased interaction may lower the interfacial tension of the mixture and provide a fluid that is more mobile.

In another embodiment, a hydrocarbon recovery composition may include polymers and/or monomers. As described above, polymers may be used to increase mobilization of at least a portion of the hydrocarbons through the formation. Suitable polymers have been described previously. Interaction between the hydrocarbons and the polymer containing hydrocarbon recovery composition may increase mobilization of at least a portion of the hydrocarbons remaining in the formation.

In terms of the range in total carbon atoms in the composition of matter, the invention preferably encompasses a composition a mixture of the secondary alcohol derivatives having a total of from 10 carbon atoms to 24 carbon atoms, more preferably from 14 carbon atoms to 24 carbon atoms, even more preferably from 18 carbon atoms to 24 carbon atoms.

Cleaning Compositions and Other Products

Another preferred composition of the invention is based on any of secondary alcohol derivatives in combination with conventional additives to form fabric or hard surface cleaning compositions, skin care compositions and personal cleansing compositions. The cleaning composition would comprise: (i) from 0.05% to 99.9%, preferably 0.5% to 95%, more preferably 1% to 90%, even more preferably 5% to 75% by weight of secondary alcohol derivatives, alone or in mixtures; and (ii) from 0.0001 to 99.99%, preferably 0.5% to 95%, more preferably 1% to 90%, even more preferably 5% to 80% by weight of conventional cleaning additive.

The skin care composition would comprise: (i) from 0.05% to 99.9%, preferably 0.5% to 95%, more preferably 1% to 90%, even more preferably 5% to 75% by weight of secondary alcohol derivatives, alone or in mixtures; and (ii) from 0.0001 to 99.99%, preferably 0.5% to 95%, more preferably 1% to 90%, even more preferably 5% to 75% by weight of a conventional skin care additive.

The personal cleansing composition would comprise: (i) from 0.05% to 99.9%, preferably 0.5% to 95%, more preferably 1% to 90%, even more preferably 5% to 75% by weight of secondary alcohol derivatives, alone or in mixtures; and (ii) from 0.0001 to 99.99%, preferably 0.5% to 95%, more preferably 1% to 90%, even more preferably 5% to 75% by weight of a conventional personal cleansing additive.

Another preferred composition of the invention is a paper article comprising at least 0.0001% by weight of said secondary alcohol derivatives, alone or in mixtures. The paper article can be any conventional paper article well known in the art. This paper article can be in the form of a toilet tissue, a disposable tissue or disposable wipe.

The fabric softening compositions described hereinbefore can optionally, but preferably comprise less than 40%, preferably from 10% to 35%, more preferably from 12% to 25%, and even more preferably from 14% to 20%, of the principal solvent, by weight of the secondary alcohol derivative composition. Said principal solvent is selected to minimize solvent odor impact in the composition and to provide a low viscosity to the final composition.

The suitability of any principal solvent for the formulation of the liquid, concentrated, preferably clear, fabric softener compositions herein with the requisite stability is surprisingly selective. Suitable solvents can be selected based upon their octanol/water partition coefficient (P). Octanol/water partition coefficient of a principal solvent is the ratio between its equilibrium concentration in octanol and in water. The partition coefficients of the principal solvent ingredients of this invention are conveniently given in the form of their logarithm to the base 10, logP.

The logP of many ingredients has been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylight CIS), Irvine, Calif., contains many, along with citations to the original literature. However, the logP values are most conveniently calculated by the "CLOGP" program, also available from Daylight CIS. This program also lists experimental logP values when they are available in the Pomona92 database. The "calculated logP" (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Ramsden, Eds., p. 295, Pergamon Press, 1990, incorporated herein by reference). The fragment approach is based on the chemical structure of each ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. These ClogP values, which are the most reliable and widely used estimates for this physicochemical property, are preferably used instead of the experimental logP values in the selection of the principal solvent ingredients which are useful in the present invention. Other methods that can be used to compute ClogP include, e.g., Crippen's fragmentation method as disclosed in J. Chem. Inf. Comput. Sci., 27, 21 (1987); Viswanadhan's fragmentation method as disclose in J. Chem. Inf. Comput. Sci., 29, 163 (1989); and Broto's method as disclosed in Eur. J. Med. Chem.--Chim. Theor., 19, 71 (1984). The principal solvents herein are selected from those having a ClogP of from 0.15 to 0.64, preferably from 0.25 to 0.62, and more preferably from 0.40 to 0.60, said principal solvent preferably being at least somewhat asymmetric, and preferably having a melting, or solidification, point that allows it to be liquid at, or near room temperature. Solvents that have a low molecular weight and are biodegradable are also desirable for some purposes. The more asymmetric solvents appear to be very desirable, whereas the highly symmetrical solvents such as 1,7-heptanediol, or 1,4-bis(hydroxymethyl)cyclohexane, which have a center of symmetry, appear to be unable to provide the essential clear compositions when used alone, even though their ClogP values fall in the preferred range.

The most preferred principal solvents can be identified by the appearance of the softener vesicles, as observed via cryogenic electron microscopy of the compositions that have been diluted to the concentration used in the rinse. These dilute compositions appear to have dispersions of fabric softener that exhibit a more unilamellar appearance than conventional fabric softener compositions. The closer to uni-lamellar the appearance, the better the compositions seem to perform. These compositions provide surprisingly good fabric softening as compared to similar compositions prepared in the conventional way with the same fabric softener active. The compositions also inherently provide improved perfume deposition as compared to conventional fabric softening compositions, especially when the perfume is added to the compositions at, or near, room temperature.

A comprehensive list of possible principal solvents can be found in U.S. Pat. No. 5,747,443, which is incorporated herein by reference.

The above fabric softeners can also be combined with other fabric softeners, such as, those in U.S. Pat. No. 3,861,870, Edwards and Diehl; U.S. Pat. No.4,308,151, Cambre; U.S. Pat. No. 3,886,075, Bernardino; U.S. Pat. No. 4,233,164, Davis; U.S. Pat. No. 4,401,578, Verbruggen; U.S. Pat. No. 3,974,076, Wiersema and Rieke; and U.S. Pat. No. 4,237,016, Rudkin, Clint, and Young, all of said patents being incorporated herein by reference. The additional softener actives herein are preferably those that are highly branched and/or unsaturated versions of the traditional softener actives, i.e., di-long chain alkyl nitrogen derivatives, normally cationic materials, such as dioleyldimethylammonium chloride and imidazolinium compounds as described hereinafter. Examples of more biodegradable fabric softeners can be found in U.S. Pat. No. 3,408,361, Mannheimer, issued Oct. 29, 1968; U.S. Pat. No. 4,709,045, Kubo et al., issued Nov. 24, 1987; U.S. Pat. No. 4,233,451, Pracht et al., issued Nov. 11, 1980; U.S. Pat. No. 4,127,489, Pracht et al., issued Nov. 28, 1979; U.S. Pat. No. 3,689,424, Berg et al., issued Sep. 5, 1972; U.S. Pat. No. 4,128,485, Baumann et al., issued Dec. 5, 1978; U.S. Pat. No. 4,161,604, Elster et al., issued

Jul. 17, 1979; U.S. Pat. No. 4,189,593, Wechsler et al., issued Feb. 19, 1980; and U.S. Pat. No. 4,339,391, Hoffman et al., issued Jul. 13, 1982, said patents being incorporated herein by reference.

Industrial Applicability

The compositions, e.g., the various secondary alcohol derivatives of the type herein can be used in all manner of compositions. Detergent compositions of the invention may also contain additional detergent components. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the cleaning composition, and the precise nature of the cleaning operation for which it is to be used. Cleaning compositions herein include, but are not limited to: granular, bar-form and liquid laundry detergents; liquid hand dishwashing compositions; automatic dishwasher compositions; liquid, gel and bar- form personal cleansing products; shampoos; dentifrices; hard surface cleaners, and the like. Such compositions can contain a variety of conventional detersive ingredients.

The compositions, e.g., the various secondary alcohol derivatives of the type herein can be used in all manner of skin care compositions. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the skin care composition, and the precise nature of the skin care operation for which it is to be used.

The secondary alcohol derivatives of this invention may be used in hard surface cleaners, laundry prespotters (aerosol and solvent based), commercial and/or industrial laundry applications, commercial and/or industrial hard surface cleanings applications, and carpet cleaning compositions. Also, one of the secondary alcohol derivatives, SAES, may be further derivatized to make a phosphate thereof which may be useful in industrial hard surface cleaners.

The following listing of such ingredients is for the convenience of the formulator, and not by way of limitation of the types of ingredients which can be used with surfactants. The cleaning compositions of the invention preferably contain one or more conventional detergent additives for example surfactants, builders, alkalinity system, organic polymeric compounds, suds suppressors, soil suspension and anti-redeposition agents and corrosion inhibitors. The skin care compositions of the invention preferably contain one or more conventional skin care additives, for example, fragrances, emollients, anti-acne actives, thickeners, structuring agents and skin conditioners.

<u>Conventional Detergent Additives Detersive Surfactants</u>:

The detergent compositions according to the present invention preferably further comprise surfactants, herein also referred to as co-surfactants. It is to be understood that surfactants prepared in the manner of the present invention may be used singly in cleaning compositions or in combination with other detersive surfactants. Typically, fully formulated cleaning compositions will contain a mixture of surfactant types in order to obtain broad-scale cleaning performance over a variety of soils and stains and under a variety of usage conditions. One advantage of the surfactants herein is their ability to be readily formulated in combination with other known surfactant types.

A wide range of these co-surfactants can be used in the detergent compositions of the present invention. A typical listing of anionic, nonionic, cationic, ampholytic and zwitterionic classes, and species of these co-surfactants, is given in U.S. Pat. No. 3,664,961 issued to Norris on May 23, 1972. Amphoteric surfactants are also described in detail in "Amphoteric Surfactants, Second Edition", E.G. Lomax, Editor (published 1996, by Marcel Dekker, Inc.) McCutcheon's, Emulsifiers and Detergents, Annually published by M. C. Publishing Co., and Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch), all of which are incorporated herein by reference.

The laundry detergent compositions of the present invention typically comprise from 0.1% to 50%, preferably from 0.5% to 35%, more preferably 0.5% to 30%, by weight of co-surfactants. Selected co-surfactants are further identified as follows.

Anionic Co-surfactants--Nonlimiting examples of anionic co-surfactants useful herein, typically at levels from 0.1% to 50%, by weight, include the conventional C11-C18 alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C10-C20 alkyl sulfates ("AS"), the C10-C18 secondary (2,3) alkyl sulfates of the formula $CH_3(CH_2)_x(CHOSO_3^- M^+)CH_3$ and $CH_3(CH_2)_y(CHOSO_3^- M^+)CH_2CH_3$ where x and (y+1) are integers of at least 7, preferably at least 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C10-C18 alpha-sulfonated fatty acid esters, the C10-C18 sulfated alkyl polyglycosides, the C10-C18 alkyl alkoxy sulfates ("AExS"; especially EO 1-7 ethoxy sulfates), and C10-C18 alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates). The C12-C18 betaines and sulfobetaines ("sultaines"), C10-C18 amine oxides, and the like, can also be included in the overall compositions. C10-C20 conventional soaps may also be used. Other conventional useful anionic co-surfactants are listed in standard texts.

The alkyl alkoxy sulfate surfactants useful herein are preferably water soluble salts or acids of the formula RO $(A)_mSO_3M$ wherein R is an unsubstituted C10-C24 alkyl or hydroxyalkyl group having a C10-C24 alkyl component, preferably a C12-C18 alkyl or hydroxyalkyl, more preferably C12-C15 alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between 0.5 and 6, more preferably between 0.5 and 3, and M is H or a cation which can be, for example, a metal cation, ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein.

The alkyl sulfate surfactants useful herein are preferably water soluble salts or acids of the formula ROSO3M wherein R preferably is a C10-C24 hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C10-C18 alkyl component, more preferably a C12-C15 alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium.

Other suitable anionic surfactants that can be used are alkyl ester sulfonate surfactants including linear esters of C8-C20 carboxylic acids (i.e., fatty acids) are sulfonated with gaseous SO3 according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

Other anionic co-surfactants useful for detersive purposes can also be included in the laundry detergent compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C8-C22 primary of secondary alkanesulfonates, C8-C24 olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C8-C24 alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates (especially saturated and unsaturated C12-C18 monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C6 -C12 diesters), sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), and alkyl polyethoxy carboxylates such as those of the formula $RO(CH_2CH_2O)_k-CH_2COO^- M^+$ wherein R is a C8-C22 alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Pat. No. 3,929,678, issued Dec. 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Other possible surfactants are the so-called Dianionics. These are surfactants which have at least two anionic groups present on the surfactant molecule. Some suitable dianionic surfactants are further described in U.S. Patent No. 5,958,858, the disclosure of which is incorporated herein by reference. Other conventional useful surfactants are listed in standard texts.

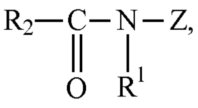
Additionally, the surfactant may be a branched alkyl sulfate, branched alkyl alkoxylate, branched alkyl alkoxylate sulfate or mid chain branched alkyl aryl sulfonate. These surfactants are further described in U.S. Patent Nos. 6,008,181, 6,228,829, 6,232,282, 6,335,312 and 6,380,143, the disclosures of which are herein incorporated herein by reference. Other suitable mid-chain branched surfactants can be found in U.S. Patent Nos. 6,015,781, 6,020,303, 6,046,152 and 6,060,443, the disclosures of which are herein incorporated herein by reference. Mixtures of these branched surfactants with conventional linear surfactants are also suitable for use in the present compositions.

Nonionic Co-surfactants--Nonlimiting examples of nonionic co-surfactants useful herein typically at levels from 0.1% to 50%, by weight include the secondary alcohol derivatives of this invention, especially alkoxylated secondary alcohols (SAA's). Conventional alkoxylated primary alcohols and alkyl phenols, polyhydroxy fatty acid amides, alkyl polyglycosides, C10-C18 glycerol ethers, and the like may also be included.

More specifically, the condensation products of secondary aliphatic and branched alcohols with from 1 to 25 moles of ethylene oxide (EO) are suitable for use as the nonionic surfactant in the present invention. The alkyl chain of the secondary alcohol can either be straight or branched, primary or secondary, and generally contains from 8 to 22 carbon atoms. Preferred are the condensation products of secondary alcohols having an alkyl group containing from 8 to 20 carbon atoms, with from 1 to 10 moles of ethylene oxide per mole of alcohol. Especially preferred nonionic surfactants of this type are the C9-C15 secondary alcohol ethoxylates containing 3-12 moles of ethylene oxide per mole of alcohol, particularly the C12-C15 secondary alcohols containing 5-10 moles of ethylene oxide per mole of alcohol.

Examples of commercially available nonionic surfactants which may be used in addition to the SAAs of this invention include: Tergitol® 24-L-6 NMW (the condensation product of C12-C14 primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), marketed by Union Carbide Corporation; Neodol® 45-9 (the condensation product of C14-C15 linear alcohol with 9 moles of ethylene oxide), Neodol® 23-3 (the condensation product of C12-C13 linear alcohol with 3 moles of ethylene oxide), Neodol® 45-7 (the condensation product of C14-C15 linear alcohol with 7 moles of ethylene oxide) and Neodol® 45-5 (the condensation product of C14-C15 linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company; Kyro® EOB (the condensation product of C13-C15 alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company; and Genapol LA O3O or O5O (the condensation product of C12-C14 alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. The preferred range of HLB in these AE nonionic surfactants is from 8-17 and most preferred from 8-14. Condensates with propylene oxide and butylene oxides may also be used.

Another class of preferred nonionic co-surfactants for use herein are the polyhydroxy fatty acid amide surfactants of the formula:



$$R_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{R^1}{|}}{N}-Z,$$

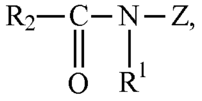
wherein R^1 is H, or C1-4 hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R_2 is C5-31 hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R^1 is methyl, R_2 is a straight C11-15 alkyl or C15-17 alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction. Typical examples include the C12-C18 and C12-C14 N-methylglucamides. See U.S. Pat. Nos. 5,194,639 and 5,298,636, incorporated herein by reference. N-alkoxy polyhydroxy fatty acid amides can also be used; see U.S. Pat. No. 5,489,393, incorporated herein by reference.

Also useful as a nonionic co-surfactant in the present invention are 1) the alkylpolysaccharides such as those disclosed in U.S. Pat. No. 4,565,647, Llenado, issued Jan. 21, 1986, and EP-Patents B 0 070 077, 0 075 996 and 0 094 118, incorporated herein by reference; 2) amide and amine ethoxylates; and 3) fatty acid alkanol amides.

Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are also suitable for use as a nonionic surfactant, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from 6 to 14 carbon atoms, preferably from 8 to 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from 2 to 25 moles of ethylene oxide per mole of alkyl phenol. Commercially available nonionic 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. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

Examples of other suitable nonionic surfactants are the commercially-available Pluronic® surfactants, marketed by BASF, the commercially available Tetronic® compounds, marketed by BASF.

Other useful nonionic surfactants include amine oxide surfactants. The compositions of the present invention may comprise amine oxide in accordance with the general formula I:



$$R_2-\underset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle R^1}{\overset{|}{N}}-Z,$$

In general, it can be seen that the structure (I) provides one long-chain moiety $R_1(EO)x(PO)_y(BO)_z$ and two short chain moieties, CH_2R'. R' is preferably selected from hydrogen, methyl and -CH2OH. In general, R1 is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated and preferably, R_1 is a primary alkyl moiety. When x+y+z=0, R_1 is a hydrocarbyl moiety having a chain length of from 8 to 18. When x+y+z is different from 0, R_1 may be somewhat longer, having a chain length in the range C12-C24. The general formula also encompasses amine oxides wherein x+y+z=0, R_1=C8-C18, R'=H and q=0-2, preferably 2. These amine oxides are illustrated by C12-14 alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, especially the dihydrates as disclosed in U.S. Pat. Nos. 5,075,501 and 5,071,594, incorporated herein by reference.

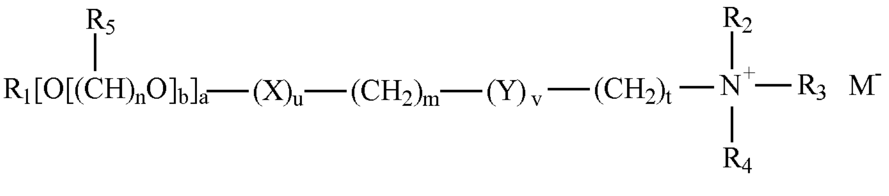
Highly preferred amine oxides herein are solutions at ambient temperature. Amine oxides suitable for use herein are made commercially by a number of suppliers, including Akzo Chemie, Ethyl Corp., and Procter & Gamble. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers.

Whereas in certain of the preferred embodiments R' is H, there is some latitude with respect to having R' slightly larger than H. Specifically, the amine oxide surfactants further encompass embodiments wherein R' is CH_2OH, such as hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oleylbis(2-hydroxyethyl)amine oxide, dodecyldimethylamine oxide dihydrate.

Cationic Co-surfactants--Nonlimiting examples of cationic co-surfactants useful herein typically at levels from 0.1% to 50%, by weight include the choline ester-type quats and alkoxylated quaternary ammonium (AQA) surfactant compounds, and the like.

Cationic co-surfactants useful as a component of the surfactant system is a cationic choline ester-type quat surfactant which are preferably water dispersible compounds having surfactant properties and comprise at least one ester (i.e.-COO-) linkage and at least one cationically charged group. Suitable cationic ester surfactants, including choline ester surfactants, have for example been disclosed in U.S. Pat. Nos. 4,228,042, 4,239,660 and 4,260,529, incorporated herein by reference.

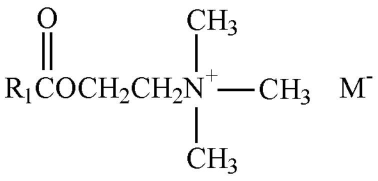
Preferred cationic ester surfactants are those having the formula:



$$R_1[O[(\overset{R_5}{\overset{|}{C}}H)_nO]_b]_a-(X)_u-(CH_2)_m-(Y)_v-(CH_2)_t-\underset{\underset{R_4}{|}}{\overset{\overset{R_2}{|}}{N^+}}-R_3\quad M^-$$

wherein R_1 is a C5-C31 linear or branched alkyl, alkenyl or alkaryl chain or M-.N+$(R_6R_7R_8)(CH_2)_s$; X and Y, independently, are selected from the group consisting of COO, OCO, O, CO, OCOO, CONH, NHCO, OCONH and NHCOO wherein at least one of X or Y is a COO, OCO, OCOO, OCONH or NHCOO group; R_2, R_3, R_4, R_6, R_7 and R_8 are independently selected from the group consisting of alkyl, alkenyl, hydroxyalkyl, hydroxyalkenyl and alkaryl groups having from 1 to 4 carbon atoms; and R_5 is independently H or a C1-3 alkyl group; wherein the values of m, n, s and t independently lie in the range of from 0 to 8, the value of b lies in the range from 0 to 20, and the values of a, u and v independently are either 0 or 1 with the proviso that at least one of u or v must be 1; and wherein M is a counter anion. Preferably R_2, R_3 and R_4 are independently selected from CH_3 and $--CH_2CH_2OH$. Preferably M is selected from the group consisting of halide, methyl sulfate, sulfate, and nitrate, more preferably methyl sulfate, chloride, bromide or iodide.

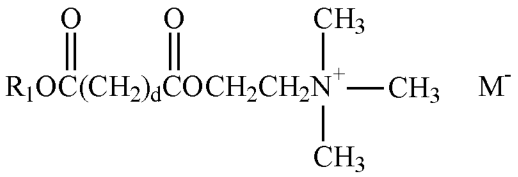
Preferred water dispersible cationic ester surfactants are the choline esters having the formula:



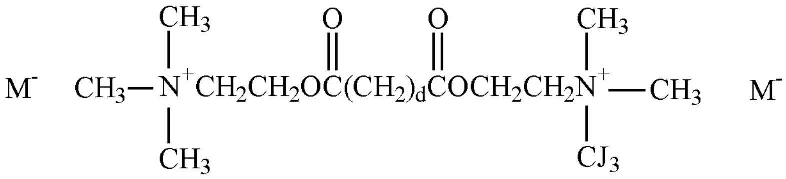
$$R_1\overset{\displaystyle O}{\overset{\|}{C}}OCH_2CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{N^+}}}}—CH_3 \quad M^-$$

wherein R_1 is a C11-19 linear or branched alkyl chain.

Other suitable cationic ester surfactants have the structural formulas below, wherein d may be from 0 to 20.



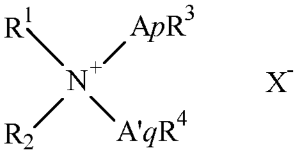
$$R_1O\overset{O}{\overset{\|}{C}}(CH_2)_d\overset{O}{\overset{\|}{C}}OCH_2CH_2\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{N^+}}}—CH_3 \quad M^-$$



$$M^- \quad CH_3—\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{N^+}}}CH_2CH_2O\overset{O}{\overset{\|}{C}}(CH_2)_d\overset{O}{\overset{\|}{C}}OCH_2CH_2\overset{CH_3}{\overset{|}{\underset{\underset{CJ_3}{|}}{N^+}}}—CH_3 \quad M^-$$

In a preferred aspect these cationic ester surfactant are hydrolysable under the conditions of a laundry wash method.

Cationic co-surfactants useful herein also include alkoxylated quaternary ammonium (AQA) surfactant compounds (referred to hereinafter as "AQA compounds") having the formula:



wherein R^1 is a linear or branched alkyl or alkenyl moiety containing from 8 to 18 carbon atoms, preferably 10 to 16 carbon atoms, most preferably from 10 to 14 carbon atoms; R^2 is an alkyl group containing from one to three carbon atoms, preferably methyl; R^3 and R^4 can vary independently and are selected from hydrogen (preferred), methyl and ethyl; X-0 is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A' can vary independently and are each selected from C1-4 alkoxy, especially ethoxy (i.e., $-CH_2CH_2O-$), propoxy, butoxy and mixed ethoxy/propoxy; p is from 0 to 30, preferably 1 to 4 and q is from 0 to 30, preferably 1 to 4, and most preferably to 4; preferably both p and q are 1. See also: EP

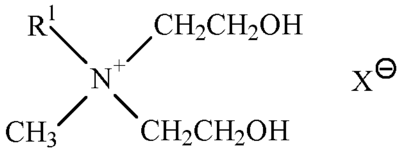
2,084, published May 30, 1979, by The Procter & Gamble Company, which describes cationic co-surfactants of this type which are also useful herein, incorporated herein by reference.

AQA compounds wherein the hydrocarbyl substituent R^1 is C8-11, especially C10, enhance the rate of dissolution of laundry granules, especially under cold water conditions, as compared with the higher chain length materials. Accordingly, the C8-11 AQA surfactants may be preferred by some formulators. The levels of the AQA surfactants used to prepare finished laundry detergent compositions can range from 0.1% to 5%, typically from 0.45% to 2.5%, by weight.

Designation	R^1	R^2	ApR^3	$A'qR^4$
AQA-1 (also referred to as Coco Methyl EO2)	C_{12}-C_{14}	CH_3	EO	EO
AQA-2	C_{12}-C_{16}	CH_3	$(EO)_2$	EO
AQA-3 (Coco Methyl EO4)	C_{12}-C_{14}	CH_3	$(EO)_2$	$(EO)_2$
AQA-4	C_{12}	CH_3	EO	EO
AQA-5	C_{12}-C_{14}	CH_3	$(EO)_2$	$(EO)_3$
AQA-6	C_{12}-C_{14}	CH_3	$(EO)_2$	$(EO)_3$
AQA-7	C_8-C_{18}	CH_3	$(EO)_3$	$(EO)_2$
AQA-8	C_{12}-C_{14}	CH_3	$(EO)_4$	$(EO)_4$
AQA-9	C_{12}-C_{14}	C_2H_5	$(EO)_3$	$(EO)_3$
AQA-10	C_{12}-C_{18}	C_3H_7	$(EO)_3$	$(EO)_4$
AQA-11	C_{12}-C_{18}	CH_3	(propoxy)	$(EO)_3$
AQA-12	C_{10}-C_{18}	C_2H_5	$(\text{iso-propoxy})_2$	$(EO)_3$
AQA-13	C_{10}-C_{18}	CH_3	$(EO/PO)_2$	$(EO)_3$
AQA-14	C_8-C_{18}	CH_3	$(EO)_{15}$*	$(EO)_{15}$*
AQA-15	C_{10}	CH_3	EO	EO
AQA-16	C_8-C_{12}	CH_3	EO	EO
AQA-17	C_9-C_{11}	CH_3	EO 3.5 Avg.	
AQA-18	C_{12}	CH_3	EO 3.5 Avg.	
AQA-19	C_8-C_{14}	CH_3	$(EO)_{10}$	$(EO)_{10}$
AQA-20	C_{10}	C_2H_5	$(EO)_2$	$(EO)_3$
AQA-21	C_{12}-C_{14}	C_2H_5	$(EO)_5$	$(EO)_3$
AQA-22	C_{12}-C_{18}	C_3H_7	Bu	$(EO)_2$

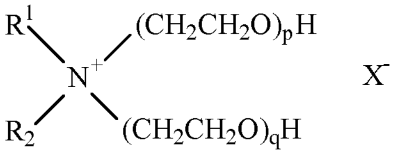
The preferred bis-ethoxylated cationic surfactants herein are available under the trade name ETHOQUAD from Akzo Nobel Chemicals Company.

Highly preferred bis-AQA compounds for use herein are of the formula:



wherein R^1 is C10-18 hydrocarbyl and mixtures thereof, preferably C10, C12, C14 alkyl and mixtures thereof, and X is any convenient anion to provide charge balance, preferably chloride. With reference to the general AQA structure noted above, since in a preferred compound R^1 is derived from coconut (C12-14 alkyl) fraction fatty acids, R^2 is methyl and ApR^3 and $A'qR^4$ are each monoethoxy, this preferred type of compound is referred to herein as "CocoMeEO$_2$" or "AQA-1" in the above list.

Other preferred AQA compounds herein include compounds of the formula:



wherein R^1 is C10-C18 hydrocarbyl, preferably C10-14 alkyl, independently p is 1 to 3 and q is 1 to 3, R^2 is C1-3 alkyl, preferably methyl, and X is an anion, especially chloride.

Other compounds of the foregoing type include those wherein the ethoxy (CH_2CH_2O) units (EO) are replaced by butoxy (Bu), isopropoxy [$CH(CH_3)CH_2O$] and [$CH_2CH(CH_3O)$] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

The following illustrates various other adjunct ingredients which may be used in the compositions of this invention, but is not intended to be limiting thereof. While the combination of the secondary alcohol derivative surfactants with such adjunct compositional ingredients can be provided as finished products in the form of liquids, gels, bars, or the like using conventional techniques, the manufacture of the granular laundry detergents herein requires some special processing techniques in order to achieve optimal performance. Accordingly, the manufacture of laundry granules will be described hereinafter separately in the Granules Manufacture section (below), for the convenience of the formulator.

Additional cationic co-surfactants are described, for example, in the "Surfactant Science Series, Volume 4, Cationic Surfactants" or in the "Industrial Surfactants Handbook", incorporated herein by reference. Classes of useful cationic surfactants described in these references include amide quats (i.e., Lexquat AMG & Schercoquat CAS), glycidyl ether quats (i.e., Cyostat 609), hydroxyalkyl quats (i.e., Dehyquart E), alkoxypropyl quats (i.e., Tomah Q-17-2), polypropoxy quats (Emcol CC-9), cyclic alkylammonium compounds (i.e., pyridinium or imidazolinium quats), and/or benzalkonium quats.

Detersive Enzymes--Enzymes are preferably included in detergent compositions for a variety of purposes, including removal of protein-based, carbohydrate- based, or triglyceride-based stains from substrates, for the prevention of refugee dye transfer in fabric laundering, and for fabric restoration. Recent enzyme disclosures in detergents useful herein include bleach/amylase/protease combinations (US

6,140,293 and US 6,147,045); chondriotinase (US 5,965,507); protease variants (US 6,455,295; US 6,475,765; US 6,451,574; WO 96/25489 A); xylanase (US 5,786,316); keratinase (EP 747,470 A); lipase (US 5,837,010 and 6,133,220); cellulase (US 5,707,951); thermitase (WO 96/28558 A), all of which are incorporated herein by reference. More generally, suitable enzymes include proteases, amylases, lipases, cellulases, peroxidases, xylanases, keratinases, chondriotinases; thermitases, cutinases and mixtures thereof of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Preferred selections are influenced by factors such as pH-activity and/or stability optima, thermostability, and stability to active detergents, builders and the like. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases. Suitable enzymes are also described in U.S. Pat. Nos. 5,677,272, 5,679,630, 5,703,027, 5,703,034, 5,705,464, 5,707,950, 5,707,951, 5,710,115, 5,710,116, 5,710.118, 5,710,119 and 5,721,202, incorporated herein by reference.

"Detersive enzyme", as used herein, means any enzyme having a cleaning, stain removing or otherwise beneficial effect in a laundry, hard surface cleaning or personal care detergent composition. Preferred detersive enzymes are hydrolases such as proteases, amylases and lipases. Preferred enzymes for laundry purposes include, but are not limited to, proteases, cellulases, lipases and peroxidases. Highly preferred are amylases and/or proteases, including both current commercially available types and improved types which, though more and more bleach compatible though successive improvements, have a remaining degree of bleach deactivation susceptibility.

Enzymes are normally incorporated into detergent or detergent additive compositions at levels sufficient to provide a "cleaning-effective amount". The term "cleaning effective amount" refers to any amount capable of producing a cleaning, stain removal, soil removal, whitening, deodorizing, or freshness improving effect on substrates such as fabrics, dishware and the like. In practical terms for current commercial preparations, typical amounts are up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. Protease enzymes are usually present in such commercial preparations at levels sufficient to provide from 0.005 to 0.1 Anson units (AU) of activity per gram of composition. For certain detergents it may be desirable to increase the active enzyme content of the commercial preparation in order to minimize the total amount of non-catalytically active materials and thereby improve spotting/filming or other end-results. Higher active levels may also be desirable in highly concentrated detergent formulations.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of B. subtilis and B. licheniformis. One suitable protease is obtained from a strain of Bacillus, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE® by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo, incorporated herein by reference. Other suitable proteases include ALCALASE® and SAVINASE® from Novo and MAXATASE® from International Bio-Synthetics, Inc., The Netherlands; as well as Protease A as disclosed in US 4,760,025 and 6,465,235, incorporated herein by reference, and Protease B as disclosed in US 4,869,150 and 6,465,235, incorporated herein by reference. See also a high pH protease from Bacillus sp. NCIMB 40338 described in US 5,531,918 to Novo, incorporated herein by reference. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 9203529 A to Novo, incorporated herein by reference. Other preferred proteases include those of US 6,599,730 to Procter & Gamble, incorporated herein by reference. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in US 5,904,451 to Procter & Gamble, incorporated herein by reference e. A recombinant trypsin-like protease for detergents suitable herein is described in 5,693,520 to Novo, incorporated herein by reference.

In more detail, an especially preferred protease, referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of Bacillus amyloliquefaciens subtilisin, as described in US 6,586,221 published Apr. 20, 1995 by Genencor International, incorporated herein by reference.

Useful proteases are also described in PCT publications: US 6,440,717published Nov. 9, 1995 by The Procter & Gamble Company; WO 95/30011 published Nov. 9, 1995 by The Procter & Gamble Company; WO 95/29979 published Nov. 9, 1995 by The Procter & Gamble Company, incorporated herein by reference.

Amylases suitable herein include, for example, alpha-amylases described in GB 1,296,839 to Novo, incorporated herein by reference; RAPIDASE®, International Bio-Synthetics, Inc. and TERMAMYL®, Novo. FUNGAMYL® from Novo is especially useful. Engineering of enzymes for improved stability, e.g., oxidative stability, is known. See, for example J. Biological Chem., Vol. 260, No. 11, June 1985, pp. 6518-6521, incorporated herein by reference. Certain preferred embodiments of the present compositions can make use of amylases having improved stability in detergents, especially improved oxidative stability as measured against a reference-point of TERMAMYL in commercial use in 1993. These preferred amylases herein share the characteristic of being "stability-enhanced" amylases, characterized, at a minimum, by a measurable improvement in one or more of: oxidative stability, e.g., to hydrogen peroxide/tetraacetylethylenediamine in buffered solution at pH 9-10; thermal stability, e.g., at common wash temperatures such as 60°C.; or alkaline stability, e.g., at a pH from 8 to 11, measured versus the above-identified reference-point amylase. Stability can be measured using any of the art-disclosed technical tests.

See, for example, references disclosed in WO 9402597, incorporated herein by reference. Stability-enhanced amylases can be obtained from Novo or from Genencor International. One class of highly preferred amylases herein have the commonality of being derived using site-directed mutagenesis from one or more of the Bacillus amylases, especially the Bacillus alpha-amylases, regardless of whether one, two or multiple amylase strains are the immediate precursors. Oxidative stability-enhanced amylases vs. the above-identified reference amylase are preferred for use, especially in bleaching, more preferably oxygen bleaching, as distinct from chlorine bleaching, detergent compositions herein. Such preferred amylases include (a) an amylase according to WO 9402597, Novo, Feb. 3, 1994, incorporated herein by reference, as further illustrated by a mutant in which substitution is made, using alanine or threonine, preferably threonine, of the methionine residue located in position 197 of the B. licheniformis alpha- amylase, known as TERMAMYL®, or the homologous position variation of a similar parent amylase, such as B. amyloliquefaciens, B. subtilis, or B. stearothermophilus; (b) stability-enhanced amylases as described by Genencor International in a paper entitled "Oxidatively Resistant alpha-Amylases" presented at the 207th American Chemical Society National Meeting, Mar. 13-17 1994, by C. Mitchinson, incorporated herein by reference. Therein it was noted that bleaches in automatic dishwashing detergents inactivate alpha-amylases but that improved oxidative stability amylases have been made by Genencor from B. licheniformis NCIB8061. Methionine (Met) was identified as the most likely residue to be modified. Met was substituted, one at a time, in positions 8, 15, 197, 256, 304, 366 and 438 leading to specific mutants, particularly important being M197L and M197T with the M197T variant being the most stable expressed variant. Stability was measured in CASCADE® and SUNLIGHT®; (c) particularly preferred amylases herein include amylase variants having additional modification in the immediate parent as described in WO 9510603 A, incorporated herein by reference, and are available from the assignee, Novo, as DURAMYL(D). Other particularly preferred oxidative stability enhanced amylase include those described in WO 9418314 to Genencor International and WO 9402597 to Novo, incorporated herein by reference. Any other oxidative stability- enhanced amylase can be used, for example as derived by site-directed mutagenesis from known chimeric, hybrid or simple mutant parent forms of available amylases. Other preferred enzyme modifications are accessible. See WO 9509909 A to Novo, incorporated herein by reference.

Other amylase enzymes include those described in WO 95/26397 and in co- pending application by Novo Nordisk PCT/DK96/00056, incorporated herein by reference. Specific amylase enzymes for use in the detergent compositions of the present invention include alpha-amylases characterized by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C. and at a pH value in the range of 8 to 10, measured by the Phadebas® alpha-amylase activity assay. (Such Phadebas® alpha-amylase activity assay is described at pages 9-10, WO 95/26397, incorporated herein by reference.) Also included herein are alpha-amylases which are at least 80% homologous with the amino acid sequences shown in the SEQ ID listings in the references. These enzymes are preferably incorporated into laundry detergent compositions at a level from 0.00018% to 0.060% pure enzyme by weight of the total composition, more preferably from 0.00024% to 0.048% pure enzyme by weight of the total composition.

Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. Pat. No. 4,435,307, Barbesgoard et al, Mar. 6, 1984, incorporated herein by reference, discloses suitable fungal cellulases from Humicola insolens or Humicola strain DSM1800 or a cellulase 212-producing fungus belonging to the genus Aeromonas, and cellulase extracted from the hepatopancreas of a marine mollusk, Dolabella Auricula Solander. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832, incorporated herein by reference. CAREZYME® and CELLUZYME® cellulases

(Novo) are especially useful. See also WO 9117243 to Novo, incorporated herein by reference.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the Pseudomonas group, such as Pseudomonas stutzeri ATCC 19.154, as disclosed in GB 1,372,034, incorporated herein by reference. See also lipases in Japanese Patent Application 53,20487, laid open Feb. 24, 1978, incorporated herein by reference. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," or "Amano-P." Other suitable commercial lipases include Amano-CES, lipases ex Chromobacter viscosum, e.g. Chromobacter viscosum var. lipolyticum NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; Chromobacter viscosum lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex Pseudomonas gladioli. LIPOLASE® enzyme derived from Humicola lanuginosa and commercially available from Novo, see also EP 341,947, is a preferred lipase for use herein. Lipase and amylase variants stabilized against peroxidase enzymes are described in WO 9414951 A to Novo, incorporated herein by reference. See also WO 9205249 and RD 94359044, incorporated herein by reference.

Cutinase enzymes suitable for use herein are described in WO 8809367 A to Genencor, incorporated herein by reference.

Peroxidase enzymes may be used in combination with oxygen sources, e.g., percarbonate, perborate, hydrogen peroxide, etc., for "solution bleaching" or prevention of transfer of dyes or pigments removed from substrates during the wash to other substrates present in the wash solution. Known peroxidases include horseradish peroxidase, ligninase, and haloperoxidases such as chloro- or bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed in

WO 89099813 A, Oct. 19, 1989 to Novo and WO 8909813 A to Novo, incorporated herein by reference.

A range of enzyme materials and means for their incorporation into synthetic detergent compositions is also disclosed in WO 9307263 A and WO 9307260 A to Genencor International, WO 8908694 A to Novo, and U.S. Pat. No. 3,553,139, Jan. 5, 1971 to McCarty et al, incorporated herein by reference. Enzymes are further disclosed in U.S. Pat. No. 4,101,457, Place et al, Jul. 18, 1978, and in U.S. Pat. No. 4,507,219, Hughes, Mar. 26, 1985, incorporated herein by reference. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Pat. No. 4,261,868, Hora et al, Apr. 14, 1981, incorporated herein by reference. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Pat. No. 3,600,319, Aug. 17, 1971, Gedge et al, EP 199,405 and EP 200,586, Oct. 29, 1986, Venegas, incorporated herein by reference. Enzyme stabilization systems are also described, for example, in U.S. Pat. No. 3,519,570, incorporated herein by reference. A useful Bacillus, sp. AC13 giving proteases, xylanases and cellulases, is described in WO 9401532 A to Novo, incorporated herein by reference.

Builders--Detergent builders are preferably included in the compositions herein, for example to assist in controlling mineral, especially Ca and/or Mg, hardness in wash water or to assist in the removal and/or suspension of particulate soils from surfaces and sometimes to provide alkalinity and/or buffering action. In solid formulations, builders sometimes serve as absorbents for surfactants. Alternately, certain compositions can be formulated with completely water-soluble builders, whether organic or inorganic, depending on the intended use.

Suitable silicate builders include water-soluble and hydrous solid types and including those having chain-, layer-, or three-dimensional- structure as well as amorphous-solid silicates or other types, for example especially adapted for use in non- structured-liquid detergents. Preferred are alkali metal silicates, particularly those liquids and solids having a SiO_2:Na_2O ratio in the range 1.6:1 to 3.2:1, including solid hydrous 2-ratio silicates marketed by PQ Corp. under the tradename BRITESIL®, e.g., BRITESIL H.sub.2O; and layered silicates, e.g., those described in U.S. Pat. No. 4,664,839, May 12, 1987, H. P. Rieck, incorporated herein by reference. NaSKS-6, sometimes abbreviated "SKS-6", is a crystalline layered aluminum-free δ-Na2SiO5 morphology silicate marketed by Hoechst and is preferred especially in granular laundry compositions. See preparative methods in German DE-A-3,417,649 and DE-A-3,742,043, incorporated herein by reference. Other layered silicates, such as those having the general formula $NaMSi_xO_{2x+1}.yH_2O$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0, can also or alternately be used herein. Layered silicates from Hoechst also include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma layer-silicate forms. Other silicates may also be useful, such as magnesium silicate, which can serve as a crisping agent in granules, as a stabilizing agent for bleaches, and as a component of suds control systems.

Also suitable for use herein are synthesized crystalline ion exchange materials or hydrates thereof having chain structure and a composition represented by the following general formula in an anhydride form: $xM_2O.ySiO_2.zM'O$ wherein M is Na and/or K, M' is Ca and/or Mg; y/x is 0.5 to 2.0 and z/x is 0.005 to 1.0 as taught in U.S. Pat. No. 5,427,711, Sakaguchi et al, Jun. 27, 1995, incorporated herein by reference.

Aluminosilicate builders, such as zeolites, are especially useful in granular detergents, but can also be incorporated in liquids, pastes or gels. Suitable for the present purposes are those having empirical formula: $[M_z(AlO_2)_z(SiO_2)_v].xH_2O$ wherein z and v are integers of at least 6, the molar ratio of z to v is in the range from 1.0 to 0.5, and x is an integer from 15 to 264. Aluminosilicates can be crystalline or amorphous, naturally-occurring or synthetically derived. An aluminosilicate production method is in U.S. Pat. No. 3,985,669, Krummel, et al, Oct. 12, 1976, incorporated herein by reference. Preferred synthetic crystalline aluminosilicate ion exchange materials are available as Zeolite A, Zeolite P (B), Zeolite X and, to whatever extent this differs from Zeolite P, the so-called Zeolite MAP. Natural types, including clinoptilolite, may be used. Zeolite A has the formula: $Na_{12}[(Al_2)_{12}(SiO_2)_{12}].xH_2O$ wherein x is from 20 to 30, especially 27. Dehydrated zeolites (x=0-10) may also be used. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

Builder level can vary widely depending upon end use and physical form of the composition. Built detergents typically comprise at least 1% builder. Liquid formulations typically comprise 5% to 50%, more typically 5% to 35% of builder. Granular formulations typically comprise from 10% to 80%, more typically 15% to 50% builder by weight of the detergent composition. Lower or higher levels of builders are not excluded. For example, certain detergent additive or high-surfactant formulations can be unbuilt.

Suitable builders herein can be selected from the group consisting of phosphates and polyphosphates, especially the sodium salts; carbonates, bicarbonates, sesquicarbonates and carbonate minerals other than sodium carbonate or sesquicarbonate; organic mono-, di-, tri-, and tetracarboxylates especially water-soluble nonsurfactant carboxylates in acid, sodium, potassium or alkanolammonium salt form, as well as oligomeric or water-soluble low molecular weight polymer carboxylates including aliphatic and aromatic types; and phytic acid. These may be complemented by borates, e.g., for pH-buffering purposes, or by sulfates, especially sodium sulfate and any other fillers or carriers which may be important to the engineering of stable surfactant and/or builder-containing detergent compositions.

Builder mixtures, sometimes termed "builder systems" can be used and typically comprise two or more conventional builders, optionally complemented by chelants, pH buffers or fillers, though these latter materials are generally accounted for separately when describing quantities of materials herein. In terms of relative quantities of surfactant and builder in the present detergents, preferred builder systems are typically formulated at a weight ratio of surfactant to builder of from 60:1 to 1:80. Certain preferred laundry detergents have said ratio in the range 0.90:1.0 to 4.0:1.0, more preferably from 0.95:1.0 to 3.0:1.0.

P-containing detergent builders often preferred where permitted by legislation include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates exemplified by the tripolyphosphates, pyrophosphates, glassy polymeric meta-phosphates; and phosphonates.

Suitable carbonate builders include alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on Nov. 15, 1973, incorporated herein by reference, although sodium bicarbonate, sodium carbonate, sodium sesquicarbonate, and other carbonate minerals such as trona or any convenient multiple salts of sodium carbonate and calcium carbonate such as those having the composition $2Na_2CO_3.CaCO_3$ when anhydrous, and even calcium carbonates including calcite, aragonite and vaterite, especially forms having high surface areas relative to compact calcite may be useful, for example as seeds or for use in synthetic detergent bars.

Suitable "organic detergent builders" for use with surfactant systems include polycarboxylate compounds, including water- soluble nonsurfactant dicarboxylates and tricarboxylates. More typically builder polycarboxylates have a plurality of carboxylate groups, preferably at least 3 carboxylates. Carboxylate builders can be formulated in acid, partially neutral, neutral or overbased form. When in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred. Polycarboxylate builders include the ether polycarboxylates, such as oxydisuccinate, see Berg, U.S. Pat. No. 3,128,287, Apr. 7, 1964, and Lamberti et al, U.S. Pat. No. 3,635,830, Jan. 18, 1972; "TMS/TDS" builders of U.S. Pat. No. 4,663,071, Bush et al, May 5, 1987; and other ether carboxylates including cyclic and alicyclic compounds, such as those described in U.S. Pat. Nos. 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903, incorporated herein by reference.

Other suitable organic detergent builders are the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether; 1,3,5-trihydroxy benzene-2,4,6-trisulphonic acid; carboxymethyloxysuccinic acid; the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid; as well as mellitic acid, succinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrates, e.g., citric acid and soluble salts thereof are important carboxylate builders e.g., for heavy duty liquid detergents, due to availability from renewable resources and biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicates. Oxydisuccinates are also especially useful in such compositions and combinations.

Where permitted, and especially in the formulation of bars used for hand-laundering operations, alkali metal phosphates such as sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates, e.g., those of U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137, incorporated herein by reference can also be used and may have desirable antiscaling properties.

Certain detersive surfactants or their short-chain homologues also have a builder action. For unambiguous formula accounting purposes, when they have surfactant capability, these materials are described as detersive surfactants. Preferred types for builder functionality are illustrated by: 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Pat. No. 4,566,984, Bush, Jan. 28, 1986, incorporated herein by reference. Succinic acid builders include the C5-20 alkyl and alkenyl succinic acids and salts thereof. Succinate builders also include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Lauryl-succinates are described in European Patent Application 0,200,263, published Nov. 5, 1986, incorporated herein by reference. Fatty acids, e.g., C12-18 monocarboxylic acids, can also be incorporated into the compositions as surfactant/builder materials alone or in combination with the aforementioned builders, especially citrate and/or the succinate builders, to provide additional builder activity. Other suitable polycarboxylates are disclosed in U.S. Pat. No. 4,144,226, Crutchfield et al, Mar. 13, 1979 and in U.S. Pat. No. 3,308,067, Diehl, Mar. 7, 1967. See also Diehl, U.S. Pat. No. 3,723,322, incorporated herein by reference.

Other types of inorganic builder materials which can be used have the formula $(M_x)_i Ca_y(CO_3)_z$ wherein x and i are integers from 1 to 15, y is an integer from 1 to 10, z is an integer from 2 to 25, Mi are cations, at least one of which is a water-soluble, and the equation ∑i=1-15(xi multiplied by the valence of Mi)+2y=2z is satisfied such that the formula has a neutral or "balanced" charge. These builders are referred to herein as "Mineral Builders", examples of these builders, their use and preparation can be found in U.S. Pat. No. 5,707,959, incorporated herein by reference. Another suitable class of inorganic builders are the Magnesiosilicates, see WO97/0179, incorporated herein by reference.

Bleaching Agents--Preferred compositions of the present invention may comprise, as part or all of the laundry or cleaning adjunct materials, a bleaching agent. Oxygen bleaching agents useful in the present invention can be any of the oxidizing agents known for laundry, hard surface cleaning, automatic dishwashing or denture cleaning purposes. Oxygen bleaches or mixtures thereof are preferred, though other oxidant bleaches, such as oxygen, an enzymatic hydrogen peroxide producing system, or hypohalites such as chlorine bleaches like hypochlorite, may also be used.

Common oxygen bleaches of the peroxygen type include hydrogen peroxide, inorganic peroxohydrates, organic peroxohydrates and the organic peroxyacids, including hydrophilic and hydrophobic mono- or di- peroxyacids. These can be peroxycarboxylic acids, peroxyimidic acids, amidoperoxycarboxylic acids, or their salts including the calcium, magnesium, or mixed-cation salts. Peracids of various kinds can be used both in free form and as precursors known as "bleach activators" or "bleach promoters" which, when combined with a source of hydrogen peroxide, perhydrolyze to release the corresponding peracid.

Also useful herein as oxygen bleaches are the inorganic peroxides such as Na_2O_2, superoxides such as KO_2, organic hydroperoxides such as cumene hydroperoxide and t- butyl hydroperoxide, and the inorganic peroxoacids and their salts such as the peroxosulfuric acid salts, especially the potassium salts of peroxodisulfuric acid and, more preferably, of peroxomonosulfuric acid including the commercial triple-salt form sold as OXONE by DuPont and also any equivalent commercially available forms such as CUROX from Akzo or CAROAT from Degussa. Certain organic peroxides, such as dibenzoyl peroxide, may be useful, especially as additives rather than as primary oxygen bleach.

Mixed oxygen bleach systems are generally useful, as are mixtures of any oxygen bleaches with the known bleach activators, organic catalysts, enzymatic catalysts and mixtures thereof; moreover such mixtures may further include brighteners, photobleaches and dye transfer inhibitors of types well-known in the art.

Preferred oxygen bleaches, as noted, include the peroxohydrates, sometimes known as peroxyhydrates or peroxohydrates. These are organic or, more commonly, inorganic salts capable of releasing hydrogen peroxide readily. Peroxohydrates are the most common examples of "hydrogen peroxide source" materials and include the perborates, percarbonates, perphosphates, and persilicates. Suitable peroxohydrates include sodium carbonate peroxyhydrate and equivalent commercial "percarbonate" bleaches, and any of the so-called sodium perborate hydrates, the "tetrahydrate" and "monohydrate" being preferred; though sodium pyrophosphate peroxyhydrate can be used. Many such peroxohydrates are available in processed forms with coatings, such as of silicate and/or borate and/or waxy materials and/or surfactants, or have particle geometries, such as compact spheres, which improve storage stability. By way of organic peroxohydrates, urea peroxyhydrate can also be useful herein.

Percarbonate bleach includes, for example, dry particles having an average particle size in the range from 500 micrometers to 1,000 micrometers, not more than 10% by weight of said particles being smaller than 200 micrometers and not more than 10% by weight of said particles being larger than 1,250 micrometers. Percarbonates and perborates are widely available in commerce, for example from FMC, Solvay and Tokai Denka.

Organic percarboxylic acids useful herein as the oxygen bleach include magnesium monoperoxyphthalate hexahydrate, available from Interox, m-chloro perbenzoic acid and its salts, 4-nonylamino-4-oxoperoxy- butyric acid and diperoxydodecanedioic acid and their salts. Such bleaches are disclosed in U.S. Pat. No. 4,483,781, U.S. Pat. Appl. 740,446, Burns et al, filed Jun. 3, 1985, EP-A 133,354, published Feb. 20, 1985, and U.S. Pat. No. 4,412,934, incorporated herein by reference. Organic percarboxylic acids usable herein include those containing one, two or more peroxy groups, and can be aliphatic or aromatic. Highly preferred oxygen bleaches also include 6-nonylamino-6-

oxoperoxycaproic acid (NAPAA) as described in U.S. Pat. No. 4,634,551, incorporated herein by reference.

An extensive and exhaustive listing of useful oxygen bleaches, including inorganic peroxohydrates, organic peroxohydrates and the organic peroxyacids, including hydrophilic and hydrophobic mono- or di- peroxyacids, peroxycarboxylic acids, peroxyimidic acids, amidoperoxycarboxylic acids, or their salts including the calcium, magnesium, or mixed-cation salts, can be found in U.S. Pat. Nos. 5,622,646 and 5,686,014, incorporated herein by reference.

Other useful peracids and bleach activators herein are in the family of imidoperacids and imido bleach activators. These include phthaloylimidoperoxycaproic acid and related arylimido-substituted and acyloxynitrogen derivatives. For listings of such compounds, preparations and their incorporation into laundry compositions including both granules and liquids, See U.S. Pat. No. 5,487,818; U.S. Pat. No. 5,470,988, U.S. Pat. No. 5,466,825; U.S. Pat. No. 5,419,846; U.S. Pat. No. 5,415,796; U.S. Pat. No. 5,391,324; U.S. Pat. No. 5,328,634; U.S. Pat. No. 5,310,934; U.S. Pat. No. 5,279,757; U.S. Pat. No. 5,246,620; U.S. Pat. No. 5,245,075; U.S. Pat. No. 5,294,362; U.S. Pat. No. 5,423,998; U.S. Pat. No. 5,208,340; U.S. Pat. No. 5,132,431 and U.S. Pat. No. 5,087,385, incorporated herein by reference.

Useful diperoxyacids include, for example, 1,12-diperoxydodecanedio- ic acid (DPDA); 1,9-diperoxyazelaic acid; diperoxybrassilic acid; diperoxysebasic acid and diperoxyisophthalic acid; 2-decyldiperoxybutane-1,4-dioic acid; and 4,4'-sulphonylbisperoxybenzoic acid.

More generally, the terms "hydrophilic" and "hydrophobic" used herein in connection with any of the oxygen bleaches, especially the peracids, and in connection with bleach activators, are in the first instance based on whether a given oxygen bleach effectively performs bleaching of fugitive dyes in solution thereby preventing fabric graying and discoloration and/or removes more hydrophilic stains such as tea, wine and grape juice--in this case it is termed "hydrophilic". When the oxygen bleach or bleach activator has a significant stain removal, whiteness-improving or cleaning effect on dingy, greasy, carotenoid, or other hydrophobic soils, it is termed "hydrophobic". The terms are applicable also when referring to peracids or bleach activators used in combination with a hydrogen peroxide source. The current commercial benchmarks for hydrophilic performance of oxygen bleach systems are: TAED or peracetic acid, for benchmarking hydrophilic bleaching. NOBS or NAPAA are the corresponding benchmarks for hydrophobic bleaching. The terms "hydrophilic", "hydrophobic" and "hydrotropic" with reference to oxygen bleaches including peracids and here extended to bleach activator have also been used somewhat more narrowly in the literature. See especially Kirk Othmer's Encyclopedia of Chemical Technology, Vol. 4., pages 284-285, incorporated herein by reference. This reference provides a chromatographic retention time and critical micelle concentration-based set of criteria, and is useful to identify and/or characterize preferred sub-classes of hydrophobic, hydrophilic and hydrotropic oxygen bleaches and bleach activators that can be used in the present invention.

While not preferred for compositions of the present invention which comprise detersive enzymes, the present invention compositions may also comprise as the bleaching agent a chlorine-type bleaching material. Such agents are well known in the art, and include for example sodium dichloroisocyanurate ("NaDCC"), or sodium hypochlorite (NaOCl).

Bleach Activators

Bleach activators useful herein include amides, imides, esters and anhydrides. Commonly at least one substituted or unsubstituted acyl moiety is present, covalently connected to a leaving group as in the structure R-C(O)-L. In one preferred mode of use, bleach activators are combined with a source of hydrogen peroxide, such as the perborates or percarbonates, in a single product. Conveniently, the single product leads to in situ production in aqueous solution (i.e., during the washing process) of the percarboxylic acid corresponding to the bleach activator. The product itself can be hydrous, for example a powder, provided that water is controlled in amount and mobility such that storage stability is acceptable. Alternately, the product can be an anhydrous solid or liquid. In another mode, the bleach activator or oxygen bleach is incorporated in a pretreatment product, such as a stain stick; soiled, pretreated substrates can then be exposed to further treatments, for example of a hydrogen peroxide source. With respect to the above bleach activator structure RC(O)L, the atom in the leaving group connecting to the peracid-forming acyl moiety R(C)O- is most typically O or N. Bleach activators can have non-charged, positively or negatively charged peracid-forming moieties and/or noncharged, positively or negatively charged leaving groups. One or more peracid-forming moieties or leaving-groups can be present. See, for example, U.S. Pat. No. 5,595,967, U.S. Pat. No. 5,561,235, U.S. Pat. No. 5,560,862 or the bis-peroxy-carbonic) system of U.S. Pat. No. 5,534,179, incorporated herein by reference. Mixtures of suitable bleach activators can also be used. Bleach activators can be substituted with electron-donating or electron-releasing moieties either in the leaving-group or in the peracid-forming moiety or moieties, changing their reactivity and making them more or less suited to particular pH or wash conditions. For example, electron-withdrawing groups such as NO.sub.2 improve the efficacy of bleach activators intended for use in mild-pH (e.g., from 7.5 to 9.5) wash conditions.

An extensive and exhaustive disclosure of suitable bleach activators and suitable leaving groups, as well as how to determine suitable activators, can be found in U.S. Pat. Nos. 5,686,014 and 5,622,646, incorporated herein by reference.

Cationic bleach activators include quaternary carbamate-, quaternary carbonate-, quaternary ester- and quaternary amide- types, delivering a range of cationic peroxyimidic, peroxycarbonic or peroxycarboxylic acids to the wash. An analogous but non-cationic palette of bleach activators is available when quaternary derivatives are not desired. In more detail, cationic activators include quaternary ammonium-substituted activators of WO 96-06915, U.S. Pat. Nos. 4,751,015 and 4,397,757, EP-A-284292, EP-A-331,229 and EP-A-03520, incorporated herein by reference. Also useful are cationic nitriles as disclosed in EP-A-303,520 and in European Patent Specification 458,396 and 464,880, incorporated herein by reference. Other nitrile types have electron-withdrawing substituents as described in U.S. Pat. No. 5,591,378, incorporated herein by reference.

Other bleach activator disclosures include GB 836,988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; U.S. Pat. Nos. 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393, incorporated herein by reference, and the phenol sulfonate ester of alkanoyl aminoacids disclosed in U.S. Pat. No. 5,523,434, incorporated herein by reference. Suitable bleach activators include any acetylated diamine types, whether hydrophilic or hydrophobic in character.

Of the above classes of bleach precursors, preferred classes include the esters, including acyl phenol sulfonates, acyl alkyl phenol sulfonates or acyl oxybenzenesulfonates (OBS leaving-group); the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

Preferred bleach activators include N,N,N'N'-tetraacetyl ethylene diamine (TAED) or any of its close relatives including the triacetyl or other unsymmetrical derivatives. TAED and the acetylated carbohydrates such as glucose pentaacetate and tetraacetyl xylose are preferred hydrophilic bleach activators. Depending on the application, acetyl triethyl citrate, a liquid, also has some utility, as does phenyl benzoate.

Preferred hydrophobic bleach activators include sodium nonanoyloxybenzene sulfonate (NOBS or SNOBS), N-(alkanoyl)aminoalkanoylox- y benzene sulfonates, such as 4-[N-(nonanoyl)aminohexanoyloxy]-benzene sulfonate or (NACA-OBS) as described in U.S. Pat. No. 5,534,642 and in EPA 0 355 384 A1, incorporated herein by reference, substituted amide types described in detail hereinafter, such as activators related to NAPAA, and activators related to certain imidoperacid bleaches, for example as described in U.S. Pat. No. 5,061,807, issued Oct. 29, 1991 and assigned to Hoechst Aktiengesellschaft of Frankfurt, Germany and Japanese Laid-Open Patent Application (Kokai) No. 4-28799, incorporated herein by reference.

Another group of peracids and bleach activators herein are those derivable from acyclic imidoperoxycarboxylic acids and salts thereof, See U.S. Pat. No. 5,415,796, and cyclic imidoperoxycarboxylic acids and salts thereof, see U.S. Pat.

Nos. 5,061,807, 5,132,431, 5,6542,69, 5,246,620, 5,419,864 and 5,438,147, incorporated herein by reference.

Other suitable bleach activators include sodium-4-benzoyloxy benzene sulfonate (SBOBS); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate (SPCC); trimethyl ammonium toluyloxy-benzene sulfonate; or sodium 3,5,5-trimethyl hexanoyloxybenzene sulfonate (STHOBS).

Bleach activators may be used in an amount of up to 20%, preferably from 0.1-10% by weight, of the composition, though higher levels, 40% or more, are acceptable, for example in highly concentrated bleach additive product forms or forms intended for appliance automated dosing.

Highly preferred bleach activators useful herein are amide-substituted and an extensive and exhaustive disclosure of these activators can be found in U.S. Pat. Nos. 5,686,014 and 5,622,646, incorporated herein by reference.

Other useful activators, disclosed in U.S. Pat. No. 4,966,723, are benzoxazin-type, such as a C_6H_4 ring to which is fused in the 1,2-positions a moiety:

-(O)OC(R1)=N-

Depending on the activator and precise application, good bleaching results can be obtained from bleaching systems having with in-use pH of from 6 to 13, preferably from 9.0 to 10.5. Typically, for example, activators with electron-withdrawing moieties are used for near-neutral or sub-neutral pH ranges. Alkalis and buffering agents can be used to secure such pH.

Acyl lactam activators are very useful herein, especially the acyl caprolactams (see for example WO 94-28102 A, incorporated herein by reference) and acyl valerolactams (see U.S. Pat. No. 5,503,639, incorporated herein by reference). See also U.S. Pat. No. 4,545,784, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam adsorbed into sodium perborate. In certain preferred embodiments of the invention, NOBS, lactam activators, imide activators or amide-functional activators, especially the more hydrophobic derivatives, are desirably combined with hydrophilic activators such as TAED, typically at weight ratios of hydrophobic activator: TAED in the range of 1:5 to 5:1, preferably about 1:1. Other suitable lactam activators are alpha-modified, see WO 96-22350 A1, Jul. 25, 1996, incorporated herein by reference. Lactam activators, especially the more hydrophobic types, are desirably used in combination with TAED, typically at weight ratios of amido-derived or caprolactam activators: TAED in the range of 1:5 to 5:1, preferably about 1:1. See also the bleach activators having cyclic amidine leaving-group disclosed in U.S. Pat. No. 5,552,556, incorporated herein by reference.

Nonlimiting examples of additional activators useful herein are to be found in U.S. Pat. No. 4,915,854, U.S. Pat. Nos. 4,412,934 and 4,634,551, incorporated herein by reference. The hydrophobic activator nonanoyloxybenzene sulfonate (NOBS) and the hydrophilic tetraacetyl ethylene diamine (TAED) activator are typical, and mixtures thereof can also be used.

Additional activators useful herein include those of U.S. Pat. No. 5,545,349, incorporated herein by reference.

<u>Transition Metal Bleach Catalysts</u>:

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. No. 5,246,621, U.S. Pat. No. 5,244,594; U.S. Pat. No. 5,194,416; U.S. Pat. No. 5,114,606; and European Pat. App. Pub. Nos. 549,271A1, 549,272A1, 544,440A2, and 544,490A1, all of which are herein incorporated by reference in their entirety. Preferred examples of these catalysts include $Mn(IV)_2(u-O_3(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(PF_6)_2$, $Mn(III)_2(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_2$, $Mn(IV)_4(u-O)_6(1,4,7\text{-triazacyclononane})_4(ClO_4)_4$, $Mn(III)-MnIV_4(u-O)_1(u-OAc)_2(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})_2(ClO_4)_3$, $Mn(IV)(1,4,7\text{-trimethyl-}1,4,7\text{-triazacyclononane})-(OCH_3)_3(PF_6)$, and mixtures thereof. Other metal- based bleach catalysts include those disclosed in U.S. Pat. Nos. 4,430,243, 5,114,611 5,622,646 and 5,686,014, incorporated herein by reference. The use of manganese with various complex ligands to enhance bleaching is also reported in the following U.S. Pat. Nos.: 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, incorporated herein by reference.

Cobalt bleach catalysts useful herein are known, and are described, for example, in M. L. To be, "Base Hydrolysis of Transition-Metal Complexes", Adv. Inorg. Bioinorg. Mech., (1983), 2, pages 1-94, incorporated herein by reference. The most preferred cobalt catalyst useful herein are cobalt pentaamine acetate salts having the formula $[Co(NH_3)_5OAc]$ Ty, wherein "OAc" represents an acetate moiety and "Ty" 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 article and the references cited therein, and in U.S. Pat. No. 4,810,410, to Diakun et al, issued Mar. 7, 1989, incorporated herein by reference.

Compositions herein may also suitably include as a bleach catalyst the class of transition metal complexes of a macropolycyclic rigid ligand. The phrase "macropolycyclic rigid ligand" is sometimes abbreviated as "MRL". One useful MRL is [MnByclamC12], where "Bcyclam" is (5,12-dimethyl-1,5,8,12-tetraaza- bicyclo[6.6.2]hexadecane). See PCT applications US 6,306,812, US 6,225,464, US 6,218,351 and US 6,906,189, incorporated herein by reference. The amount used is a catalytically effective amount, suitably 1 ppb or more, for example up to 99.9%, more typically 0.001 ppm or more, preferably from 0.05 ppm to 500 ppm (wherein "ppb" denotes parts per billion by weight and "ppm" denotes parts per million by weight).

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 0.01 ppm to 25 ppm, more preferably from 0.05 ppm to 10 ppm, and most preferably from 0.1 ppm to 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 0.0005% to 0.2%, more preferably from 0.004% to 0.08%, of bleach catalyst, especially manganese or cobalt catalysts, by weight of the cleaning compositions.

Enzymatic Sources of Hydrogen Peroxide

On a different track from the bleach activators illustrated hereinabove, another suitable hydrogen peroxide generating system is a combination of a C1-4 alkanol oxidase and a C1-4 alkanol, especially a combination of methanol oxidase (MOX) and ethanol. Such combinations are disclosed in US 5,237,611, incorporated herein by reference. Other enzymatic materials related to bleaching, such as peroxidases, haloperoxidases, oxidases, superoxide dismutases, catalases and their enhancers or, more commonly, inhibitors may be used as optional ingredients in the instant compositions.

Oxygen Transfer Agents and Precursors

Also useful herein are any of the known organic bleach catalysts, oxygen transfer agents or precursors therefor. These include the compounds themselves and/or their precursors, for example any suitable ketone for production of dioxiranes and/or any of the hetero-atom containing analogs of dioxirane precursors or dioxiranes, such as sulfonimines R1R2C=NSO2R3, see EP 446 982 A, published 1991 and sulfonyloxaziridines, see EP 446,981 A, published 1991, incorporated herein by reference. Preferred examples of such materials include hydrophilic or hydrophobic ketones, used especially in conjunction with monoperoxysulfates to produce dioxiranes in situ, and/or the imines described in U.S. Pat. No. 5,576,282 and references described therein. Oxygen bleaches preferably used in conjunction with such oxygen transfer agents or precursors include percarboxylic acids and salts, percarbonic acids and salts, peroxymonosulfuric acid and salts, and mixtures thereof. See also U.S. Pat. No. 5,360,568; U.S. Pat. No. 5,360,569; U.S. Pat. No. 5,370,826 and U.S. Pat. No. 5,442,066, incorporated herein by reference.

Although oxygen bleach systems and/or their precursors may be susceptible to decomposition during storage in the presence of moisture, air (oxygen and/or carbon dioxide) and trace metals (especially rust or simple salts or colloidal oxides of the transition metals) and when subjected to light, stability can be improved by adding common sequestrants (chelants) and/or polymeric dispersants and/or a small amount of antioxidant to the bleach system or product. See, for example, U.S. Pat. No. 5,545,349, incorporated herein by reference. Antioxidants are often added to detergent ingredients ranging from enzymes to surfactants. Their presence is not necessarily inconsistent with use of an oxidant bleach; for example, the introduction of a phase barrier may be used to stabilize an apparently incompatible combination of an enzyme and antioxidant, on one hand, and an oxygen bleach, on the other. Although commonly known substances can be used as antioxidants, For example see U.S. Pat. Nos. 5,686,014, 5,622,646, 5,055,218, 4,853,143, 4,539,130 and 4,483,778, incorporated herein by reference. Preferred antioxidants are 3,5-di-tert-butyl-4-hydroxytoluene, 2,5-di-tert-butylhydroquinone and D,L-alpha-tocopherol.

Polymeric Soil Release Agent--The compositions according to the present invention may optionally comprise one or more soil release agents. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of the laundry cycle and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

If utilized, soil release agents will generally comprise from 0.01% to 10% preferably from 0.1% to 5%, more preferably from 0.2% to 3% by weight, of the composition.

The following, all included herein by reference, describe soil release polymers suitable for us in the present invention. U.S. Pat. No. 5,691,298 Gosselink et al., issued Nov. 25, 1997; U.S. Pat. No. 5,599,782 Pan et al., issued Feb. 4, 1997; U.S. Pat. No. 5,415,807 Gosselink et al., issued May 16, 1995; U.S. Pat. No. 5,182,043 Morrall et al., issued Jan. 26, 1993; U.S. Pat. No. 4,956,447 Gosselink et al., issued Sep. 11, 1990; U.S. Pat. No. 4,976,879 Maldonado et al. issued Dec. 11, 1990; U.S. Pat. No. 4,968,451 Scheibel et al., issued Nov. 6, 1990; U.S. Pat. No. 4,925,577 Borcher, Sr. et al., issued May 15, 1990; U.S. Pat. No. 4,861,512 Gosselink, issued Aug. 29, 1989; U.S. Pat. No. 4,877,896 Maldonado et al., issued Oct. 31, 1989; U.S. Pat. No. 4,702,857 Gosselink et al., issued Oct. 27, 1987; U.S. Pat. No. 4,711,730 Gosselink et al., issued Dec. 8, 1987; U.S. Pat. No. 4,721,580 Gosselink issued Jan. 26, 1988; U.S. Pat. No. 4,000,093 Nicol et al., issued Dec. 28, 1976; U.S. Pat. No. 3,959,230 Hayes, issued May 25, 1976; U.S. Pat. No. 3,893,929 Basadur, issued Jul. 8, 1975; and European Patent Application 0 219 048, published Apr. 22, 1987 by Kud et al.

Further suitable soil release agents are described in U.S. Pat. No. 4,201,824 Voilland et al.; U.S. Pat. No. 4,240,918 Lagasse et al.; U.S. Pat. No. 4,525,524 Tung et al.; U.S. Pat. No. 4,579,681 Ruppert et al.; U.S. Pat. No. 4,220,918; U.S. Pat. No. 4,787,989; EP 279,134 A, 1988 to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N.V., 1974; all incorporated herein by reference.

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

A preferred soil release and anti-redeposition agent is ethoxylated tetraethylene pentamine. Exemplary ethoxylated amines are further described in U.S. Pat. No. 4,597,898, VanderMeer, issued Jul. 1, 1986, incorporated herein by reference. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in European Patent Application 111,965, Oh and Gosselink, published Jun. 27, 1984, incorporated herein by reference. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in European Patent Application 111,984, Gosselink, published Jun. 27, 1984, incorporated herein by reference; the zwitterionic polymers disclosed in European Patent Application 112,592, Gosselink, published Jul. 4, 1984, incorporated herein by reference; and the amine oxides disclosed in U.S. Pat. No. 4,548,744, Connor, issued Oct. 22, 1985, incorporated herein by reference. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. See U.S. Pat. No. 4,891,160, VanderMeer, issued Jan. 2, 1990 and WO 95/32272, published Nov. 30, 1995, incorporated herein by reference. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

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

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

Particularly suitable polymeric polycarboxylates can be derived from acrylic acid. The average molecular weight of such polymers in the acid form preferably ranges from 2,000 to 10,000, more preferably from 4,000 to 7,000 and most preferably from 4,000 to 5,000. Soluble polymers of this type are known materials. Use of polyacrylates of this type in detergent compositions has been disclosed, for example, in Diehl, U.S. Pat. No. 3,308,067, issued Mar. 7, 1967, incorporated herein by reference.

Acrylic/maleic-based copolymers may also be used as a preferred component of the dispersing/anti-redeposition agent. The average molecular weight of such copolymers in the acid form preferably ranges from 2,000 to 100,000, more preferably from 5,000 to 75,000, most preferably from 7,000 to 65,000. The ratio of acrylate to maleate segments in such copolymers will generally range from 30:1 to 1:1, more preferably from 10:1 to 2:1. Soluble acrylate/maleate copolymers of this type are known materials which are described in European Patent Application No. 66915, published

Dec. 15, 1982, as well as in EP 193,360, published Sep. 3, 1986, which also describes such polymers comprising hydroxypropylacrylate, incorporated herein by reference. Still other useful dispersing agents include the maleic/acrylic/vinyl alcohol terpolymers. Such materials are also disclosed in EP 193,360, including, for example, the 45/45/10 terpolymer of acrylic/maleic/vinyl alcohol.

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

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

Other polymer types which may be more desirable for biodegradability, improved bleach stability, or cleaning purposes include various terpolymers and hydrophobically modified copolymers, including those marketed by Rohm & Haas, BASF Corp., Nippon Shokubai and others for all manner of water-treatment, textile treatment, or detergent applications.

Brightener--Any optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from about 0.01% to about 1.2%, by weight, into the detergent compositions herein when they are designed for fabric washing or treatment.

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Pat. No. 4,790,856, issued to Wixon on Dec. 13, 1988, incorporated herein by reference. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Arctic White CC and Arctic White CWD, the 2-(4-styryl-phenyl)-2H-naptho[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-- yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(benzimidazol-2-yl)ethylene; 1,3-diphenyl-pyrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naptho[1,2-d]oxazole; and 2-(stilben-4-yl)-2H-naphtho[1,2-d]triazole. See also U.S. Pat. No. 3,646,015, issued Feb. 29, 1972 to Hamilton, incorporated herein by reference.

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

The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to

500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO". See U.S. Pat. No. 5,633,255 to Fredj, incorporated herein by reference.

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

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

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

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

The hydrophilic optical brighteners useful in the present invention include, for example 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-tria- zine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt (Tinopal-UNPA-GX), 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)- -s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt (Tinopal 5BM-GX) and 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-s- tilbenedisulfonic acid, sodium salt (Tinopal AMS-GX) all by Ciba Geigy Corporation.

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

Other, conventional optical brightener types can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a dye transfer inhibiting effect. Such usage is conventional and well known to detergent formulations.

Chelating Agents--The detergent compositions herein may also optionally contain one or chelating agents, particularly chelating agents for adventitious transition metals. Those commonly found in wash water include iron and/or manganese in water-soluble, colloidal or particulate form, and may be associated as oxides or hydroxides, or found in association with soils such as humic substances. Preferred chelants are those which effectively control such transition metals, especially including controlling deposition of such transition metals or their compounds on fabrics and/or controlling undesired redox reactions in the wash medium and/or at fabric or hard surface interfaces. Such chelating agents include those having low molecular weights as well as polymeric types, typically having at least one, preferably two or more donor heteroatoms such as O or N, capable of co-ordination to a transition-metal, Common chelating agents can be selected from the group consisting of aminocarboxylates, aminophosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof, all as hereinafter defined.

Aminocarboxylates useful as optional chelating agents include ethylenediaminetetraacetates, N-hydroxyethylethylenediaminetriacetates, nitrilo- triacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexaacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, their alkali metal, ammonium, and substituted ammonium salts, and mixtures thereof.

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

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Pat. No. 3,812,044, issued May 21, 1974, to Connor et al, incorporated herein by reference. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Pat. No. 4,704,233, Nov. 3, 1987, to Hartman and Perkins, incorporated herein by reference.

The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like.

If utilized, chelating agents will generally comprise from about 0.001% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, chelating agents will comprise from about 0.01% to about 3.0% by weight of such compositions.

Suds Suppressors--Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention when required by the intended use, especially washing of laundry in washing appliances. Other compositions, such as those designed for hand-washing, may desirably be high-sudsing and may omit such ingredients Suds suppression can be of particular importance in the so-called "high concentration cleaning process" as described in U.S. Pat. Nos. 4,489,455 and 4,489,574, incorporated herein by reference, and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors and are well known in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (Wiley, 1979), incorporated herein by reference.

The compositions herein will generally comprise from 0% to about 10% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts thereof, will be present typically in amounts up to about 5%, preferably 0.5%-3% by weight, of the detergent composition, although higher amounts may be used. Preferably from about 0.01% to about 1% of silicone suds suppressor is used, more preferably from about 0.25% to about 0.5%. These weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any suds suppressor adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from about 0.1% to about 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from about 0.01% to about 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

Alkoxylated Polycarboxylates--Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Fabric Softeners--Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Pat. No. 4,062,647, Storm and Nirschl, issued Dec. 13, 1977, incorporated herein by reference, as well as other softener clays known in the art, can optionally be used typically at levels of from about 0.5% to about 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Pat. No. 4,375,416, Crisp et al, Mar. 1, 1983 and U.S. Pat. No. 4,291,071, Harris et al, issued Sep. 22, 1981, incorporated herein by reference. Moreover, in laundry cleaning methods herein, known fabric softeners, including biodegradable types, can be used in pretreat, mainwash, post-wash and dryer-added modes.

Perfumes--Perfumes and perfumery ingredients useful in the present compositions and processes comprise a wide variety of natural and synthetic chemical ingredients, including, but not limited to, aldehydes, ketones, esters, and the like. Also included are various natural extracts and essences which can comprise complex mixtures of ingredients, such as orange oil, lemon oil, rose extract, lavender, musk, patchouli, balsamic essence, sandalwood oil, pine oil, cedar, and the like. Finished perfumes can comprise extremely complex mixtures of such ingredients. Finished perfumes typically comprise from about 0.01% to about 2%, by weight, of the detergent compositions herein, and individual perfumery ingredients can comprise from about 0.0001% to about 90% of a finished perfume composition.

Non-limiting examples of perfume ingredients useful herein include: 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; ionone methyl; ionone gamma methyl; methyl cedrylone; methyl dihydrojasmonate; methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert- butyl-1,1-dimethyl indane; para-hydroxy-phenyl-butanone; benzophenone; methyl beta- naphthyl ketone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; 7-hydroxy-3,7-dimethyl ocatanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecane; condensation products of hydroxycitronellal and methyl anthranilate, condensation products of hydroxycitronellal and indol, condensation products of phenyl acetaldehyde and indol; 2-methyl-3-(para-tert- butylphenyl)-propionaldehy- de; ethyl vanillin; heliotropin; hexyl cinnamic aldehyde; amyl cinnamic aldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; coumarin; decalactone gamma; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-b- enzopyrane; beta- naphthol methyl ether; ambroxane; dodecahydro-3a,6,6,9a-tetramethyl-naphtho[2,1b]furan; cedrol, 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol;

tricyclodecenyl propionate; tricyclodecenyl acetate; benzyl salicylate; cedryl acetate; and para-(tert-butyl)cyclohex- yl acetate.

Particularly preferred perfume materials are those that provide the largest odor improvements in finished product compositions containing cellulases. These perfumes include but are not limited to: hexyl cinnamic aldehyde; 2-methyl-3-(para-tert- butylphenyl)-propionaldehyde; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; benzyl salicylate; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; para-tert-butyl cyclohexyl acetate; methyl dihydro jasmonate; beta-napthol methyl ether; methyl beta- naphthyl ketone; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-gamma-2-benzopyra- ne; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; anisaldehyde; coumarin; cedrol; vanillin; cyclopentadecanolide; tricyclodecenyl acetate; and tricyclodecenyl propionate.

Other perfume materials include essential oils, resinoids, and resins from a variety of sources including, but not limited to: Peru balsam, Olibanum resinoid, styrax, labdanum resin, nutmeg, cassia oil, benzoin resin, coriander and lavandin. Still other perfume chemicals include phenyl ethyl alcohol, terpineol, linalool, linalyl acetate, geraniol, nerol, 2-(1,1-dimethylethyl)-cyclohexanol acetate, benzyl acetate, and eugenol. Carriers such as diethylphthalate can be used in the finished perfume compositions.

Other Detergent Ingredients--A wide variety of other ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C10-16 alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C10-14 monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, water-soluble magnesium and/or calcium salts such as $MgCl_2$, $MgSO_4$, $CaCl_2$, $CaSO_4$ and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance, especially for liquid dishwashing purposes.

Various detersive ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the detersive ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the detersive ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended detersive function.

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

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between about 6.5 and about 11, preferably between about 7.0 and 10.5, more preferably between about 7.0 to about 9.5. Liquid dishwashing product formulations preferably have a pH between about 6.8 and about 9.0. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

Conventional Skin Care Additives

The skin care compositions of the present invention may contain a variety of other ingredients such as are conventionally used in a given product type provided they do not unacceptably alter the benefits of the invention. These optional components should be suitable for application to human skin, that is, when incorporated into the composition they are suitable for use in contact with human skin without undue toxicity, incompatibility, instability, allergic response, and the like within the scope of sound medical or formulator's judgment. The CTFA Cosmetic Ingredient Handbook, Second Edition (1992) describes a wide variety of nonlimiting cosmetic and pharmaceutical ingredients commonly used in the skin care industry, which are suitable for use in the compositions of the present invention. Examples of these ingredient classes include: abrasives, absorbents, aesthetic components such as perfumes, pigments, colorings/colorants, essential oils, skin sensates, astringents, etc. (e.g., clove oil, menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate), anti-acne agents (e.g., resorcinol, sulfur, salicylic acid, erythromycin, zinc, etc.), anti-caking agents, antifoaming agents, antimicrobial agents (e.g., iodopropyl butylcarbamate), antioxidants, binders, biological additives, buffering agents, bulking agents, chelating agents, chemical additives, colorants, cosmetic astringents, cosmetic biocides, denaturants, drug astringents, external analgesics, film formers or materials, e.g., polymers, for aiding the film-forming properties and substantivity of the composition (e.g., copolymer of eicosene and vinyl pyrrolidone), humectants, opacifying agents, pH adjusters, propellants, reducing agents, sequestrants, skin bleaching agents (or lightening agents) (e.g., hydroquinone, kojic acid, ascorbic acid, magnesium ascorbyl phosphate, ascorbyl glucosamine), skin-conditioning agents (humectants, including miscellaneous and occlusive), skin soothing and/or healing agents (e.g., panthenol and derivatives (e.g., ethyl panthenol), aloe vera, pantothenic acid and its derivatives, allantoin, bisabolol, and dipotassium glycyrrhizinate), skin treating agents including agents for preventing, retarding, arresting, and/or reversing skin wrinkles (e.g., alpha-hydroxy acids such as lactic acid and glycolic acid and beta-hydroxy acids such as salicylic acid), thickeners, and vitamins and derivatives thereof (e.g. tocopherol, tocopherol acetate, retinoic acid, retinol, retinoids, retinyl palmitate, niacin, niacinamide, and the like).

The skin care compositions of the present invention may contain one or more of such optional components. Preferred skin care compositions optionally contain one or more materials selected from UVB sunscreen actives, anti-acne actives, artificial tanning agents, humectants, moisturizers, skin conditioners, and thickening/structuring agents.

UVB Sunscreen Active

The skin care compositions of the present invention can comprise a UVB sunscreen active which absorbs UV radiation having a wavelength of from 290 nm to 320 nm. As used herein, the UVB sunscreen active means an active other than the dibenzoylmethane sunscreen active which itself may possess UVB absorption properties. The skin care compositions should comprise an amount of the UVB active effective to provide UVB protection either independently or in combination with other UV protective actives which may be present in the skin care composition, preferably from 0.1% to 10%, more preferably from 0.1% to 4%, and most preferably from 0.5% to 2.5% by weight of the composition.

A wide variety of UVB sunscreen actives, including both organic sunscreen actives and inorganic physical sunblocks, are suitable for use herein. Nonlimiting examples of such sunscreen actives are described in U.S. Pat. No. 5,087,445 issued Feb. 11, 1992 to Haffey et al.; and U.S. Pat. Nos. 5,073,371 and 5,073,372, both issued on Dec. 17, 1991 to Turner et al, incorporated herein by reference. Nonlimiting examples of suitable physical sunblocks are described in CTFA International Cosmetic Ingredient Dictionary, Sixth edition, 1995, pp. 1026-28, and 1103, incorporated herein by reference.

Preferred UVB sunscreen actives are selected from group consisting of 2-phenyl- benzimidazole-5-sulfonic acid, octocrylene, TEA salicylate, octyl dimethyl PABA, zinc oxide, titanium dioxide, and mixtures thereof. A preferred organic sunscreen active is 2-phenyl-benzimidazole-5-sulfonic acid while preferred inorganic physical sunblocks are zinc oxide, titanium dioxide, and mixtures thereof. Salt and acid-neutralized forms of the acidic sunscreens are also contemplated herein.

When used, the physical sunblocks are present in an amount such that the present skin care compositions are transparent on the skin (i.e., non-whitening), preferably less than or equal to 5%. When titanium dioxide is used, it can have an anatase, rutile, or amorphous structure. Physical sunblock particles, e.g., titanium dioxide and zinc oxide, can be uncoated or coated with a variety of materials including, but not limited to, amino acids; aluminum compounds such as alumina, aluminum stearate, aluminum laurate, and the like; carboxylic acids and their salts, e.g., stearic acid and its salts; phospholipids such as lecithin; organic silicone compounds; inorganic silicone compounds such as silica and silicates; and mixtures thereof. A preferred titanium dioxide is commercially available from Tayca (Japan) and is distributed by Tri-K Industries (Emerson, N.J.) under the MT micronized series (e.g., MT 100SAS).

Anti-Acne Actives

The skin care compositions of the present invention may comprise one or more anti-acne actives. Examples of useful anti-acne actives are described in further detail in U.S. Pat. No. 5,607,980, issued to McAtee et al., on Mar. 4, 1997, incorporated herein by reference.

Artificial Tanning Agents

The skin care compositions of the present invention can comprise one or more artificial tanning agents. Suitable tanning agents include dihydroxyacetone, tyrosine, tyrosine esters and phopho-pho-DOPA. See The Merck Index, Tenth Edition, entry 3167, p. 463 (1983), and "Dihydroxyacetone for Cosmetics", E. Merck Technical Bulletin, 03-304 110, 319 897, 180 588, incorporated herein by reference.

Structuring Agent

The skin care compositions of the present invention may contain a structuring agent. Structuring agents are particularly preferred in the oil-in-water emulsions of the present invention. Without being limited by theory, it is believed that the structuring agent assists in providing rheological characteristics to the skin care composition which contribute to the stability of the composition. For example, the structuring agent tends to assist in the formation of the liquid crystalline gel network structures. The structuring agent may also function as an emulsifier or surfactant. Preferred skin care compositions of this invention comprise from 0.5% to 20%, more preferably from 1% to 10%, most preferably from 1% to 5%, of one or more structuring agents.

The preferred structuring agents for use in the skin care compositions of the present invention are selected from the group consisting of stearic acid, palmitic acid, stearyl alcohol, cetyl alcohol, behenyl alcohol, stearic acid, palmitic acid, the polyethylene glycol ether of stearyl alcohol having an average of 1 to 21 ethylene oxide units, the polyethylene glycol ether of cetyl alcohol having an average of 1 to 5 ethylene oxide units, and mixtures thereof. More preferred structuring agents for use in the skin care compositions of the present invention are selected from the group consisting of stearyl alcohol, cetyl alcohol, behenyl alcohol, the polyethylene glycol ether of stearyl alcohol having an average of about 2 ethylene oxide units (steareth-2), the polyethylene glycol ether of stearyl alcohol having an average of about 21 ethylene oxide units (steareth-21), the polyethylene glycol ether of cetyl alcohol having an average of about 2 ethylene oxide units, and mixtures thereof. Even more preferred structuring agents are selected from the group consisting of stearic acid, palmitic acid, stearyl alcohol, cetyl alcohol, behenyl alcohol, steareth-2, steareth-21, and mixtures thereof.

Thickening Agent (Including Thickeners and Gelling Agents)

The skin care compositions of the present invention can comprise one or more thickening agents, preferably from about 0.1% to about 5%, more preferably from about 0.1% to about 3%, and most preferably from about 0.25% to about 2%, by weight of the composition.

Nonlimiting classes of thickening agents include those selected from the group consisting of:

Carboxylic Acid Polymers--These polymers are crosslinked compounds containing one or more monomers derived from acrylic acid, substituted acrylic acids, and salts and esters of these acrylic acids and the substituted acrylic acids, wherein the crosslinking agent contains two or more carbon-carbon double bonds and is derived from a polyhydric alcohol. Polymers useful in the present invention are more fully described in U.S. Pat. No. 5,087,445, to Haffey et al., issued Feb. 11, 1992; U.S. Pat. No. 4,509,949, to Huang et al., issued Apr. 5, 1985; U.S. Pat. No. 2,798,053, to Brown, issued Jul. 2, 1957; and in CTFA International Cosmetic Ingredient Dictionary, Fourth edition, 1991, pp. 12 and 80, incorporated herein by reference.

Examples of commercially available carboxylic acid polymers useful herein include the carbomers, which are homopolymers of acrylic acid crosslinked with allyl ethers of sucrose or pentaerytritol. The carbomers are available as the Carbopol® 900 series from B.F. Goodrich (e.g., Carbopol®954). In addition, other suitable carboxylic acid polymeric agents include copolymers of C10-30 alkyl acrylates with one or more monomers of acrylic acid, methacrylic acid, or one of their short chain (i.e. C1-4 alcohol) esters, wherein the crosslinking agent is an allyl ether of sucrose or pentaerytritol. These copolymers are known as acrylates/C10-30 alkyl acrylate crosspolymers and are commercially available as Carbopol® 1342, Carbopol® 1382, Pemulen TR-1, and Pemulen TR-2, from B. F. Goodrich. In other words, examples of carboxylic acid polymer thickeners useful herein are those selected from the group consisting of carbomers, acrylates/C10-C30 alkyl acrylate crosspolymers, and mixtures thereof.

Crosslinked Polyacrylate Polymers--The skin care compositions of the present invention can optionally comprise crosslinked polyacrylate polymers useful as thickeners or gelling agents including both cationic and nonionic polymers, with the cationics being generally preferred. Examples of useful crosslinked nonionic polyacrylate polymers and crosslinked cationic polyacrylate polymers are those described in U.S. Pat. No. 5,100,660, to Hawe et al., issued Mar. 31, 1992; U.S. Pat. No. 4,849,484, to Heard, issued Jul. 18, 1989; U.S. Pat. No. 4,835,206, to Farrar et al., issued May 30, 1989; U.S. Pat. No. 4,628,078 to Glover et al. issued Dec. 9, 1986; U.S. Pat. No. 4,599,379 to Flesher et al. issued Jul. 8, 1986; and EP 228,868, to Farrar et al., published Jul. 15, 1987, incorporated herein by reference.

Polyacrylamide Polymers--The skin care compositions of the present invention can optionally comprise polyacrylamide polymers, especially nonionic polyacrylamide polymers including substituted branched or unbranched polymers. Most preferred among these polyacrylamide polymers is the nonionic polymer given the CTFA designation polyacrylamide and isoparaffin and laureth-7, available under the Tradename Sepigel 305 from Seppic Corporation (Fairfield, N.J.).

Other polyacrylamide polymers useful herein include multi-block copolymers of acrylamides and substituted acrylamides with acrylic acids and substituted acrylic acids. Commercially available examples of these multi-block copolymers include Hypan SR150H, SS500V, SS500W, SSSA100H, from Lipo Chemicals, Inc., (Patterson, N.J.).

Polysaccharides--A wide variety of polysaccharides are useful herein. "Polysaccharides" refer to gelling agents which contain a backbone of repeating sugar (i.e. carbohydrate) units. Nonlimiting examples of polysaccharide gelling agents include those selected from the group consisting of cellulose, carboxymethyl hydroxyethylcellulose, cellulose acetate propionate carboxylate, hydroxyethylcellulose, hydroxyethyl ethylcellulose, hydroxypropylcellulose, hydroxypropyl methylcellulose, methyl hydroxyethylcellulose, microcrystalline cellulose, sodium cellulose sulfate, and mixtures thereof. Also useful herein are the alkyl-substituted celluloses. In these polymers, the hydroxy groups of the cellulose polymer is hydroxyalkylated (preferably hydroxyethylated or hydroxypropylated) to form a hydroxyalkylated cellulose which is then further modified with a C10-30 straight chain or branched chain alkyl group through an ether linkage. Typically these polymers are ethers of C10-C30 straight or branched chain alcohols with hydroxyalkylcelluloses. Examples of alkyl groups useful herein include those selected from the group consisting of stearyl, isostearyl, lauryl, myristyl, cetyl, isocetyl, cocoyl (i.e. alkyl groups derived from the alcohols of coconut oil), palmityl, oleyl, linoleyl, linolenyl, ricinoleyl, behenyl, and mixtures thereof. Preferred among the alkyl hydroxyalkyl cellulose ethers is the material given the CTFA designation cetyl hydroxyethylcellulose, which is the ether of cetyl alcohol and hydroxyethylcellulose. This material is sold under the tradename Natrosol® CS Plus from Aqualon Corporation (Wilmington, Del.).

Other useful polysaccharides include scleroglucans comprising a linear chain of (1-3) linked glucose units with a (1-6) linked glucose every three units, a commercially available example of which is Clearogel® CS11 from Michel Mercier Products Inc. (Mountainside, N.J.).

Gums--Other thickening and gelling agents useful herein include materials which are primarily derived from natural sources. Nonlimiting examples of these gelling agent gums include materials selected from the group consisting of acacia, agar, algin, alginic acid, ammonium alginate, amylopectin, calcium alginate, calcium carrageenan, camitine, carrageenan, dextrin, gelatin, gellan gum, guar gum, guar hydroxypropyltrimonium chloride, hectorite, hyaluroinic acid, hydrated silica, hydroxypropyl chitosan, hydroxypropyl guar, karaya gum, kelp, locust bean gum, natto gum, potassium alginate, potassium carrageenan, propylene glycol alginate, sclerotium gum, sodium carboxymethyl dextran, sodium carrageenan, tragacanth gum, xanthan gum, and mixtures thereof.

Preferred skin care compositions of the present invention include a thickening agent selected from the group consisting of carboxylic acid polymers, crosslinked polyacrylate polymers, polyacrylamide polymers, and mixtures thereof, more preferably selected from the group consisting of carboxylic acid polymers, polyacrylamide polymers, and mixtures thereof.

Humectants, Moisturizers, and Skin Conditioners

Preferred skin care compositions optionally comprise one or more humectants, moisturizers, or skin conditioners. A variety of these materials can be employed and each can be present at a level of from about 0.01% to about 20%, more preferably from about 0.1% to about 10%, and most preferably from about 0.5% to about 7%. These materials include, but are not limited to, guanidine; glycolic acid and glycolate salts (e.g. ammonium and quaternary alkyl ammonium); lactic acid and lactate salts (e.g. ammonium and quaternary alkyl ammonium); aloe vera in any of its variety of forms (e.g., aloe vera gel); polyhydroxy alcohols such as sorbitol, glycerol, hexanetriol, propylene glycol, butylene glycol, hexylene glycol and the like; polyethylene glycols; sugars and starches; sugar and starch derivatives (e.g., alkoxylated glucose); hyaluronic acid; lactamide monoethanolamine;

acetamide monoethanolamine; and mixtures thereof. Also useful herein are the propoxylated glycerols described in U.S. Pat. No. 4,976,953, to Orr et al., issued Dec. 11, 1990, incorporated herein by reference.

Also useful are various C.sub.1-C.sub.30 monoesters and polyesters of sugars and related materials. These esters are derived from a sugar or polyol moiety and one or more carboxylic acid moieties. Such ester materials are further described in, U.S. Pat. No. 2,831,854, U.S. Pat. No. 4,005,196, to Jandacek, issued Jan. 25, 1977; U.S. Pat. No. 4,005,195, to Jandacek, issued Jan. 25, 1977, U.S. Pat. No. 5,306,516, to Letton et al., issued Apr. 26, 1994; U.S. Pat. No. 5,306,515, to Letton et al., issued Apr. 26, 1994; U.S. Pat. No. 5,305,514, to Letton et al., issued Apr. 26, 1994; U.S. Pat. No. 4,797,300, to Jandacek et al., issued Jan. 10, 1989; U.S. Pat. No. 3,963,699, to Rizzi et al, issued Jun. 15, 1976; U.S. Pat. No. 4,518,772, to Volpenhein, issued May 21, 1985; and U.S. Pat. No. 4,517,360, to Volpenhein, issued May 21, 1985, incorporated herein by reference.

Emulsifiers

The skin care compositions of the present invention can also comprise one or more emulsifiers. Emulsifiers generally serve to reduce the in interfacial tension between phases and improve the formulation and stability of an emulsion. Suitable emulsifiers include a wide variety of nonionic, cationic, anionic, and zwitterionic emulsifiers. See McCutcheon's, Detergents and Emulsifiers, North American Edition (1986), published by Allured Publishing Corporation; U.S. Pat. No. 5,011,681 issued to Ciotti et al. on Apr. 30, 1991; U.S. Pat. No. 4,421,769 issued to Dixon et al. on Dec. 20, 1983; and U.S. Pat. No. 3,755,560 issued to Dickert et al. on Aug. 28, 1973, incorporated herein by reference.

Suitable emulsifier types include esters of glycerin, esters of propylene glycol, fatty acid esters of polyethylene glycol, fatty acid esters of polypropylene glycol, esters of sorbitol, esters of sorbitan anhydrides, carboxylic acid copolymers, esters and ethers of glucose, ethoxylated ethers, ethoxylated alcohols, alkyl phosphates, polyoxyethylene fatty ether phosphates, fatty acid amides, acyl lactylates, soaps and mixtures thereof.

Suitable emulsifiers can include, but are not limited to, TEA stearate, DEA oleth-3 phosphate, polyethylene glycol 20 sorbitan monolaurate (polysorbate 20), polyethylene glycol 5 soya sterol, steareth-2, steareth-20, steareth-21, ceteareth-20, PPG-2 methyl glucose ether distearate, ceteth-10, polysorbate 80, cetyl phosphate, potassium cetyl phosphate, diethanolamine cetyl phosphate, polysorbate 60, glyceryl stearate, PEG-100 stearate, and mixtures thereof. Preferred emulsifiers are steareth-2, steareth-21, TEA stearate, diethanolamine cetyl phosphate, potassium cetyl phosphate, and mixtures thereof. The emulsifier can be used individually or as a mixture of two or more and comprises from about 0.1% to about 10%, more preferably from about 0.15% to about 7%, and most preferably from about 0.25% to about 5% of the compositions of the present invention.

Conventional Personal Cleansing Additive

These are additives which are conventionally used in personal cleansing compositions, such as toilet soaps, body washes, shampoos and medicated wipes. Examples of these are conditioning agents, conventional personal care polymer, antidandruff agent, surfactant; and mixtures thereof. These conventional personal cleansing additives are just some of the possible ingredients which can be conventionally added to personal cleansing compositions.

The conditioning agents, useful in the present invention can be further selected from the group comprising non-volatile hydrocarbons conditioning agents, silicone conditioning agents and mixtures thereof.

The conventional personal care polymers useful in the present invention can be further selected from the group comprising deposition polymers, styling polymers and solvent, dispersed phase polymers, and mixtures thereof.

The personal cleansing compositions of the present invention is in the form of a liquid or a liquid gel. It can contain for example, suspended ingredients, more than one phase etc. Effectively the personal cleansing compositions of the present invention can be in the form of any type of liquid or liquid gel and contain any additive conventionally added to personal cleansing compositions, such as shampoos, body wash gels, bath gels etc.

For more information and additional examples of conventional personal cleansing additives see U.S. Patent No. 6,335,312, incorporated herein by reference.

Suitable conventional personal cleansing additives include anti static agents, dyes, diluents, emollient oils (such as polyisobutylene, mineral oil, petrolatum and isocetyl stearyl stearate), pearlescent aids, foam boosters, styling polymer, pediculocides, dispersed phase polymers, hydrotropes, hair or skin conditioning agents such as nonvolatile silicone conditioning agents and nonvolatile organic conditioning agents, solvent pH adjusting agents, perfumes, preservatives, low viscosity surfactant soluble conditioning oil, electrolytes, amphiphiles, proteins, phase separation initiator, cationic spreading agents, such as cationic surfactants, antioxidants; chelators and sequestrants, surfactants, antidandruff agent such as platelet pyridinethione salt crystal, sulfur, octopirox, selenium sulfide, ketoconazole and pyridinethione salts, organic deposition polymers and aesthetic components such as fragrances, colorings, essential oils, skin sensates, astringents, suspending agent skin soothing agents, aqueous liquid carrier, skin healing agents and the like, nonlimiting examples of these aesthetic components include panthenol and derivatives (e.g. ethyl panthenol), pantothenic acid and its derivatives, clove oil, menthol, camphor, eucalyptus oil, eugenol, menthyl lactate, witch hazel distillate, allantoin, bisabolol, dipotassium glycyrrhizinate and the like, sunscreens, thickeners, vitamins and derivatives thereof (e.g., ascorbic acid, vitamin E, tocopheryl acetate, retinoic acid, retinol, retinoids, and the like), and viscosity adjusting agents. This list of conventional personal cleansing additives is not meant to be exclusive, and other conventional personal cleansing additives can be used.

For more information and additional examples of conditioning agents see U.S. Patent No. 6,200,554 and U.S. Patent No. 6,248,317. See also U.S Patent No. 4,741,855. All three of these references are incorporated herein by reference.

Suitable suspending agents are described in U.S. Pat. Nos. 4,741,855, 4,788,006, 2,798,053, and 4,704,272, which description is incorporated herein by reference.

Examples of some suitable styling polymers are described in U.S. Pat. No. 5,120,531, to Wells et al., issued Jun. 9, 1992; U.S. Pat. No. 5,120,532, to Wells et al., issued Jun. 9, 1992; U.S. Pat. No. 5,104,642, to Wells et al., issued Apr. 14, 1992; U.S. Pat. No. 4,272,511, to Papantoniou et al., issued Jun. 9, 1981; U.S. Pat. No. 4,963,348, to Bolich et al., issued Oct. 16, 1990, EPO Application 90307528.1, published as EPO Application 0 408 311 A2 on Jan. 11, 1991, Hayama, et al.; U.S. Pat. No. 5,061,481, issued Oct. 29, 1991, Suzuki et al.; U.S. Pat. No. 5,106,609, Bolich et al., issued Apr. 21, 1992; U.S. Pat. No. 5,100,658, Bolich et al., issued Mar. 31, 1992; U.S. Pat. No. 5,100,657, Ansher-Jackson, et al., issued Mar. 31, 1992; U.S. Pat. No. 5,104,646, Bolich et al., issued Apr. 14, 1992; U.S. Ser. No. 07/758,319, Bolich et al, filed Aug. 27, 1991, U.S. Ser. No. 07/758,320, Torgerson et al., filed Aug. 27, 1991, and U.S. Pat. No. 4,196,190, to Gehman et al., issued Apr. 1, 1980, which descriptions are incorporated herein by reference.

For suitable dispersed phase polymers see also copending U.S. Patent No. 5,783,200, which is incorporated herein by reference.

For suitable phase separation initiators see copending U.S. Patent No. 6,335,312, incorporated herein by reference.

For suitable antidandruff agents see also U.S. Pat. No. 4,948,576 to Verdicchio et al, and copending U.S. Patent Nos. 5,932,202, 4,379,753, 2,694,668, 3,152,046, 4,089,945, 4,885,107, 2,809,971, 3,236,733, 3,753,196, 3,761,418, 4,345,080, 4,323,683, 4,379,753 and 4,470,982 all of which are incorporated herein by reference.

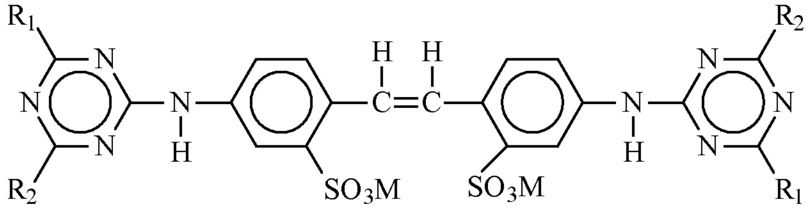
Optional Fabric Softener Ingredients

The fabric softening composition of the invention can also contain optional ingredients. A comprehensive list of possible optional ingredients can be found in U.S. Pat. No. 5,747,443, which is incorporated herein by reference.

Low molecular weight water soluble solvents--can also be used at levels of from 0% to about 12%, preferably from about 1% to about 10%, more preferably from about 2% to about 8%. The water soluble solvents cannot provide a clear product at the same low levels of the principal solvents described hereinbefore but can provide clear product when the principal solvent is not sufficient to provide completely clear product. The presence of these water soluble solvents is therefore highly desirable. Such solvents include: ethanol; isopropanol; 1,2-propanediol; 1,3-propanediol; propylene carbonate; etc. but do not include any of the principal solvents (B). These water soluble solvents have a greater affinity for water in the presence of hydrophobic materials like the softener active than the principal solvents.

Brighteners--The fabric softening compositions herein can also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.001% to 1% by weight of such optical brighteners.

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



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

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

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

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

Dispersibility Aids

Optional Viscosity/Dispersibility Modifiers--Relatively concentrated fabric softening compositions containing both saturated and unsaturated diester quaternary ammonium compounds can be prepared that are stable without the addition of concentration aids. However, the fabric softening compositions of the present invention may require organic and/or inorganic concentration aids to go to even higher concentrations and/or to meet higher stability standards depending on the other ingredients. These concentration aids, which typically can be viscosity modifiers, may be needed, or preferred, for ensuring stability under extreme conditions when particular softener active levels are used. The surfactant concentration aids are typically selected from the group consisting of (1) single long chain alkyl cationic surfactants; (2) nonionic surfactants; (3) amine oxides; (4) fatty acids; and (5) mixtures thereof. These aids are described in US Patent No. 5,545,340, specifically on page 14, line 12 to page 20, line 12, which is herein incorporated by reference.

When said dispersibility aids are present, the total level is from about 2% to about 25%, preferably from about 3% to about 17%, more preferably from about 4% to about 15%, and even more preferably from 5% to about 13% by weight of the composition. These materials can either be added as part of the active softener raw material e.g., the mono-long chain alkyl cationic surfactant and/or the fatty acid which are reactants used to form the biodegradable fabric softener active as discussed hereinbefore, or added as a separate component.

Mono-Alkyl Cationic Quaternary Ammonium Compound--When the mono-alkyl cationic quaternary ammonium compound is present, it is typically present at a level of from about 2% to about 25%, preferably from about 3% to about 17%, more preferably from about 4% to about 15%, and even more preferably from 5% to about 13% by weight of the composition, the total mono-alkyl cationic quaternary ammonium compound being at least at an effective level.

Such mono-alkyl cationic quaternary ammonium compounds useful in the present invention are, preferably, quaternary ammonium salts of the general formula:

$$[R^4N^+(R^5)_3]X^-$$

wherein R^4 is C8-22 alkyl or alkenyl group, preferably C10-18 alkyl or alkenyl group, more preferably C10-14 or C16-18 alkyl or alkenyl group; each R^5 is a C1-6 alkyl or substituted alkyl group (e.g., hydroxy alkyl), preferably C1-3 alkyl group, e.g., methyl (most preferred), ethyl, propyl, and the like, a benzyl group, hydrogen, a polyethoxylated chain with from about 2 to about 20 oxyethylene units, preferably from about 2.5 to about 13 oxyethylene units, more preferably from about 3 to about 10 oxyethylene units, and mixtures thereof; and X^- is as defined hereinbefore.

Especially preferred dispersibility aids are monolauryl trimethyl ammonium chloride and monotallow trimethyl ammonium chloride available from Witco under the trade name Varisoft® 471 and monooleyl trimethyl ammonium chloride available from Witco under the tradename Varisoft® 417.

The R^4 group can also be attached to the cationic nitrogen atom through a group containing one, or more, ester, amide, ether, amine, etc., linking groups which can be desirable for increased concentratability of fabric softening compositions components. Such linking groups are preferably within from about one to about three carbon atoms of the nitrogen atom.

Mono-alkyl cationic quaternary ammonium compounds also include C8-22 alkyl choline esters. The preferred dispersibility aids of this type have the formula:

$$R^1C(O)\text{-}O\text{-}CH_2CH_2N^+(R)_3X^-$$

wherein R^1, R and X^- are as defined previously.

Highly preferred dispersibility aids include C12-14 coco choline ester and C16-18 tallow choline ester.

Suitable biodegradable single-long-chain alkyl dispersibility aids containing an ester linkage in the long chains are described in U.S. Pat. No. 4,840,738, Hardy and Walley, issued Jun. 20, 1989, said patent being incorporated herein by reference.

When the dispersibility aid comprises alkyl choline esters, preferably the compositions also contain a small amount, preferably from about 2% to about 5% by weight of the composition, of organic acid. Organic acids are described in European Patent Application No. 404,471, Machin et al., published on Dec. 27, 1990, which is herein incorporated by reference. Preferably the organic acid is selected from the group consisting of glycolic acid, acetic acid, citric acid, and mixtures thereof.

Ethoxylated quaternary ammonium compounds which can serve as the dispersibility aid include ethylbis(polyethoxy ethanol)alkylammonium ethyl-sulfate with 17 moles of ethylene oxide, available under the trade name Variquat® 66 from Sherex Chemical Company; polyethylene glycol (15) oleammonium chloride, available under the trade name Ethoquad® 0/25 from Akzo; and polyethylene glycol (15) cocomonium chloride, available under the trade name Ethoquad® C/25 from Akzo.

Although the main function of the dispersibility aid is to increase the dispersibility of the ester softener, preferably the dispersibility aids of the present invention also have some softening properties to boost softening performance of the composition. Therefore, preferably the compositions of the present invention are essentially free of non- nitrogenous ethoxylated nonionic dispersibility aids which will decrease the overall softening performance of the compositions.

Also, quaternary compounds having only a single long alkyl chain, can protect the cationic softener from interacting with anionic surfactants and/or detergent builders that are carried over into the rinse from the wash solution.

Amine Oxides--Suitable amine oxides include those with one alkyl or hydroxyalkyl moiety of about 8 to about 22 carbon atoms, preferably from about 10 to about 18 carbon atoms, more preferably from about 8 to about 14 carbon atoms, and two alkyl moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups with about 1 to about 3 carbon atoms.

Examples include dimethyloctylamine oxide, diethyldecylamine oxide, bis-(2-hydroxyethyl)dodecyl-amine oxide, dimethyldodecylamine oxide, dipropyl- tetradecylamine oxide, methylethylhexadecylamine oxide, dimethyl-2-hydroxyoctadecylamine oxide, and coconut fatty alkyl dimethylamine oxide.

<u>Stabilizers</u>--Stabilizers can be present in the fabric softening compositions of the present invention. The term "stabilizer," as used herein, includes antioxidants and reductive agents. These agents are present at a level of from 0% to about 2%, preferably from about 0.01% to about 0.2%, more preferably from about 0.035% to about 0.1% for antioxidants, and more preferably from about 0.01% to about 0.2% for reductive agents. These assure good odor stability under long term storage conditions. Antioxidants and reductive agent stabilizers are especially critical for unscented or low scent products (no or low perfume).

Examples of antioxidants that can be added to the compositions of this invention include a mixture of ascorbic acid, ascorbic palmitate, propyl gallate, available from Eastman Chemical Products, Inc., under the trade names Tenox® PG and Tenox® S-1; a mixture of BHT (butylated hydroxytoluene), BHA (butylated hydroxyanisole), propyl gallate, and citric acid, available from Eastman Chemical Products, Inc., under the trade name Tenox®-6; butylated hydroxytoluene, available from UOP Process Division under the trade name Sustane® BHT; tertiary butylhydroquinone, Eastman Chemical Products, Inc., as Tenox® TBHQ; natural tocopherols, Eastman Chemical Products, Inc., as Tenox® GT-1/GT-2; and butylated hydroxyanisole, Eastman Chemical Products, Inc., as BHA; long chain esters (C8-22) of gallic acid, e.g., dodecyl gallate; Irganox® 1010; Irganox® 1035; Irganox® B 1171;

Irganox® 1425; Irganox® 3114; Irganox® 3125; and mixtures thereof; preferably Irganox® 3125, Irganox® 1425, Irganox® 3114, and mixtures thereof; more preferably Irganox® 3125 alone or mixed with citric acid and/or other chelators such as isopropyl citrate, Dequest® 2010, available from Monsanto with a chemical name of 1-hydroxyethylidene-1,1-diphosphonic acid (etidronic acid), and Tiron®, available from Kodak with a chemical name of 4,5-dihydroxy-m-benzene- sulfonic acid/sodium salt, and DTPA®, available from Aldrich with a chemical name of diethylenetriaminepentaace- tic acid.

Soil Release Agent--In the present fabric softening compositions, an optional soil release agent can be added. The addition of the soil release agent can occur in combination with the premix, in combination with the acid/water seat, before or after electrolyte addition, or after the final composition is made. The softening composition prepared by the process of the present invention herein can contain from 0% to about 10%, preferably from 0.2% to about 5%, of a soil release agent. Suitable soil release agents are described hereinbefore.

Examples of suitable soil release agents include the commercially available materials Zelcon 4780® (from Dupont) and Milease T® (from ICI).

A more complete disclosure of soil release agents is contained in U.S. Pat. No. 4,661,267, Decker, Konig, Straathof, and Gosselink, issued Apr. 28, 1987; U.S. Pat. No. 4,711,730, Gosselink and Diehl, issued Dec. 8, 1987; U.S. Pat. No. 4,749,596, Evans, Huntington, Stewart, Wolf, and Zimmerer, issued Jun. 7, 1988; U.S. Pat. No. 4,818,569, Trinh, Gosselink, and Rattinger, issued Apr. 4, 1989; U.S. Pat. No. 4,877,896, Maldonado, Trinh, and Gosselink, issued Oct. 31, 1989; U.S. Pat. No. 4,956,447, Gosselink et al., issues Sep. 11, 1990; and U.S. Pat. No. 4,976,879, Maldonado, Trinh, and Gosselink, issued Dec. 11, 1990, all of said patents being incorporated herein by reference.

These soil release agents can also act as scum dispersants.

Scum Dispersant--In the present invention, the premix can be combined with an optional scum dispersant, other than the soil release agent, and heated to a temperature at or above the melting point(s) of the components.

The preferred scum dispersants herein are formed by highly ethoxylating hydrophobic materials. The hydrophobic material can be a fatty alcohol, fatty acid, fatty amine, fatty acid amide, amine oxide, quaternary ammonium compound, or the hydrophobic moieties used to form soil release polymers. The preferred scum dispersants are highly ethoxylated, e.g., more than about 17, preferably more than about 25, more preferably more than about 40, moles of ethylene oxide per molecule on the average, with the polyethylene oxide portion being from about 76% to about 97%, preferably from about 81% to about 94%, of the total molecular weight.

The level of scum dispersant is sufficient to keep the scum at an acceptable, preferably unnoticeable to the consumer, level under the conditions of use, but not enough to adversely affect softening. For some purposes it is desirable that the scum is nonexistent. Depending on the amount of anionic or nonionic detergent, etc., used in the wash cycle of a typical laundering process, the efficiency of the rinsing steps prior to the introduction of the compositions herein, and the water hardness, the amount of anionic or nonionic detergent surfactant and detergency builder (especially phosphates and zeolites) entrapped in the fabric (laundry) will vary. Normally, the minimum amount of scum dispersant should be used to avoid adversely affecting softening properties. Typically scum dispersion requires at least about 2%, preferably at least about 4% (at least 6% and preferably at least 10% for maximum scum avoidance) based upon the level of softener active. However, at levels of about 10% (relative to the softener material) or more, one risks loss of softening efficacy of the product especially when the fabrics contain high proportions of nonionic surfactant which has been absorbed during the washing operation.

Preferred scum dispersants are: Brij 700®; Varonic U-250®; Genapol T-500®, Genapol T-800®; Plurafac A-79®; and Neodol 25-50®.

Bactericides--Examples of bactericides used in the compositions of this invention include glutaraldehyde, formaldehyde, 2-bromo-2-nitro-propane-1,3-diol sold by Inolex Chemicals, located in Philadelphia, Pa., under the trade name Bronopol®, and a mixture of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazoline-3-on- e sold by Rohm and Haas Company under the trade name Kathon about 1 to about 1,000 ppm by weight of the agent.

Perfume--The present invention can contain any softener compatible perfume. Suitable perfumes are disclosed in U.S. Pat. No. 5,500,138, Bacon et al., issued Mar. 19, 1996, said patent being incorporated herein by reference.

As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such as fixatives, extenders, stabilizers and solvents. These auxiliaries are also included within the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds. Other suitable perfumes are described hereinbefore

Examples of perfume ingredients useful in the perfumes of the present invention compositions include, but are not limited to, hexyl cinnamic aldehyde; amyl cinnamic aldehyde; amyl salicylate; hexyl salicylate; terpineol; 3,7-dimethyl-cis-2,6-octadien-1-ol; 2,6-dimethyl-2-octanol; 2,6-dimethyl-7-octen-2-ol; 3,7-dimethyl-3-octanol; 3,7-dimethyl-trans-2,6-octadien-1-ol; 3,7-dimethyl-6-octen-1-ol; 3,7-dimethyl-1-octanol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; tricyclodecenyl propionate; tricyclodecenyl acetate; anisaldehyde; 2-methyl-2-(para-iso- propylphenyl)-propionaldehyde; ethyl-3-methyl-3-phenyl glycidate; 4-(para-hydroxyphenyl)-butan-2-one; 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; para-methoxyacetophenone; para-methoxy-alpha-phenylpropene; methyl-2-n-hexyl-3-oxo-cyclopentane carboxylate; undecalactone gamma.

Additional examples of fragrance materials include, but are not limited to, orange oil; lemon oil; grapefruit oil; bergamot oil; clove oil; dodecalactone gamma; methyl-2-(2-pentyl-3-oxo-cyclopentyl)acetate; beta-naphthol methylether; methyl- beta-naphthylketone; coumarin; decylaldehyde; benzaldehyde; 4-tert- butylcyclohexyl acetate; alpha,alpha-dimethylphenethyl acetate; methylphenylcarbinyl acetate; Schiff's base of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldeh- yde and methyl anthranilate; cyclic ethyleneglycol diester of tridecandioic acid; 3,7-dimethyl-2,6-octadiene-1-nitrile; ionone gamma methyl; ionone alpha; ionone beta; petitgrain; methyl cedrylone; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene; ionone methyl; methyl-1,6,10-trimethyl-2,5,9-

cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1- ,1-dimethyl indane; benzophenone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecan; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8- -hexamethylcyclopenta-gamma-2-benzopyrane; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho-[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; cedryl acetate; para-tert-butylcyclohexyl acetate; patchouli; olibanum resinoid; labdanum; vetivert; copaiba balsam; fir balsam; and condensation products of: hydroxycitronellal and methyl anthranilate; hydroxycitronellal and indol; phenyl acetaldehyde and indol; 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate.

More examples of perfume components are geraniol; geranyl acetate; linalool; linalyl acetate; tetrahydrolinalool; citronellol; citronellyl acetate; dihydromyrcenol; dihydromyrcenyl acetate; tetrahydromyrcenol; terpinyl acetate; nopol; nopyl acetate; 2-phenylethanol; 2-phenylethyl acetate; benzyl alcohol; benzyl acetate; benzyl salicylate; benzyl benzoate; styrallyl acetate; dimethylbenzylcarbinol; trichloromethylphenylcarbinyl methylphenylcarbinyl acetate; isononyl acetate; vetiveryl acetate; vetiverol; 2-methyl-3-(p-tert- butylphenyl)-propanal; 2-methyl-3-(p-isopropylphenyl)-propanal; 3-(p-tert-butylphenyl)-propanal; 4-(4-methyl-3-pentenyl)-3-cyclohexeneca- rbaldehyde; 4-acetoxy-3-pentyltetrahydropyran; methyl dihydrojasmonate; 2-n- heptylcyclopentanone; 3-methyl-

2-pentyl-cyclopentanone; n-decanal; n-dodecanal; 9-decenol-1; phenoxyethyl isobutyrate; phenylacetaldehyde dimethylacetal; phenylacetaldehyde diethylacetal; geranonitrile; citronellonitrile; cedryl acetal; 3-isocamphylcyclohexanol; cedryl methylether; isolongifolanone; aubepine nitrile; aubepine; heliotropine; eugenol; vanillin; diphenyl oxide; hydroxycitronellal ionones; methyl ionones; isomethyl ionones; irones; cis-3-hexenol and esters thereof; indane musk fragrances; tetralin musk fragrances; isochroman musk fragrances; macrocyclic ketones; macrolactone musk fragrances; ethylene brassylate.

The perfumes useful in the present invention compositions are substantially free of halogenated materials and nitromusks.

Suitable solvents, diluents or carriers for perfumes ingredients mentioned above are for examples, ethanol, isopropanol, diethylene glycol, monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, etc. The amount of such solvents, diluents or carriers incorporated in the perfumes is preferably kept to the minimum needed to provide a homogeneous perfume solution.

Perfume can be present at a level of from 0% to about 10%, preferably from about 0.1% to about 5%, and more preferably from about 0.2% to about 3%, by weight of the finished composition. Fabric softener compositions of the present invention provide improved fabric perfume deposition.

Chelating Agents--The compositions and processes herein can optionally employ one or more copper and/or nickel chelating agents ("chelators"). Such water-soluble 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. The whiteness and/or brightness of fabrics are substantially improved or restored by such chelating agents and the stability of the materials in the compositions are improved. Suitable chelating agents are described hereinbefore.

Amino carboxylates useful as chelating agents herein include ethylenedi- aminetetraacetates (EDTA), N-hydroxyethylethylenediaminetriac- etates, nitrilotriacetates (NTA), ethylenediamine tetraproprionates, ethylenediamine-N,N'-diglutamates, 2-hyroxypropylenediamine-N,N'-disuccinates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates (DETPA), and ethanoldiglycines, including their water-soluble salts such as the 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, and include ethylenediaminetetrakis (methylenephosphonates), diethylenetriamine-N,N,N- ',N",N"-pentakis(methane phosphonate) (DETMP) and 1hydroxyethane-1,1-dipho- sphonate (HEDP). Preferably, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

The chelating agents are typically used in the present rinse process at levels from about 2 ppm to about 25 ppm, for periods from 1 minute up to several hours' soaking.

The preferred EDDS chelator used herein (also known as ethylenediamine-N,N'-disuccinate) is the material described in U.S. Pat. No. 4,704,233, herein incorporated by reference.

As can be seen from the foregoing, a wide variety of chelators can be used herein. Indeed, simple polycarboxylates such as citrate, oxydisuccinate, and the like, can also be used, although such chelators are not as effective as the amino carboxylates and phosphonates, on a weight basis. Accordingly, usage levels may be adjusted to take into account differing degrees of chelating effectiveness. The chelators herein will preferably have a stability constant (of the fully ionized chelator) for copper ions of at least about 5, preferably at least about 7. Typically, the chelators will comprise from about 0.5% to about 10%, more preferably from about 0.75% to about 5%, by weight of the compositions herein. Preferred chelators include DETMP, DETPA, NTA, EDDS and mixtures thereof.

Other Optional Ingredients--The present invention can include optional components conventionally used in textile treatment compositions, for example: colorants; preservatives; surfactants; anti-shrinkage agents; fabric crisping agents; spotting agents; germicides; fungicides; anti-oxidants such as butylated hydroxy toluene, anti-corrosion agents, and the like.

Particularly preferred ingredients include water soluble calcium and/or magnesium compounds, which provide additional stability. The chloride salts are preferred, but acetate, nitrate, etc. salts can be used. The level of said calcium and/or magnesium salts is from 0% to about 2%, preferably from about 0.05% to about 0.5%, more preferably from about 0.1% to about 0.25%.

The present invention can also include other compatible ingredients, including those as disclosed in copending applications Ser. No.: 08/372,068, filed Jan. 12, 1995, Rusche, et al.; Ser. No. 08/372,490, filed Jan. 12, 1995, Shaw, et al.; and Ser. No. 08/277,558, filed Jul. 19, 1994, Hartman, et al., incorporated herein by reference.

Form of the Cleaning Compositions

The cleaning compositions in accordance with the invention can take a variety of physical forms including granular, gel, tablet, bar, paste, cream and liquid forms. The form can be dependent upon the end use of the composition. The compositions include the so-called concentrated granular detergent compositions adapted to be added to a washing machine by means of a dispensing device placed in the machine drum with the soiled fabric load.

The mean particle size of the components of granular compositions in accordance with the invention should preferably be such that no more that 5% of particles are greater than 1.7 mm in diameter and not more than 5% of particles are less than 0.15 mm in diameter.

The term mean particle size as defined herein is calculated by sieving a sample of the composition into a number of fractions (typically 5 fractions) on a series of Tyler sieves. The weight fractions thereby obtained are plotted against the aperture size of the sieves. The mean particle size is taken to be the aperture size through which 50% by weight of the sample would pass.

Certain preferred granular detergent compositions in accordance with the present invention are the high-density types, now common in the marketplace; these typically have a bulk density of at least 600 g/liter, more preferably from 650 g/liter to 1200 g/liter.

Surfactant Agglomerate Particles

One of the preferred methods of delivering surfactant in consumer products is to make surfactant agglomerate particles, which may take the form of flakes, prills, marumes, noodles, ribbons, but preferably take the form of granules. A preferred way to process the particles is by agglomerating powders (e.g. aluminosilicate, carbonate) with high active surfactant pastes and to control the particle size of the resultant agglomerates within specified limits. Such a process involves mixing an effective amount of powder with a high active surfactant paste in one or more agglomerators such as a pan agglomerator, a Z-blade mixer or more preferably an in-line mixer such as those manufactured by Schugi (Holland) BV, 29 Chroomstraat 8211 AS, Lelystad, Netherlands, and Gebruder Lodige Maschinenbau GmbH, D-4790 Paderborn 1, Elsenerstrasse 7-9, Postfach 2050, Germany. Most preferably a high shear mixer is used, such as a Lodige CB (Trade Name).

A high active surfactant paste comprising from 50% by weight to 95% by weight, preferably 70% by weight to 85% by weight of surfactant is typically used. The paste may be pumped into the agglomerator at a temperature high enough to maintain a pumpable viscosity, but low enough to avoid degradation of the anionic surfactants used. An operating temperature of the paste of 50°C to 80°C is typical.

Laundry Washing Method

Machine laundry methods herein typically comprise treating soiled laundry with an aqueous wash solution in a washing machine having dissolved or dispensed therein an effective amount of a machine laundry detergent composition in accord with the invention. By an effective amount of the detergent composition it is here meant from 40g to 300g of product dissolved or dispersed in a wash solution of volume from 5 to 65 liters, as are typical product dosages and wash solution volumes commonly employed in conventional machine laundry methods.

As noted, surfactants are used herein in detergent compositions, preferably in combination with other detersive surfactants, at levels which are effective for achieving at least a directional improvement in cleaning performance. In the context of a fabric laundry composition, such "usage levels" can vary widely, depending not only on the type and severity of the soils and stains, but also on the wash water temperature, the volume of wash water and the type of washing machine.

In a preferred use aspect a dispensing device is employed in the washing method. The dispensing device is charged with the detergent product, and is used to introduce the product directly into the drum of the washing machine before the commencement of the wash cycle. Its volume capacity should be such as to be able to contain sufficient detergent product as would normally be used in the washing method.

Once the washing machine has been loaded with laundry the dispensing device containing the detergent product is placed inside the drum. At the commencement of the wash cycle of the washing machine water is introduced into the drum and the drum periodically rotates. The design of the dispensing device should be such that it permits containment of the dry detergent product but then allows release of this product during the wash cycle in response to its agitation as the drum rotates and also as a result of its contact with the wash water.

Alternatively, the dispensing device may be a flexible container, such as a bag or pouch. The bag may be of fibrous construction coated with a water impermeable protective material so as to retain the contents, such as is disclosed in European published Patent Application No. 0018678. Alternatively it may be formed of a water-insoluble synthetic polymeric material provided with an edge seal or closure designed to rupture in aqueous media as disclosed in European published Patent Application Nos. 0011500, 0011501, 0011502, and 0011968, herein incorporated by reference. A convenient form of water frangible closure comprises a water-soluble adhesive disposed along and sealing one edge of a pouch formed of a water impermeable polymeric film such as polyethylene or polypropylene.

Machine Dishwashing Method

Any suitable methods for machine washing or cleaning soiled tableware, particularly soiled silverware are envisaged.

A preferred machine dishwashing method comprises treating soiled articles selected from crockery, glassware, hollowware, silverware and cutlery and mixtures thereof, with an aqueous liquid having dissolved or dispensed therein an effective amount of a machine dishwashing composition in accord with the invention. By an effective amount of the machine dishwashing composition it is meant from 8g to 60g of product dissolved or dispersed in a wash solution of volume from 3 to 10 liters, as are typical product dosages and wash solution volumes commonly employed in conventional machine dishwashing methods.

Packaging for the Compositions

Commercially marketed executions of the bleaching compositions can be packaged in any suitable container including those constructed from paper, cardboard, plastic materials and any suitable laminates.

Form of the Skin Care Compositions

The skin care compositions in accordance with the invention can take a variety of physical forms including powder, gel, tablet, bar, paste, cream and liquid forms. The form can be dependent upon the end use of the composition. The skin care composition can also be in a tissue, baby wipe, or other similar articles.

Form of the Personal Cleansing Compositions

The personal cleansing compositions in accordance with the invention can take a variety of physical forms including powder, gel, tablet, bar, paste, cream and liquid forms. The form can be dependent upon the end use of the composition.

Form of the Fabric Softener Compositions

Solid particulate compositions--The invention also comprises solid particulate composition comprising:

a) from 50% to 95%, preferably from 60% to 90%, of said biodegradable fabric softening active;
b) optionally, from 0% to 30%, preferably from 3% to 15%, of dispersibility modifier; and
c) from 0% to 10% of a pH modifier.

Optional pH Modifier

Since the biodegradable ester fabric softener actives are somewhat labile to hydrolysis, it is preferable to include optional pH modifiers in the solid particulate fabric softener compositions to which water is to be added, to form stable dilute or concentrated liquid softener compositions. Said stable liquid fabric softener compositions should have a pH (neat) of from about 2 to about 5, preferably from about 2 to about 4.5, more preferably from about 2 to about 4.

The pH can be adjusted by incorporating a solid, water-soluble Bronsted acid. Examples of suitable Bronsted acids include inorganic mineral acids, such as boric acid, sodium bisulfate, potassium bisulfate, sodium phosphate monobasic, potassium phosphate monobasic, and mixtures thereof; organic acids, such as citric acid, fumaric acid, maleic acid, malic acid, tannic acid, gluconic acid, glutamic acid, tartaric acid, glycolic acid, chloroacetic acid, phenoxyacetic acid, 1,2,3,4-butane tetracarboxylic acid, benzene sulfonic acid, benzene phosphonic acid, ortho-toluene sulfonic acid, para-toluene sulfonic acid, phenol sulfonic acid, naphthalene sulfonic acid, oxalic acid, 1,2,4,5-pyromellitic acid, 1,2,4-trimellitic acid, adipic acid, benzoic acid, phenylacetic acid, salicylic acid, succinic acid, and mixtures thereof;

and mixtures of mineral inorganic acids and organic acids. Preferred pH modifiers are citric acid, gluconic acid, tartaric acid, 1,2,3,4-butane tetracarboxylic acid, malic acid, and mixtures thereof.

Optionally, materials that can form solid clathrates such as cyclodextrins and/or zeolites, etc., can be used as adjuvants in the solid particulate composition as host carriers of concentrated liquid acids and/or anhydrides, such as acetic acid, HCl, sulfuric acid, phosphoric acid, nitric acid, carbonic acid, etc. An example of such solid clathrates is carbon dioxide adsorbed in zeolite A, as disclosed in U.S. Pat. No. 3,888,998, Whyte and Samps, issued Jun. 10, 1975 and U.S. Pat. No. 4,007,134, Liepe and Japikse, issued Feb. 8, 1977, both of said patents being incorporated herein by reference. Examples of inclusion complexes of phosphoric acid, sulfuric acid, and nitric acid, and process for their preparation are disclosed in U.S. Pat. No. 4,365,061, issued Dec. 21, 1982 to Szejtli et al., said patent being incorporated herein by reference.

When used, the pH modifier is typically used at a level of from about 0.01% to about 10%, preferably from about 0.1% to about 5%, by weight of the composition.

Preparation of Solid Particulate Granular Fabric Softener

The granules can be formed by preparing a melt, solidifying it by cooling, and then grinding and sieving to the desired size. In a three-component mixture, e.g., nonionic surfactant, single-long-chain cationic, and DEQA, it is more preferred, when forming the granules, to pre-mix the nonionic surfactant and the more soluble single-long-chain alkyl cationic compound before mixing in a melt of the diester quaternary ammonium cationic compound.

It is highly preferred that the primary particles of the granules have a diameter of from about 50 to about 1,000, preferably from about 50 to about 400, more preferably from about 50 to about 200, microns. The granules can comprise smaller and larger particles, but preferably from about 85% to about 95%, more preferably from about 95% to about 100%, are within the indicated ranges. Smaller and larger particles do not provide optimum emulsions/dispersions when added to water. Other methods of preparing the primary particles can be used including spray cooling of the melt. The primary particles can be agglomerated to form a dust-free, non-tacky, free-flowing powder. The agglomeration can take place in a conventional agglomeration unit (i.e., Zig-Zag Blender, Lodige) by means of a water-soluble binder. Examples of water-soluble binders useful in the above agglomeration process include glycerol, polyethylene glycols, polymers such as PVA, polyacrylates, and natural polymers such as sugars.

The flowability of the granules can be improved by treating the surface of the granules with flow improvers such as clay, silica or zeolite particles, water-soluble inorganic salts, starch, etc.

Method of Use

Water can be added to the particulate, solid, granular compositions to form dilute or concentrated liquid softener compositions for later addition to the rinse cycle of the laundry process with a concentration of said biodegradable cationic softening compound of from about 0.5% to about 50%, preferably from about 1% to about 35%, more preferably from about 4% to about 32%. The particulate, rinse-added solid composition (1) can also be used directly in the rinse bath to provide adequate usage concentration (e.g., from about 10 to about 1,000 ppm, preferably from about 50 to about 500 ppm, of total softener active ingredient). The liquid compositions can be added to the rinse to provide the same usage concentrations.

The water temperature for preparation should be from about 20°C to about 90°C, preferably from about 25°C to about 80°C Single-long-chain alkyl cationic surfactants as the viscosity/dispersibility modifier at a level of from 0% to about 15%, preferably from about 3% to about 15%, more preferably from about 5% to about 15%, by weight of the composition, are preferred for the solid composition. Nonionic surfactants at a level of from about 5% to about 20%, preferably from about 8% to about 15%, as well as mixtures of these agents can also serve effectively as the viscosity/dispersibility modifier.

The emulsified/dispersed particles, formed when the said granules are added to water to form aqueous concentrates, typically have an average particle size of less than about 10 microns, preferably less than about 2 microns, and more preferably from about 0.2 to about 2 microns, in order that effective deposition onto fabrics is achieved. The term "average particle size," in the context of this specification, means a number average particle size, i.e., more than 50% of the particles have a diameter less than the specified size.

Particle size for the emulsified/dispersed particles is determined using, e.g., a Malvern particle size analyzer.

Depending upon the particular selection of nonionic and cationic surfactant, it may be desirable in certain cases, when using the solids to prepare the liquid, to employ an efficient means for dispersing and emulsifying the particles (e.g., blender).

Solid particulate compositions used to make liquid compositions can, optionally, contain electrolytes, perfume, antifoam agents, flow aids (e.g., silica), dye, preservatives, and/or other optional ingredients described hereinbefore.

The benefits of adding water to the particulate solid composition to form aqueous compositions to be added later to the rinse bath include the ability to transport less weight thereby making shipping more economical, and the ability to form liquid compositions similar to those that are normally sold to consumers, e.g., those that are described herein, with lower energy input (i.e., less shear and/or lower temperature). Furthermore, the particulate granular solid fabric softener compositions, when sold directly to the consumers, have less packaging requirements and smaller, more disposable containers. The consumers will then add the compositions to available, more permanent, containers, and add water to pre-dilute the compositions, which are then ready for use in the rinse bath, just like the liquid compositions herein. The liquid form is easier to handle, since it simplifies measuring and dispensing.

Dryer Activated compositions--The present invention also relates to improved solid dryer-activated fabric softener compositions which are either incorporated into articles of manufacture, e.g., on a substrate, or, are in the form of particles similar to those disclosed above. (including, where appropriate, agglomerates, pellets, and tablets of said particles). Such compositions typically contain from about 10% to about 95% of fabric softening agent.

Substrate Articles--In preferred embodiments, the present invention encompasses articles of manufacture. Representative articles are those that are adapted for use to provide unique perfume benefits and to soften fabrics in an automatic laundry dryer, of the types disclosed in U.S. Pat. No. 3,989,631 Marsan, issued Nov. 2, 1976; U.S. Pat. No. 4,055,248, Marsan, issued Oct. 25, 1977; U.S. Pat. No. 4,073,996, Bedenk et al., issued Feb. 14, 1978; U.S. Pat. No. 4,022,938, Zaki et al., issued May 10, 1977; U.S. Pat. No.

4,764,289, Trinh, issued Aug. 16, 1988; U.S. Pat. No. 4,808,086, Evans et al., issued Feb. 28, 1989; U.S. Pat. No. 4,103,047, Zaki et al., issued Jul. 25, 1978; U.S. Pat. No. 3,736,668, Dillarstone, issued Jun. 5, 1973; U.S. Pat. No. 3,701,202, Compa et al., issued Oct. 31, 1972; U.S. Pat. No. 3,634,947, Furgal, issued Jan. 18, 1972; U.S. Pat. No. 3,633,538, Hoeflin, issued Jan. 11, 1972; and 3,435,537, Rumsey, issued Apr. 1, 1969; and U.S. Pat. No. 4,000,340, Murphy et al., issued Dec. 28, 1976, all of said patents being incorporated herein by reference.

Typical articles of manufacture of this type include articles comprising:

I. a fabric conditioning composition comprising from about 30% to about 95% of normally solid, dryer softenable fabric softening agent comprising said biodegradable fabric softening active; and

II. a dispensing means which provides for release of an effective amount of said composition including an effective amount of ii, sufficient to provide odor control, to fabrics in an automatic laundry dryer at automatic laundry dryer operating temperatures, e.g., from about 35°C to 115°C.

When the dispensing means is a flexible substrate, e.g., in sheet configuration, the fabric conditioning composition is releasably affixed on the substrate to provide a weight ratio of conditioning composition to dry substrate ranging from about 10:1 to about 0.5:1, preferably from about 5:1 to about 1:1.

The solid fabric softener compositions herein can include cationic and nonionic fabric softener actives used in combination with each other.

In the following Examples, the abbreviations for the various ingredients used for the compositions have the following meanings.

SAE Secondary alcohol ethoxylate - C_{11-15} secondary alcohol 7 mole ethoxylate.

SAES Secondary alcohol ethoxylate sulfate - C_{11-15} secondary alcohol 3 mole ethoxysulfate, sodium salt.

SAEC Secondary alcohol ethoxylate carboxylate - C_{11-15} secondary alcohol 3 mole ethoxycarboxylate, sodium salt.

NaPS Sodium paraffin sulfonate

C45AS Sodium C14-15 linear alkyl sulfate

CxyAS Sodium C_{1x}-C_{1y} alkyl sulfate (or other salt if specified)

CxyEzS Sodium C_{1x}-C_{1y} alkyl sulfate condensed

LAS Sodium linear alkyl benzene sulfonate

Citric acid Anhydrous citric acid

LMFAA C12-14 alkyl N-methyl glucamide

CxyFA C_{1x}-C_{1y} fatty acid

CxyEz A C_{1x}-C_{1y} branched primary alcohol condensed with an average of z moles of ethylene oxide

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

Citrate Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425 µm and 850 µm

TFAA C16-18 alkyl N-methyl glucamide

Fatty Acid (C12/14) C12-C14 fatty acid

Fatty Acid (TPK) Topped palm kernel fatty acid

Fatty Acid (RPS) Rapeseed fatty acid

Borax Na tetraborate decahydrate

PAA Polyacrylic Acid (mw=4500)

PEG Polyethylene glycol (mw=4600) with z moles of ethylene oxide (or other salt if specified)

CxyEz A C_{1x}-C_{1y} branched primary alcohol condensed with an average of z moles of ethylene oxide

AQA $R_2.N^+(CH_3)_x((C._2H_4O_yH)_z$ with $R_2=C_{8-18}$, x+z=3, x=0 to 3, z=0 to 3, y=1 to 15.

STPP Anhydrous sodium tripolyphosphate

Zeolite A Hydrated Sodium Aluminosilicate of formula $Na_{12}(A1O_2SiO_2)_{12}.27H_2O$ having a primary particle size in the range from 0.1 to 10 micrometers

NaSKS-6	Crystalline layered silicate of formula delta-$Na_2Si_2O_5$
Carbonate	Anhydrous sodium carbonate with a particle size between 200 µm and 900 µm
Bicarbonate	Anhydrous sodium bicarbonate with a particle size distribution between 400 µm and 1200 µm
Silicate	Amorphous Sodium Silicate (SiO_2:Na_2O; 2.0 ratio)
Sulfate	Anhydrous sodium sulfate
PAE	ethoxylated tetraethylene pentamine
PIE	ethoxylated polyethylene imine
PAEC	methyl quaternized ethoxylated dihexylene triamine
MA/AA	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000.
CMC	Sodium carboxymethyl cellulose
Protease	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
Cellulase	Cellulytic enzyme of activity 1000 CEVU/g sold by NOVO Industries A/S under the tradename Carezyme
Amylase	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T

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

PB 1 Anhydrous sodium perborate bleach of nominal formula NaBO.sub.2.H.sub.2O.sub.2

Percarbonate Sodium Percarbonate of nominal formula 2Na.sub.2CO.sub.3.3H.sub.2O.sub.2

NaDCC Sodium dichloroisocyanurate

NOBS Nonanoyloxybenzene sulfonate, sodium salt

TAED Tetraacetylethylenediamine

DTPMP Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under Trade name Dequest 2060

Photoactivated bleach Sulfonated Zinc Phthalocyanine bleach encapsulated in dextrin soluble polymer

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

Brightener 2 Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin- -2-yl)amino) stilbene-2:2'-disulfonate.

HEDP 1,1-hydroxyethane diphosphonic acid

SRP 1 Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone

SRP 2 sulfonated ethoxylated terephthalate polymer

SRP 3 methyl capped ethoxylated terephthalate polymer

Silicone antifoam Polydimethylsiloxane foam controller with siloxane- oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.

DTPA Diethylene triamine pentaacetic acid

Endolase Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S

MEA Monoethanolamine

PG Propaneglycol

BPP Butoxy-propoxy-propanol

EtOH Ethanol

NaOH Solution of sodium hydroxide

NaTS Sodium toluene sulfonate

TFAA C16-18 alkyl N-methyl glucamide

LMFAA C12-14 alkyl N-methyl glucamide

APA C8-C10 amido propyl dimethyl amine

Isofol 16 Condea trademark for C16 (average) Guerbet alcohols

In the following Examples all levels are quoted as % by weight of the composition. The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

EXAMPLE 1

The following powder laundry detergent compositions A to D are prepared in accord with the invention:

TABLE 1-1

	A	B	C	D
SAES or SAEC	2	4.0	4.0	8.0
C45 AS	6	4.0	2.8	--
LAS	--	--	1.2	--
SAE	3.4	3.4	3.4	3.4
AQA	0.4	0.5	0.6	0.8
Zeolite A	18.1	18.1	18.1	18.1
Carbonate	13.0	13.0	13.0	27.0
Silicate	1.4	1.4	1.4	3.0
Sulfate	26.1	26.1	26.1	26.1
PB1	9.0	9.0	9.0	9.0
TAED	1.5	1.5	1.5	1.5
DTPMP	0.25	0.25	0.25	0.25
HEDP	0.3	0.3	0.3	0.3
Protease	0.26	0.26	0.26	0.26
Amylase	0.1	0.1	0.1	0.1
MA/AA	0.3	0.3	0.3	0.3
CMC	0.2	0.2	0.2	0.2
Photoactivated beach	15 ppm	15 ppm	15 ppm	15 ppm
Brightener 1	0.09	0.09	0.09	0.09
Perfume	0.3	0.3	0.3	0.3
Silicone antifoam	0.5	0.5	0.5	0.5

EXAMPLE 2

The following powder laundry detergent compositions E to I are prepared in accord with the invention:

TABLE 2-1

	E	F	G	H	I
SAES or SAEC	22	16.5	11	1-5.5	10-25
Any Combination of: C45 AS C45E1S LAS C16 SAS C14-17 NaPS C14-18 MES	0	1-5.5	11	16.5	0-5
AQA	0-5	0-2	0-2	0-2	0-4
SAE	1.5	1.5	1.5	1.5	0-4
Zeolite A	27.8	27.8	27.8	27.8	20-30
PAA	2.3	2.3	2.3	2.3	0-5
Carbonate	27.3	27.3	27.3	27.3	20-30
Silicate	0.6	0.6	0.6	0.6	0-2
PB1	1.0	1.0	1.0	1.0	0-3
Protease	0-0.5	0-0.5	0-0.5	0-0.5	0-0.5
Cellulase	0-0.3	0-0.3	0-0.3	0-0.3	0-0.5
Amylase	0-0.5	0-0.5	0-0.5	0-0.5	0-1
SRP 1	0.4	0.4	0.4	0.4	0-1
Brightener 1 or 2	0.2	0.2	0.2	0.2	0-0.3
PEG	1.6	1.6	1.6	1.6	0-2
Sulfate	5.5	5.5	5.5	5.5	0-6
Silicone Antifoam	0.42	0.42	0.42	0.42	0-0.5
Moisture & Minors			Balance		

EXAMPLE 3

The following powder laundry detergent compositions J to N are prepared in accord with the invention:

TABLE 3-1

	J	K	L	M	N
SAES or SAEC	16.5	12.5	8.5	4	1-25
Any Combination of: C45 AS C45E1S LAS C16 SAS C14-17 NaPS C14-18 MES	0-6	10	14	18.5	0-20
AQA	0-2	0-2	0-2	0-2	0-4
TFAA	1.6	1.6	1.6	1.6	0-4
SAE	5	5	5	5	0-6
Zeolite A	15	15	15	15	10-30
NaSKS-6	11	11	11	11	5-15
Citrate	3	3	3	3	0-8
MA/AA	4.8	4.8	4.8	4.8	0-8
HEDP	0.5	0.5	0.5	0.5	0-1
Carbonate	8.5	8.5	8.5	8.5	0-15
Percarbonate or PB1	20.7	20.7	20.7	20.7	0-25
TAED	4.8	4.8	4.8	4.8	0-8
Protease	0.9	0.9	0.9	0.9	0-1
Lipase	0.15	0.15	0.15	0.15	0-0.3
Cellulase	0.26	0.26	0.26	0.26	0-0.5
Amylase	0.36	0.36	0.36	0.36	0-0.5
SRP 1	0.2	0.2	0.2	0.2	0-0.5
Brightener 1 or 2	0.2	0.2	0.2	0.2	0-0.4
Sulfate	2.3	2.3	2.3	2.3	0-25
Silicone Antifoam		0.4	0.4	0.4	0-1
Moisture & Minors	Balance				

EXAMPLE 4

The following powder laundry detergent compositions O to T are prepared in accord with the invention:

TABLE 4-1

	O	P	Q	R	S	T
SAES or SAEC	32	24	16	8	4	1-35
Any Combination of: C45 AS C45E1S LAS C16 SAS C14-17 NaPS C14-18 MES	0	8	16	24	28	0-35
SAE	3.6	3.6	3.6	3.6	3.6	0-6
AQA	0-1	0-1	0-1	0-1	0-1	0-4
Zeolite A	9.0	9.0	9.0	9.0	9.0	0-20
PAA or MA/AA	7.0	7.0	7.0	7.0	7.0	0-10
Carbonate	18.4	18.4	18.4	18.4	18.4	5-25
Silicate	11.3	11.3	11.3	11.3	11.3	5-25
PB1	3.9	3.9	3.9	3.9	3.9	1-6
NOBS	4.1	4.1	4.1	4.1	4.1	0-6
Protease	0.9	0.9	0.9	0.9	0.9	0-1.3
Amylase	0-0.5	0-0.5	0-0.5	0-0.5	0-0.5	0-0.5
Cellulase	0-0.3	0-0.3	0-0.3	0-0.3	0-0.3	0-0.3
SRP1	0.5	0.5	0.5	0.5	0.5	0-1
Brightener 1 or 2	0.3	0.3	0.3	0.3	0.3	0-0.5
PEG	0.2	0.2	0.2	0.2	0.2	0-0.5
Sulfate	5.1	5.1	5.1	5.1	5.1	0-10
Silicone Antifoam	0.2	0.2	0.2	0.2	0.2	0-0.5
Moisture & Minors	Balance					

EXAMPLE 5

The following powder detergent formulations U to X, according to the present invention, are prepared:

TABLE 5-1

	U	V	W	X
Agglomerate				
SAES or SAEC	11.0	7.0	4	14.0
MBFS	3.0	10.0	17.0	3.0
Zeolite A	15.0	12.0	10.0	10.0
Carbonate	4.0	4.0	4.0	8.0
PAA or MA/AA	4.0	4.0	4.0	2.0
CMC	0.5	0.5	0.5	0.5
DTPMP	0.4	0.4	0.4	0.4
Spray On				
SAE	5.0	5.0	5.0	5.0
Perfume	0.5	0.5	0.5	0.5
Dry Adds				
SAE	6.0	6.0	3.0	3.0
HEDP	0.5	0.5	0.5	0.3
SKS-6	13.0	13.0	13.0	6.0
Citrate	3.0	3.0	3.0	1.0
TAED	5.0	5.0	5.0	7.0
Percarbonate	20.0	20.0	20.0	20.0
SRP 1	0.3	0.3	0.3	0.3
Protease	1.4	1.4	1.4	1.4
Lipase	0.4	0.4	0.4	0.4
Cellulase	0.6	0.6	0.6	0.6
Amylase	0.6	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0	5.0
Brightener 1	0.2	0.2	0.2	0.2
Brightener 2	0.2	0.2	0.2	--
Balance (Water/Miscellaneous)	100	100	100	100

EXAMPLE 6

The following powder laundry detergent compositions Y to BB suitable for hand-washing soiled fabrics are prepared in accord with the invention:

TABLE 6-1

	Y	Z	AA	BB
SAEC OR SAES	5	10	18	22
LAS	20	10	11	--
STPP	15	30	11	28
Carbonate	15	8	20	15
Silicates	15	10	15	10
Protease	0	0	0.3	0.3
Perborate	0	0	0	10
Sodium Chloride	25	15	20	10
Brightener, Perfume	0-0.3	0.2	0.2	0.2
Moisture & Minors		Balance		

EXAMPLE 7

The following powder laundry detergent compositions CC to FF suitable for hand-washing soiled fabrics are prepared in accord with the invention:

TABLE 7-1

	CC	DD	EE	FF
SAES or SAEC	22	16	11	1-6
Any Combination of: C45 AS C45E1S C45E3S LAS	0	0-5	5-15	10-20
AQA	0-5	0-1	0-5	0-3
SAE	0-2	0-4	0-2	0-2
STPP	5-45	5-45	5-45	5-45
PAA	0-2	0-2	0-2	0-2
CMC	0-0.5	0-0.5	0-0.5	0-0.5
Protease	0-0.5	0-0.5	0-0.5	0-0.5
Cellulase	0-0.3	0-0.3	0-0.3	0-0.3
Amylase	0-0.5	0-0.5	0-0.5	0-0.5
SRP	0-0.5	0.4	0-0.5	0-0.5
Brightener, perfume	0-0.3	0-0.2	0-0.3	0-0.2
Photobleach	0-0.1	0-0.1	0-0.1	0-0.1
Carbonate	15	10	20	15
Silicate	7	15	10	8
Sulfate	5	5	5	5
Moisture & Minors	Balance			

EXAMPLE 8

Light-duty liquid dishwashing detergent compositions are prepared:

TABLE 8-1

Ingredient	Wt. % GG	Wt. % HH	Wt. % II	Wt. % JJ
C23E0.6S	25	20	15	0
SAE	1	1	1	1
SAES or SAEC	5	10	15	30
LMFAA	4	4	4	4
Coconut	4	4	4	4
Amine Oxide EO/PO Block	0.5	0.5	0.5	0.5
Co-polymer - Tetronic® 704 EtOH	6	6	6	6
Calcium xylene	5	5	5	5
Sulfonate Magnesium (added as chloride)	3.0	3.0	3.0	3.0
Water, thickeners and minors	to 100%	to 100%	to 100%	to 100%
pH @ 10% (as made)	7.5	7.5	7.5	7.5

EXAMPLE 9

This example illustrates the preparation and performance advantages of the secondary alcohol ethoxylate sulfate containing non-aqueous liquid detergent compositions of the instant invention. Such examples, however, are not necessarily meant to limit or otherwise define the scope of the invention herein. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

Preparation of LAS Powder for Use as a Structurant

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

NaLAS powder is produced by taking a slurry of NaLAS in water (approximately 40-50% active) combined with dissolved sodium sulfate (3-15%) and hydrotrope, sodium 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 9-1.

TABLE 9-1

	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

TABLE 9-2

Non-Aqueous based heavy duty liquid laundry detergent compositions (KK to OO) are presented below.

Non-Aqueous Liquid Detergent Composition with Bleach

Component	Wt % KK	Wt % LL	Wt % MM	Wt % NN	Wt % OO
LAS, From Above	16	13	8	8	2
SAES or SAEC	22	25	28	30	34
BPP	19	19	19	19	19
Citrate	3	3	3	3	3
Beach activator	5.9	5.9	5.9	5.9	5.9
Carbonate	9	9	9	9	9
MA/AA	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
Perborate	15	15	15	15	15
Optionals including: brightener, colorant, perfume, thickener, suds suppressor, colored speckles etc.	balance	balance	balance	balance	balance

The resulting Table 9-2 composition is a stable, anhydrous heavy-duty liquid laundry detergent which provides excellent stain and soil removal performance when used in normal fabric laundering operations.

EXAMPLE 10

The following heavy duty liquid laundry detergent compositions PP to TT which comprise the SAES and SAE of the present invention are prepared are presented below.

TABLE 10-1

Ingredient	PP	QQ	RR	SS	TT
SAES or SAEC	10	8	6	4	2
Na C25AE1.8S	10	12	14	16	18
SAE	2	2	2	2	2
LMFAA	5	5	5	5	0
Citric acid builder	3	3	3	3	3
Fatty acid builder	0	1	2	4	5
PAE	1	1	1.2	1.2	0.5
PG	8	8	8	8	4.5
EtOH	4	4	4	4	2
Boric Acid	3.5	3.5	3.5	3.5	2
Sodium Cumene Sulfonate	3	3	3	3	0
Enzymes, dyes, water	balance	balance	balance	balance	balance
	100%	100%	100%	100%	100%

EXAMPLE 11

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

TABLE 11-1

	UU	VV	WW	XX	ZZ
SAES or SAEC	1-7	7-12	12-17	17-22	1-35
Any combination of: C25 AExS*Na (x = 1.8-2.5) C25 AS (linear to high 2-alkyl) C14-17 NaPS C12-16 SAS C18 1,4 disulfate LAS C12-16 MES	15-21	10-15	5-10	0-5	0-25
LMFAA	0-3.5	0-3.5	0-3.5	0-3.5	0-8
SAE	0-2	0-2	0-2	0-2	0-8
APA	0.5	0.5	0.5	0.5	0.5-2
Citric Acid	5	5	3	3	0-8
Fatty Acid (TPK or C12/14)	4	3	2	1	0-14
EtOH	4	4	4	4	0-8
PG	6	6	6	6	0-10
MEA	1	1	1	1	0-3
NaOH	3	3	3	3	0-7
Na TS	2.3	2.3	2.3	2.3	0-4
Na formate	0.1	0.1	0.1	0.1	0-1
Borax	2.5	2.5	2.5	2.5	0-5
Protease	0.9	0.9	0.9	0.9	0-1.3
Lipase	0.06	0.06	0.06	0.06	0-0.3
Amylase	0.15	0.15	0.15	0.15	0-0.4
Cellulase	0.05	0.05	0.05	0.05	0-0.2
PAE	0-0.6	0-0.6	0-0.6	0-0.6	0-2.5
PIE	1.2	1.2	1.2	1.2	0-2.5
PAEC	0-0.4	0-0.4	0-0.4	0-0.4	0-2
SRP2	0.2	0.2	0.2	0.2	0-0.5
Brightener 1 or 2	0.15	0.15	0.15	0.15	0-0.5
Silicone Antifoam	0.12	0.12	0.12	0.12	0-0.3
Fumed Silica	0.0015	0.0015	0.0015	0.0015	0-0.003
Perfume	0.3	0.3	0.3	0.3	0-0.6
Dye	0.0013	0.0013	0.0013	0.0013	0-0.003
Moisture/minors	Balance	Balance	Balance	Balance	Balance

EXAMPLE 12

Clear fabric softening compositions with various fabric softener levels and solvent systems are prepared.

TABLE 12-1

Component (Wt %)	A1	B1	C1	D1	E1	F1	G1	H1	I1
TEA Diester Quat	30	35	30	30	30	35	30	35	30
Ethanol (from active)	2.47	2.88	2.47	2.47	2.47	2.88	2.47	2.88	2.47
Hexylene Glycol (from active)	2.7	3.1	2.7	2.7	2.7	3.1	2.7	3.1	2.7
TMPD	4	5	--	5	5	--	--	--	5.5
Hexylene Glycol	--	--	6	--	--	10	--	2	--
2-Ethgyl-1,3-Hexanediol	--	--	--	--	--	--	6	--	--
SAE	5	6	4	6	6	5	5	5	6
Pluronic L-350	1	1	1	1	1	1	1	1	1
HC1	0-0.25	0-0.25	0-0.25	0-0.25	0-0.25	0-0.25	0-0.25	0-0.25	0-0.25
MgCl2	1.75	1.75	2.00	1.75	1.75	2.20	1.50	1.75	1.75
Perfume	2.2	2.5	2.5	2	2.5	3	2	2	2
DTPA	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Blue Dye	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003	0.0003
Deionized Water & Minors	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance	Balance

EXAMPLE 13

A clear fabric softening composition with hexylene glycol as the principal solvent is prepared.

TABLE 13-1

Component Wt %	X1	Y1	Z1	A2	B2	C2	D2	E2	F2	G2	H2
TEA Diester Quat.	45	45	45	45	45	30	28	32	32	36	36
Ethanol (from active)	3.7	3.7	3.7	3.7	3.7	2.5	2.3	2.6	2.6	3.3	3.3
Hexylene Glycol (from active)	4	4	4	4	4	2.7	2.5	2.8	2.8	--	--
Hexylene Glycol	3	6	9	7.3	3	9	3	3.3	6.1	6.5	6.5
Rewopal C6	3.5	2.5	1.5	3.1	2.9	3	--	--	--	1.8	1.8
SAE	--	--	--	--	--	--	3.1	3.0	4.9	--	--
CaC12	1.1	1.1	0.8	2	1	0.95	2.1	2	1	--	1.2
Sodium Cumene Sulfonate	--	--	--	--	--	--	--	--	--	1	--
Perfume	2.0	2.0	2.0	2.0	1.5	1.5	1.0	1.1	.2	1.2	1.2
Deionized Water	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.

LIQUID PHASE

The liquid phase will generally comprise from about 35% to 99% by weight of the liquid detergent compositions herein. More preferably, the liquid phase will comprise from about 50% to 95% by weight of the compositions. Most preferably, the liquid phase will comprise from about 45% to 75% by weight of the compositions herein. The liquid phase of the detergent compositions herein essentially contains relatively high concentrations of a certain type anionic surfactant combined with a certain type of nonaqueous, liquid diluent.

(A) Essential Anionic Surfactant

The anionic surfactant essentially utilized as an essential component of the nonaqueous liquid phase is one selected from the alkali metal salts of alkylbenzene sulfonic acids in which the alkyl group contains from about 10 to 16 carbon atoms, in straight chain or branched chain configuration. (See U.S. Pat. Nos. 2,220,099 and 2,477,383, incorporated herein by reference). Especially preferred are the sodium and potassium linear straight chain alkylbenzene sulfonates (LAS) in which the average number of carbon atoms in the alkyl group is from about 11 to 14. Sodium C11 -14 LAS is especially preferred.

The alkylbenzene sulfonate anionic surfactant will be dissolved in the nonaqueous liquid diluent which makes up the second essential component of the nonaqueous phase. To form the structured liquid phase required for suitable phase stability and acceptable rheology, the alkylbenzene sulfonate anionic surfactant is generally present to the extent of from about 30% to 65% by weight of the liquid phase. More preferably, the alkylbenzene sulfonate anionic surfactant will comprise from about 35% to 50% by weight of the nonaqueous liquid phase of the compositions herein. Utilization of this anionic surfactant in these concentrations corresponds to an anionic surfactant concentration in the total composition of from about 15% to 60% by weight, more preferably from about 20% to 40% by weight, of the composition.

(B) Nonaqueous Liquid Diluent

To form the liquid phase of the detergent compositions, the hereinbefore described alkylbenzene sulfonate anionic surfactant is combined with a nonaqueous liquid diluent which contains two essential components. These two components are a liquid alcohol alkoxylate material and a nonaqueous, low-polarity organic solvent.

i) Alcohol Alkoxylates

One essential component of the liquid diluent used to form the compositions herein comprises an alkoxylated fatty alcohol material. Secondary alcohol ethoxylates are preferred for use herein but other alkoxylated alcohols may also be used. Such materials are themselves also nonionic surfactants. Such materials correspond to the general formula:

$$R^1(OC_mH_{2m})_nOH$$

wherein R^1 is a C8-16 alkyl group, m is from 2 to 4, and n ranges from about 2 to 12. Preferably R^1 is a secondary alkyl group 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 component of the liquid diluent 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 as one of the essential components of the nonaqueous liquid diluent in 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. An example of a preferred alkoxylate for use herein is a 7 mole ethoxylate of a secondary alcohol such as C_{11-15} secondary alcohol. Shell Chemical Company has commercially marketed other alcohol ethoxylates under the trade names Neodol 25-7 and Neodol 23-6.5. 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 C12 -13 alcohol having about 9 moles of ethylene oxide and Neodol 91-10, an ethoxylated C9-11 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 C9-11 fatty alcohol with an average of 5 moles ethylene oxide and Dobanol 25-7 is an ethoxylated C12-C15 fatty alcohol with an average of 7 moles of ethylene oxide per mole of fatty alcohol.

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.

The alcohol alkoxylate component which is essentially utilized as part of the liquid diluent in the nonaqueous compositions herein will generally be present to the extent of from about 1% to 60% of the liquid phase composition. More preferably, the alcohol alkoxylate component will comprise about 5% to 40% of the liquid phase. Most preferably, the essentially utilized alcohol alkoxylate component will comprise from about 5% to 30% of the detergent composition 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.

ii) Nonaqueous Low-Polarity Organic Solvent

A second essential component of the liquid diluent which forms part of the liquid phase of the detergent compositions herein comprises nonaqueous, low-polarity organic solvent(s). The term "solvent" is used herein to connote the non-surface active carrier or diluent portion of the liquid phase of the composition. 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 nonaqueous organic materials which are employed as solvents herein are those which are liquids 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 should not be utilized. Suitable types of low-polarity solvents useful in the nonaqueous liquid detergent compositions herein do include non-vicinal C4-8 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 nonaqueous, low-polarity solvent for use in the compositions herein comprises the non-vicinal C4-8 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 nonaqueous, low-polarity solvent for use herein comprises the mono-, di-, tri-, or tetra-C2-3 alkylene glycol mono C2-6 alkyl ethers. The specific examples of such compounds include diethylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, dipropylene glycol monoethyl ether, and dipropylene glycol monobutyl ether. Diethylene glycol monobutyl ether and dipropylene glycol monobutyl ether are especially preferred. Compounds of the type have been commercially marketed under the tradenames Dowanol, Carbitol, and Cellosolve.

Another preferred type of nonaqueous, 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, nonaqueous 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 nonaqueous, low-polarity 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 will generally be utilized in an amount of from about 1% to 70% by weight of the liquid phase. More preferably, the nonaqueous, low-polarity organic solvent will comprise from about 10% to 60% by weight of the liquid phase, most preferably from about 20% to 50% by weight, of the liquid phase of the composition.

Utilization of this organic solvent in these concentrations in the liquid phase corresponds to a 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) Alcohol Alkoxylate To Solvent Ratio

The ratio of alcohol alkoxylate to organic solvent within the liquid diluent can be used to vary the rheological properties of the detergent compositions eventually formed. Generally, the weight ratio of alcohol alkoxylate to organic solvent will range from about 50:1 to 1:50. More preferably, this ratio will range from about 3:1 to 1:3.

iv) Liquid Diluent Concentration

As with the concentration of the alkylbenzene sulfonate anionic surfactant mixture, the amount of total liquid diluent in the nonaqueous liquid phase herein will be determined by the type and amounts of other composition components and by the desired composition properties. Generally, the liquid diluent will comprise from about 35% to 70% of the nonaqueous liquid phase of the compositions herein. More preferably, the liquid diluent will comprise from about 50% to 65% of the nonaqueous liquid phase. This corresponds to a nonaqueous liquid diluent 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.

SOLID PHASE

The nonaqueous detergent compositions herein also essentially comprise from about 1% to 65% by weight, more preferably from about 5% to 50% by weight, of a solid phase of 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 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 nonaqueous liquid phase of the composition. The types of particulate materials which can be utilized are described in detail as follows:

COMPOSITION PREPARATION AND USE

The nonaqueous liquid detergent compositions herein can be prepared by combining the essential and optional components thereof 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 the first step of such a typical preparation process, an admixture of the alkylbenzene sulfonate anionic surfactant and the two essential components of the nonaqueous diluent is formed by heating a combination of these materials to a temperature from about 30°C. to 100°C.

In a second process step, the heated admixture formed as hereinbefore described is maintained under shear agitation at a temperature from about 40°C to 100°C for a period of from about 2 minutes to 20 hours. Optionally, a vacuum can be applied to the admixture at this point. This second process step serves to completely dissolve the anionic surfactant in the nonaqueous liquid phase.

In a third process step, this liquid phase combination of materials is cooled to a temperature of from about 0°C to 35°C. This cooling step serves to form a structured, surfactant-containing liquid base into which the particulate material of the detergent compositions herein can be added and dispersed.

Particulate material is added in a fourth process step by combining the particulate material with the liquid base which is maintained under conditions of shear agitation. When more than one type of particulate material is to be added, it is preferred that a certain order of addition be observed. For example, while shear agitation is maintained, essentially all of any optional surfactants in solid particulate form can be added in the form of particles ranging in size from about 0.2 to 1,000 microns. After addition of any optional surfactant particles, 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. Other solid form optional ingredients can then be added to the composition at this point. 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 bleaching agent can be added to the composition, again while the mixture is maintained under shear agitation. By adding the 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 bleach can be realized. If enzyme prills are incorporated, they are preferably added to the nonaqueous 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 and phase stability characteristics. Frequently this will involve agitation for a period of from about 1 to 30 minutes.

As a variation of the composition preparation procedure hereinbefore described, one or more of the solid components may be added to the agitated mixture as a slurry of particles premixed with a minor portion of one or more of the liquid components. Thus a premix of a small fraction of the alcohol alkoxylate and/or nonaqueous, low-polarity solvent with particles of the organic builder material and/or the particles of the inorganic alkalinity source and/or particles of a bleach activator may be separately formed and added as a slurry to the agitated mixture of composition components. Addition of such slurry premixes should precede addition of bleaching agent and/or enzyme particles which may themselves be part of a premix slurry formed in analogous fashion.

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.

EXAMPLE 14

A bleach-containing nonaqueous liquid laundry detergent is prepared having the composition as set forth in Table 14-1.

TABLE 14-1

Component	Wt %	Range (% wt.)
Liquid Phase		
Na C_{12} Linear Alkylbenzene sulfonate (LAS)	25.3	18-35
SAES or SAEC	2.0	1-10
SAE	13.6	10-20
Hexylene Glycol	27.3	20-30
Perfume	0.4	0-1.0
Solids		
Protease enzyme	0.4	0-1.0
Na_3 Citrate, anhydrous	4.3	3-6
Sodium Perborate	3.4	2-7
Sodium Nonanoyloxybenzene Sulfonate (NOBS)	8.0	2-12
Sodium Carbonate	13.9	5-20
Diethyl Triamine Pentaacetic Acid (DTPA)	0.9	0-1.5
Brightener	0.4	0-0.6
Suds Suppressor	0.1	0-0.3
Minors	Balance	--

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

EXAMPLE 15

The following Example illustrates the invention herein with respect to a hand dishwashing liquid which is prepared having the composition as set forth in Table 15-1.

TABLE 15-1

Ingredient	% (wt.)	Range (% wt.)
SAES or SAEC	2.0	0.15-15
Ammonium C_{12-13} Alkyl Sulfate	7.0	2-35
C_{12}-C_{14} Ethoxy (1) Sulfate	20.5	5-35
Coconut Amine Oxide	2.6	2-5
Betaine/Tetronic 704®**	0.87-0.10	0-2 (mix)
SAE	5.0	2-10
Ammonium Xylene Sulfonate	4.0	1-6
Ethanol	4.0	0-7
Ammonium Citrate	0.06	0-1.0
Magnesium Chloride	3.3	0-4.0
Calcium Chloride	2.5	0-4.0
Ammonium Sulfate	0.08	0-4.0
Hydrogen Peroxide	200 ppm	10-300 ppm
Perfume	0.18	0-0.5
Maxatase® Protease	0.50	0-1.0
Water and Minors	Balance	

** Cocoalkyl Betaine

EXAMPLE 16

The following Example further illustrates the invention herein with respect to a granular phosphate-containing automatic dishwashing detergent.

TABLE 16-1

	% by weight of active material	
Ingredient	A	B
STPP (Anhydrous)[1]	31	26
SAES or SAEC	1	1
Sodium Carbonate	22	32
Silicate (% S_iO_2)	9	7
SAE	3	1.5
NaDCC Bleach[2]	2	--
Sodium Perborate	--	5
TAED	--	1.5
Savinase (Au/g)	--	0.04
Termamyl (Amu/g)		425
Sul fate	25	25
Perfume/Minors	to 100%	to 100%

[1] Sodium tripoly phosphate
[2] Sodium dichloro cyanurate

The following examples illustrate the present invention. It will be appreciated that other modifications of the present invention within the skill of those in the personal cleansing formulation art can be undertaken without departing from the spirit and scope of this invention. All of the formulations exemplified hereinafter are prepared via conventional formulation and mixing methods unless specific methods are given.

All parts, percentages, and ratios herein are by weight unless otherwise specified. Some components may come from suppliers as dilute solutions. The levels given reflect the weight percent of the active material, unless otherwise specified. The excluded diluents and other materials are included as "Minors".

EXAMPLE 17

The following personal cleansing composition of the present invention is made as follows:

TABLE 17-1

Components	Weight % A	 B
TEA C12-C14 Alkyl Sulfate	10.00	--
NH4 C12-C14 Alkyl (Ethoxy)3 Sulfate	--	7.90
SAES or SAEC	5	7.90
Cocamide MEA	3.00	1.50
Dimethicone DC-200*	3.00	3.00
Ethylene Glycol Disterate	1.50	1.50
Citric Acid	0.60	0.60
Trisodium Citrate	0.30	--
Q.S. Color, Preservative, Perfume and Water	q.s. to 100%	q.s. to 100%

EXAMPLE 18

The following personal cleansing composition of the present invention is made as follows:

TABLE 18-1

Component	Weight % C	Weight % D
Ammonium Lauryl Sulfate	2.5	8.5
Ammonium Laureth (3) Sulfate	8.5	8.5
JAGUAR C-17[1]	0.5	0.5
SAES or SAEC	6.0	2.0
Coconut Monoethanol Amide	1.0	1.0
Ethylene Glycol Distearate	2.0	2.0
Isocetyl Stearoyl Stearate	1.0	1.0
Tricetyl Methyl Ammonium Chloride	0.5	0.5
Polydimethylsiloxane[2]	2.0	2.0
Cetyl Alcohol	0.4	0.4
Stearyl Alcohol	0.2	0.2
Perfume	1.0	1.0
Color Solution	0.6	0.6
Preservative	0.4	0.4
Water and Minors	q.s. to 100%	q.s. to 100%

[1] Tradename for guar hydroxypropyltrimonium chloride, a cationic polymer available from Rhone-Poulenc (Cranbury, NJ, USA).

[2] A 40/60 weight ratio blend of polydimethylsiloxane gum (GE SE 76, available from General Electric Co., Silicone Products Div., Waterford, NY, USA) and polydimethylsiloxane fluid (about 350 centistokes).

The composition can provide excellent in-use hair cleaning and conditioning. As an alternative, the JAGUAR C-17 can be replaced with LUVIQUAT FC 370.

EXAMPLE 19

The following personal cleansing composition of the present invention is made as follows:

TABLE 19-1

Component	Weight % E	 F
Ammonium Lauryl Sulfate	4.2	2.2
Ammonium Laureth (3) Sulfate	9.2	9.2
POLYMER LR 400[1]	1.0	1.0
SAES or SAEC	4.0	6.0
Coconut Monoethanol Amide	1.0	1.0
Ethylene Glycol Distearate	2.0	2.0
Light Mineral Oil	1.0	1.0
Tricetyl Methyl Ammonium Chloride	0.5	0.5
Polydimethylsiloxane[2]	1.5	1.5
Cetyl Alcohol	0.4	0.4
Stearyl Alcohol	0.2	0.2
Perfume	1.2	1.2
Color Solution	0.6	0.6
Preservative	0.4	0.4
Water and Minors	q.s. to 100%	q.s. to 100%

[1] Cellulose, 2-[2-hydroxy-3-(trimethyl ammonio)propoxy] ethyl ether, chloride, a cationic polymer available from Amerchol Corp. (Edison, NJ, USA).

[2] A 40/60 weight ratio blend of polydimethylsiloxane gum (GE SE 76, available from General Electric Co., Silicone Products Div., Waterford, NY, USA) and polydimethylsiloxane fluid (about 350 centistokes).

The composition can provide excellent in-use hair cleaning and conditioning.

EXAMPLE 20

The following personal cleansing composition of the present invention wherein the cationic polymer and anionic surfactant component form a complex coacervate phase is made as follows:

TABLE 20-1

Component	Weight % G
Ammonium Laureth (3) Sulfate	4.0
LUVIQUAT FC 370[1]	0.5
SAES or SAEC	13.5
Coconut Monoethanol Amide	1.0
Ethylene Glycol Distearate	2.0
Light Mineral Oil	0.5
Tricetyl Methyl Ammonium Chloride	0.5
Polydimethylsiloxane[2]	3.0
Cetyl Alcohol	0.4
Stearyl Alcohol	0.2
Perfume	1.0
Color Solution	0.6
Preservative	0.4
Water and Minors	73.8

[1] Tradename of BASF Wyandotte Corporation (Parsippany, NJ, USA) for copolymer of vinyl pyrrolidone and methyl vinyl imidazolium chloride.

[2] A 40/60 weight ratio blend of polydimethylsiloxane gum (GE SE 76, available from General Electric Co., Silicone Products Div., Waterford, NY, USA) and polydimethylsiloxane fluid (about 350 centistokes).

The composition can provide excellent in-use hair cleaning and conditioning. As an alternative, the LUVIQUAT FC 370 can be replaced with JAGUAR C-17.

EXAMPLE 21

The following personal cleansing composition of the present invention is made as follows:

TABLE 21-1

Component	Weight % H
Cocoamidopropyl Betaine	4.0
Ammonium Laureth (3) Sulfate	8.0
Coconut Monoethanol Amide	2.0
Ethylene Glycol Distearate	2.0
Polymer JR-125[1]	1.0
SAEC or SAES	4.0
Isopropyl Isostearate	1.0
Tricetyl Methyl Ammonium Chloride	0.5
Polydimethylsiloxane[2]	1.5
Cetyl Alcohol	0.4
Stearyl Alcohol	0.2
Perfume	1.0
Color Solution	0.6
Preservative	0.4
Water and Minors	q.s. to 100%

[1] Cellulose, 2-[2-hydroxy-3-(trimethyl ammonio)propoxy] ethyl ether, chloride, a cationic polymer available from Amerchol Corp. (Edison, NJ, USA).

[2] VISCASIL, 12,500 cS silicone fluid, available from General Electric (Waterford, NY, USA).

EXAMPLE 22

The following personal cleansing composition of the present invention is made as follows:

TABLE 22-1

	Weight %	
Component	I	J
Ammonium Lauryl Sulfate	8.5	2.0
Ammonium Laureth (3) Sulfate	4.0	4.0
Polymer LM 200[1]	1.0	1.0
SAES or SAEC	5.0	11.5
Light Mineral Oil	1.0	1.0
Coconut Monoethanol Amide	1.0	1.0
Ethylene Glycol Distearate	2.0	2.0
Tricetyl Methyl Ammonium Chloride	0.5	0.5
Polydimethylsiloxane[2]	3.0	3.0
Cetyl Alcohol	0.4	0.4
Stearyl Alcohol	0.2	0.2
Perfume	1.0	1.0
Color Solution	0.6	0.6
Preservative	0.4	0.4
Water and Minors	q.s. to 100%	q.s. to 100%

[1] Polyquaternium 24, a polymeric quaternary ammonium salt of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, available from Amerchol Corp. (Edison, NJ, USA).

[2] The Mid-Chain Branched surfactants according to Examples VII.

[3] A 40/60 weight ratio blend of polydimethylsiloxane gum (GE SE 76, available from General Electric Co., Silicone Products Div., Waterford, NY, USA) and polydimethylsiloxane fluid (about 350 centistokes).

EXAMPLE 23

The following personal cleansing composition of the present invention wherein the cationic polymer and anionic surfactant component form a complex coacervate phase is made as follows:

TABLE 23-1

Component	Weight % K
Ammonium Laureth (3) Sulfate	8.5
GAFQUAT 755N[1]	0.5
FLEXAN 130[3]	0.5
Coconut Monoethanol Amide	1.0
Ethylene Glycol Distearate	2.0
SAES or SAEC	8.5
Isocetyl Stearoyl Stearate	1.0
Tricetyl Methyl Ammonium Chloride	0.5
Polydimethylsiloxane[2]	2.0
Cetyl Alcohol	0.4
Stearyl Alcohol	0.2
Perfume	1.0
Color Solution	0.6
Preservative	0.4
Water and Minors	q.s. to 100%

[1] Copolymer of 1-vinyl-w-pyrrolidone and dimethylaminoethylmethacrylate, available from GAF Corp., Wayne, NJ, USA.

[2] VISCASIL, 600,000 cS, from General Electric, Waterford, NY, USA.

[3] Sodium polystyrene sulfonate, an anionic polymer available from National Starch and Chemical Corp. Bridgewater, NJ, USA.

The composition can provide excellent in-use hair cleaning and conditioning. The example compositions hereof can be made by preparing a premix of the entire amount of silicone conditioning agent to be incorporated into the personal cleansing composition, along with sufficient ammonium sulfate and cetyl and stearyl alcohol such that the premix comprises about 30% silicone conditioning agent, about 69% surfactant, and about 1% of the alcohols. The premix ingredients are heated and stirred at 72°C for about 10 minutes and the premix is then conventionally mixed with the remaining ingredients. The composition is then pumped through a high shear mixer and cooled.

EXAMPLE 24

The following examples (L to Z) further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. These exemplified embodiments of the shampoo compositions of the present invention provide cleansing of hair and improved hair conditioning performance. Ingredients are hereinafter identified by chemical, trade, or CTFA name.

Preparation: The shampoo compositions of the present invention can be prepared by using conventional mixing and formulating techniques. The shampoo compositions illustrated hereinafter in Examples L to Z are prepared in the following manner.

About one-third to all of the total sulfate surfactant (added as a 25% solution) is added to a jacketed mix tank and heated to about 74°C with slow agitation to form a surfactant solution. Cocamide MEA and fatty alcohol, as applicable, are added to the tank and allowed to disperse. Ethylene glycol distearate (EGDS), as applicable, is then added to the mixing vessel, and melted. After the EGDS is well dispersed (usually about 5 to 20 minutes), polyethylene glycol and the preservative, if used, are added and mixed into the surfactant solution. This mixture is passed through a heat exchanger where it is cooled to about 35°C and collected in a finishing tank. As a result of this cooling step, the ethylene glycol distearate crystallizes to form a crystalline network in the product. The remainder of the surfactant and other ingredients including the silicone emulsions are added to the finishing tank with ample agitation to insure a homogeneous mixture. A sufficient amount of the silicone emulsions are added to provide the desired level of dimethicone in the final product. Water dispersible polymers are typically dispersed in water as a 1% to 10% solution before addition to the final mix. Once all ingredients have been added, ammonium xylene sulfonate or additional sodium chloride can be added to the mixture to thin or thicken respectively to achieve a desired product viscosity. Preferred viscosities range from about 2500 to about 9000 cS at 25°C (as measured by a Wells-Brookfield cone and plate viscometer at 15/s).

TABLE 24-1

Component	L	M	N	O	P
SAES or SAEC	10	10	16	15	16
Cocamidopropylbetaine	0	0	2.5	0	1
Jaguar C17[8]	0.05	0.05	0.05	0.30	0.15
Cocamide MEA	0.5	0.5	0.80	0.80	0
Cetyl Alcohol	0	0	0.42	0.42	0.42
Stearyl Alcohol	0	0	0.18	0.18	0.18
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
EP Silicone[4]	3.0	2.5	3.0	2.0	3.0
Perfume Solution	0.70	0.70	0.70	0.70	0.70
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64
Water and Minors	----q.s. to 100%----				

Component	Q	R	S	T	U
SAES or SAEC	9.00	9.00	14.0	14.85	12.50
Cocamidopropylbetaine	1.70	1.70	2.70	1.85	4.20
Polyquaternium-10[3]	0.05	0.02	0.15	0.15	0.15
Cocamide MEA	0.80	0.80	0.80	0.80	0
Cetyl Alcohol	0	0	0.42	0.42	0.42
Stearyl Alcohol	0	0	0.18	0.18	0.18
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
EP Silicone[4]	3.0	2.5	3.0	2.0	3.0
Perfume Solution	0.70	0.70	0.70	0.70	0.70
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64
Water and Minors	----q.s. to 100%----				

Component	V	W	X	Y	Z
SAES or SAEC	14.0	14.00	14.00	9.00	9.00
Cocamidopropylbetaine	2.70	2.70	2.70	1.70	1.70
Polyquaternium-10[6]	0	0.15	0.15	0.05	0.02
Cocamide MEA	0.80	0.80	0	0.80	0.80
Cetyl Alcohol	0	0.42	0	0	0
Stearyl Alcohol	0	0.18	0	0	0
Ethylene Glycol Distearate	0	0	0	1.50	1.50
Carbopol 981[2]	0.50	0.50	0.50	0	0
EP Silicone[1]	3.0	2.5	3.0	2.0	3.0
Perfume Solution	0.70	0.70	0.70	0.70	0.70
DMDM Hydantoin	0.37	0.37	0.37	0.37	0.37
Color Solution (ppm)	64	64	64	64	64
Water and Minors	----q.s. to 100%----				

[1] EP Silicone is an experimental emulsion polymerized polydimethyl siloxane of about 97,000 csk with particle size

of approximately 300 nm made via linear feedstock available from Dow Corning (2-1520; 13556-34).

[2] Carbopol 981 is a crosslinked polyacrylate available from B. F. Goodrich.

[3] Polyquaternium-10 is JR30M, a cationic cellulose derived polymer available from Amerchol.

[4] EP Silicone is an experimental emulsion polymerized polydimethyl siloxane of about 335,000 csk with particle size of approximately 500 nm made via linear feedstock available from Dow Corning (2-1520); PE106004).

[5] Jaguar C17 is a cationic polymer available from Rhone-Poulenc.

[6] Polyquaternium-10 is JR400, a cationic cellulose derived polymer available from Amerchol.

EXAMPLE 25

The following shampoo composition of the present invention is made as follows:

TABLE 25-1

Component	% Weight AA
SAES or SAEC	17
Zinc Pyridinethione*	2.0
Coconut Monoethanolamide	3.0
Ethylene Glycol Distearate	5.0
Sodium Citrate	0.5
Citric Acid	0.2
Color Solution	0.1
Perfume	0.5
Water	q.s. to 100.00%
Component	% Weight BB
Triethanolamine Alkyl Sulfate	10%
SAEC or SAES	9
Zinc Pyridinethione*	2.0
Coconut Monoethanolamide	2.0
Triethanolamine	3.0
Magnesium/Aluminum Silicate	0.5
Hydroxy Methyl Cellulose	0.6y
Color Solution	0.1
Perfume	0.3
Water	q.s. to 100.00%
Component	% Weight CC
Sodium Alkyl Glyceryl Sulfonate	5%
SAES or SAEC	15
Zinc Pyridinethione*	2.0
Sodium Chloride	5.0
Sodium N-Lauryl Sarcosinate	12.0
N-Cocoyl Sarcosine Acid	1.0
Lauric Diethanolamide	2.0
Color Solution	0.12
Perfume	0.5
Water	q.s. to 100.00%

*The Zinc pyridinethione salt crystals prepared according to the method described in U.S. Pat. No. 4,379,753 to Bolich.

EXAMPLE 26

The compositions illustrated in Example 26 (DD to TT), illustrate specific embodiments of the shampoo compositions of the present invention, but are not intended to be limiting thereof Other modifications can be undertaken by the skilled artisan without departing from the spirit and scope of this invention. These exemplified embodiments of the shampoo compositions of the present invention provide excellent cleansing of hair and dandruff control.

All exemplified compositions can be prepared by conventional formulation and mixing techniques. Component amounts are listed as weight percents and exclude minor materials such as diluents, filler, and so forth. The listed formulations, therefore, comprise the listed components and any minor materials associated with such components.

TABLE 26-1

Component	DD	EE	FF	GG	HH
Ammonium Laureth Sulfate	15.00	15.00	15.00	15.00	15.00
SAES or SAEC	5.00	5.00	5.00	5.00	2.50
Sodium Lauroyl Sarcosinate	1.50	1.50	1.50	1.50	0.75
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
Zinc Pyrithione	1.00	1.00	1.00	--	1.00
Selenium Disulfide	--	--	--	1.00	--
Jaguar C17S	0.10	0.05	0.50	0.10	0.10
Fragrance	q.s.	q.s.	q.s.	q.s.	q.s.
Color	q.s.	q.s.	q.s.	q.s.	q.s.
pH Adjustment (Mono/Di Sodium Phosphate)	q.s.	q.s.	q.s.	q.s.	q.s.
Viscosity Adjustment (Sodium Chloride)	q.s.	q.s.	q.s.	q.s.	q.s.
Preservative (DMDM Hydantoin)	q.s.	q.s.	q.s.	q.s.	q.s.
Water	q.s.	q.s.	q.s.	q.s.	q.s.
Component	JJ	KK	LL	MM	NN
SAES	10.00	20.00	20.00	12.50	12.50
Cocamidopropyl Betaine	--	--	--	2.50	2.50
Sodium Lauroyl Sarcosinate	0.75	--	--	--	--
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50
Ketoconazole	1.00	1.00	1.00	1.00	1.00
Jaguar C13S	--	0.10	--	0.10	--
Jaguar C17S	0.05	--	0.10	--	0.10
Fragrance	q.s.	q.s.	q.s.	q.s.	q.s.
Color	q.s.	q.s.	q.s.	q.s.	q.s.
pH Adjustment (Mono/Di Sodium Phosphate)	q.s.	q.s.	q.s.	q.s.	q.s.
Sodium Sulfate, PEG-600, (Ammonium Xylene Sulfonate)	q.s.	q.s.	q.s.	q.s.	q.s.
Preservative (DMDM Hydantoin)	q.s.	q.s.	q.s.	q.s.	q.s.
Water	q.s.	q.s.	q.s.	q.s.	q.s.

Component	OO	PP	QQ	RR	SS	TT
Ammonium Laureth Sulfate	0	15.00	0	15.00	15.00	0
SAES	20.00	--	20.00	--	--	20.00
Cocamidopropyl Betaine	2.00	--	--	--	--	--
Sodium Lauroyl Sarcosinate	--	1.50	1.50	--	--	--
Sodium Cocoyl Glutamate	--	--	--	--	--	1.50
Ethylene Glycol Distearate	1.50	1.50	1.50	1.50	1.50	1.50
Stearyl Alcohol	--	--	--	--	--	--
Zinc Pyrithione	1.00	0.30	0.30	0.30	0.30	1.00
Jaguar C13S	0.20	--	--	0.10	0.05	--
Jaguar C17S	--	0.10	0.05	--	--	0.10
Fragrance	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Color	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
pH Adjustment (Mono/Di Sodium Phosphate)	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Viscosity Adjustment (Sodium Chloride)	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Preservative (DMDM Hydantoin)	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.

In preparing each of the compositions described in Examples DD to TT, about one-third of the surfactant (added as 25 wt % solution) is added to a jacketed mix tank and heated to about 74°C with slow agitation to form a surfactant solution. Salts (sodium chloride) and pH modifiers (disodium phosphate, monosodium phosphate) are added to the tank and allowed to disperse. Ethylene glycol distearate (EGDS) is added to the mixing vessel and allowed to melt. After the EGDS is melted and dispersed (e.g., after about 5-20 minutes), preservative and additional viscosity modifier are added to the surfactant solution. The resulting mixture is passed through a heat exchanger where it is cooled to about 35°C and collected in a finishing tank. As a result of this cooling step, the EGDS crystallizes to form a crystalline network in the product. The remainder of the surfactant and other components are added to the finishing tank with agitation to ensure a homogeneous mixture. Cationic guar polymer is dispersed in water as a 0.5-2.5% aqueous solution before addition to the final mix. Once all components have been added, viscosity and pH modifiers are added to the mixture to adjust product viscosity and pH to the extent desired.

Each exemplified composition will provide excellent hair cleansing, lathering, antimicrobial agent deposition on the scalp and dandruff control.

EXAMPLES 27 - 29

Component	Eample 27	Example 28	Example 29
SAES or SAEC	14.00	14.00	14.00
Cocamidopropyl Betaine	--	2.50	2.50
Cocoamphodiacetate	2.50	--	--
Cocamide MEA	1.00	1.00	1.00
Ethylene Glycol Distearate	1.50	1.50	1.50
Cetyl Alcohol	0.42	0.42	0.42
Stearyl Alcohol	0.18	0.18	0.18
Zinc Pyrithione	1.00	1.00	1.00
Jaguar C13S	0.15	0.15	--
Jaguar C17S	--	--	0.15
Fragrance	q.s.	q.s.	q.s.
Color	q.s.	q.s.	q.s.
pH Adjustment (Mono/Di Sodium Phosphate)	q.s.	q.s.	q.s.
Viscosity Adjustment (Sodium Chloride)	q.s.	q.s.	q.s.
Preservative (DMDM Hydantoin)	q.s.	q.s.	q.s.
Water	q.s.	q.s.	q.s.

In preparing each of the compositions described in Examples 27 to 29, from 50% to 100% by weight of the detersive surfactants are added to a jacketed mix tank and heated to about 74°C with slow agitation to form a surfactant solution. If used, pH modifiers (monosodium phosphate, disodium phosphate) are added to the tank and allowed to disperse. Ethylene glycol distearate (EGDS) and fatty alcohols (cetyl alcohol, stearyl alcohol) are then added to the mixing vessel and allowed to melt. After the EGDS is melted and dispersed (usually about 5-10 minutes), preservative (if used) is added and mixed into the surfactant solution. Additional viscosity modifiers are added to the surfactant solution if necessary. The resulting mixture is passed through a heat exchanger where it is cooled to about 35°C and collected in a finishing tank. As a result of this cooling step, the EGDS crystallizes to form a crystalline network in the product. Any remaining surfactant and other components are added to the finishing tank with agitation to ensure a homogeneous mixture. Cationic guar polymer is dispersed in water as a 0.5-2.5% aqueous solution before addition to the final mix. Once all components have been added, viscosity and pH modifiers are added to the mixture to adjust product viscosity and pH to the extent desired.

Each exemplified composition will provide excellent hair cleansing, lathering, antimicrobial agent deposition on the scalp, and dandruff control.

EXAMPLE 30

Table 30-1

	Weight %				
Component	UU	VV	WW	XX	YY
SAES or SAEC	2.0	2.0	3.0	2.0	3.0
Cocamidopropyl Betaine FB	6.0	6.0	9.0	6.0	9.0
Alkyl Glyceryl Sulfonate	10.0	10.0	6.0	10.0	6.0
Mixture A	3.0	6.0	--	--	--
Mixture B	--	--	3.0	--	6.0
Mixture C	--	--	--	3.0	--
Dihydrogenated Tallowamidoethyl Hydroxyethylmonium Methosulfate (1)	0.25	0.50	--	0.25	--
Ditallowamidoethyl Hydroxypropylmonium Methosulfate (2)	--	--	0.25	--	0.25
Polyquaternium-16 (Luviquat 905)	--	--	--	0.25	--
Monosodium Phosphate	0.1	0.1	0.1	0.1	0.1
Disodium Phosphate	0.2	0.2	0.2	0.2	0.2
Glycol Distearate	2.0	2.0	2.0	2.0	2.0
Cocomonoethanol amide	0.6	0.6	0.6	0.6	0.6
Fragrance	1.0	1.0	1.0	1.0	1.0
Cetyl Alcohol	0.42	0.42	0.42	0.42	0.60
Stearyl Alcohol	0.18	0.18	0.18	0.18	--
PEG-150 Pentaerythrityl Tetrastearate	0.1	0.1	0.1	0.1	0.1
Polyquaternium 10 (JR30M)	0.3	--	--	0.1	--
Polyquaternium 10 (JR400)	--	0.3	--	--	--
Polyquaternium 10 (JR125)	--	--	0.3	--	0.1
Dimethicone	--	0.3	0.3	--	--
DMDM Hydantoin	0.2	0.2	0.2	0.2	0.2
Water	q.s. 100	q.s. 100	q.s. 100	q.s. 100	q.s. 100

(1) Available under the tradename Varisoft 110 from Sherex Chemical Co. (Dublin, Ohio, USA)

(2) Available under the tradename Varisoft 238 from Sherex Chemical Co. (Dublin, Ohio, USA)

Table 30-2

	Weight %				
Component	ZZ	AAA	BBB	CCC	DDD
SAES or SAEC	5.0	6.0	7.0	4.0	5.0
Ammonium Laureth Sulfate	5.5	4.5	3.5	3.5	4.5
Sodium Lauroamphoacetate	7.5	7.5	7.5	8.5	7.5
Mixture A	4.0	6.0	--	--	4.0
Mixture B	--	--	4.0	--	--
Mixture C	--	--	--	4.0	--
Dihydrogenated Tallowamidoethyl Hydroxyethylmonium Methosulfate (1)	1.0	--	--	--	--
Ditallowamidoethyl Hydroxypropylmonium Methosulfate (2)	--	0.75	--	--	--
Ditallow Dimethyl Ammonium Chloride (3)	--	--	1.0	--	1.0
Ditallowamidoethyl Hydroxyethylmonium Methosulfate (4)	--	--	--	0.75	--
Polyquaternium-16 (Luviquat 905)	--	--	--	0.25	--
Monosodium Phosphate	0.1	0.1	0.1	0.1	0.1
Disodium Phosphate	0.2	0.2	0.2	0.2	0.2
Glycol Distearate	2.0	2.0	2.0	2.0	2.0
Cocomonoethanol amide	0.6	0.6	0.6	0.6	0.6
Fragrance	1.0	0.8	1.0	1.0	1.0
Cetyl Alcohol	0.42	0.42	0.42	0.42	0.42
Stearyl Alcohol	0.18	0.18	0.18	0.18	0.18
PEG-150 Pentaerythrityl Tetrastearate	0.08	0.1	0.1	0.1	0.1
Polyquaternium 10 (JR30M)	0.3	--	--	0.1	0.3
Polyquaternium 10 (JR400)	--	0.3	--	--	--
Polyquaternium 10 (JR125)	--	--	0.3	--	--
Dimethicone	--	0.5	0.3	--	--
DMDM Hydantoin	0.2	0.2	0.2	0.2	0.2
Water	q.s. 100	q.s. 100	q.s. 100	q.s. 100	q.s. 100

(1) Available under the tradename Varisoft 110 from Sherex Chemical Co. (Dublin, Ohio, USA)

(2) Available under the tradename Varisoft 238 from Sherex Chemical Co. (Dublin, Ohio, USA)

(3) Available under the tradename Adogen 442-110P from Witco (Dublin, Ohio, USA)

(4) Available under the tradename Varisoft 222 from Sherex Chemical Co. (Dublin, Ohio, USA)

Table 30-3

	Weight %				
Component	EEE	FFF	GGG	HHH	III

SAES or SAEC	2.0	4.0	0	3.0	4.0
Ammonium Laureth Sulfate	0	6.5	4.0	7.0	6.0
Cocamidopropyl Betaine FB	6.0	--	4.7	--	--
Sodium Lauroamphoacetate	--	7.5	--	7.5	7.5
Alkyl Glyceryl Sulfonate	10.0	--	--	--	--
Mixture A	--	--	--	4.0	--
Mixture C	--	--	--	--	4.0
Mixture D	6.0	4.0	8.0	--	--
Dihydrogenated Tallowamidoethyl Hydroxyethylmonium Methosulfate (1)	0.25	--	--	0.5	--
Ditallow Dimethyl Ammonium Chloride (3)	--	1.0	--	--	--
Di(partially hardened soyoylethyl) Hydroxyethylmonium Methosulfate (5)	--	--	0.75	--	1.0
Polyquaternium-16 (Luviquat 905)	--	--	--	0.25	--
Monosodium Phosphate	0.1	0.1	0.1	0.1	0.1
Disodium Phosphate	0.2	0.2	0.2	0.2	0.2
Glycol Distearate	2.0	2.0	2.0	2.0	2.0
Cocomonoethanol amide	0.6	0.6	0.6	0.6	0.6
Fragrance	1.0	0.8	1.0	1.0	1.0
Cetyl Alcohol	0.42	0.42	0.42	0.42	0.42
Stearyl Alcohol	0.18	0.13	0.18	0.18	0.18
PEG-150 Pentaerythrityl Tetrastearate	0.10	0.08	1.0	0.10	0.08
Polyquaternium 10 (JR30M)	--	--	0.3	--	--
Polyquaternium 10 (JR400)	--	0.3	--	--	--
Polyquaternium 10 (JR125)	0.3	--	--	--	--
Guar Hydroxypropyltrimonium Chloride	--	--	--	0.25	0.5
Dimethicone	--	0.5	--	--	--
DMDM Hydantoin	0.2	0.2	0.2	0.2	0.2
Water	q.s. 100	q.s. 100	q.s. 100	q.s. 100	q.s. 100

(1) Available under the tradename Varisoft 110 from Sherex Chemical Co. (Dublin, Ohio, USA)

(3) Available under the tradename Adogen 442-110P from Witco (Dublin, Ohio, USA)

(4) Available under the tradename Armocare EQ-S from Akzo-Nobel Chemicals Inc. (Chicago, Illinois, USA)

EXAMPLE 31

The compositions of the present invention, in general, can be made by mixing together at elevated temperature, e.g., about 72°C water and surfactants along with any solids (e.g., amphiphiles) that need to be melted, to speed mixing into the personal cleansing composition. Additional ingredients including the electrolytes can be added either to this hot premix or after cooling the premix. The nonionic or anionic polymers can be added as a water solution after cooling the premix. The ingredients are mixed thoroughly at the elevated temperature and then pumped through a high shear mill and then through a heat exchanger to cool them to ambient temperature. The silicone may be emulsified at room temperature in concentrated surfactant and then added to the cooled product. Alternately, for example, the silicone conditioning agent can be mixed with anionic surfactant and fatty alcohol, such as cetyl and stearyl alcohols, at elevated temperature, to form a premix containing dispersed silicone. The premix can then be added to and mixed with the remaining materials of the personal cleansing composition, pumped through a high shear mill, and cooled.

The personal cleansing compositions illustrated in Example XXII (JJJ to QQQ) illustrate specific embodiments of the personal cleansing compositions of the present invention, but are not intended to be limiting thereof. Other modifications can be undertaken by the skilled artisan without departing from the spirit and scope of this invention. These exemplified embodiments of the personal cleansing compositions of the present invention provide cleansing of hair and/or skin and improved conditioning.

All exemplified compositions can be prepared by conventional formulation and mixing techniques. Component amounts are listed as weight percents and exclude minor materials such as diluents, filler, and so forth. The listed formulations, therefore, comprise the listed components and any minor materials associated with such components.

Table 31-1

Ingredients	JJJ	KKK	LLL	MMM	NNN

SAES or SAEC	10.0	--	--	--	--
Sodium Alkyl Glycerol Sulfonate	2.50	2.50	2.50	2.50	2.50
Cocoamidopropyl Betaine	--	--	--	--	--
Glycol Distearate	2.00	1.50	2.00	2.00	2.00
Cocomonoethanol Amide	0.60	0.85	0.85	0.85	0.85
Cetyl Alcohol	0.42	0.42	0.42	0.42	0.42
Stearyl Alcohol	0.18	0.18	0.18	0.18	0.18
EDTA (Ethylenediamine Tetra Acetic Acid)	0.10	0.10	0.10	0.10	0.10
Monosodium Phosphate	0.10	0.10	0.10	0.10	0.10
Disodium Phosphate	0.20	0.20	0.20	0.20	0.20
Sodium Benzoate	0.25	0.25	0.25	0.25	0.25
Hydroxyethylcellulose[1]	0.10	0.25	--	--	--
Hydroxypropyl Guar[2]	--	--	0.25	--	--
Hydroxyethylethylcellulose[3]	--	--	--	0.25	--
Polystyrene Sulfonate	--	--	--	--	0.25
Tricetyl Methylammonium Chloride	0.58	--	--	--	--
Perfule	0.60	0.60	0.60	0.60	0.60
Dimethicone	1.00	1.50	1.50	1.50	1.50
Glydant	0.20	0.20	0.20	0.20	0.20
NaCl	0.20	0.30	0.30	1.00	0.30
Water and Minors	-----q.s. to 100%-----				

EXAMPLE 32

Low-temperature alkaline-surfactant-polymer flooding enhanced oil recovery (EOR):

The following EOR composition of the present invention is made as follows. The injection fluid to relase crude oil is introduced followed by a polymer flushing solution:

0.5% SAES
1.0% sodium carbonate
98.5% reservoir brine

EXAMPLE 33

High-temperature alkaline-surfactant-polymer flooding EOR

The following EOR composition of the present invention is made as follows. The injection fluid to relase crude oil is introduced followed by a polymer flushing solution:

0.5% SAEC
1.0% sodium carbonate
98.5% reservoir brine

EXAMPLE 34

The following laundry bar formulation is made as follows:

24% LAS
6% SAES or SAEC
10% soap
25% soda ash
30% calcium carbonate
5% water

EXAMPLE 35

The following detergent gel formulations are made as follows:

	A	B	C	D
Mg (SAES)2	25%	13	24	24
Mg (LAS)2	8%	4	8	1
SAE	0	4	0	1
Mg(AE3S)2	0	12	2	1
C10-16 amine oxide	0	2	4	4
water	balance	balance	balance	balance

EXAMPLE 36

The following laundry prespotter formulations are made as follows:

	A	B	C	D
SAES	0	1	4	4
SAE	10%	10	15	5
Alcohol ethoxylate, NEODOL 25-5 or equivalent	10	10	5	20
Solvent, Shell sol 71 or 72 or equivalent	20	20	25	20
Isopropyl alcohol	12	15	15	15
Triethanolamine oleate	3	4	4	4
water	balance	balance	balance	balance

EXAMPLE 37

The following dishwash liquid formulations, including magnesium salts to improve grease removal, are made as follows:

	A	B	C	D
SAES	20	20	25	10
SAE	1	1	0	1
Mg (LAS)2	10	10	0	5
Mg(AE3S)2	5	4	10	15
Fatty acid diethanol amide or fatty acid monoethanol amide	5	0	5	0
Amine oxide	1	10	0	8
Ethanol and/or sodium xylene sulfonate	8	6	8	8
Water, dye, and/or perfume	balance	balance	balance	balance

EXAMPLE 38

The following household or industrial & institutional hard surface cleaner formulations, are made as follows:

	A	B	C	D
SAES	0	1	3	1
SAE	5	4	5	4
C-12-LAS	0	1	3	1
Pine oil	0	5	20	1
Triethanol amine	0	3	6	1
Phosphate, carbonate, and/or silicate builder	7	0	0	5
Ethanol and/or sodium xylene sulfonate	6	12	12	6
Water, dye, and/or perfume	balance	balance	balance	balance

EXAMPLE 39

The following detergent gel formulations are made as follows:

	A	B	C	D
Mg $(SAES)_2$	25%	13	24	24
Mg $(LAS)_2$	8%	4	8	1
SAE	0	4	0	1
$Mg(AE3S)_2$	0	12	2	1
C10-16 amine oxide	0	2	4	4
water	balance	balance	balance	balance

EXAMPLE 40

The following laundry prespotter formulations are made as follows:

	A	B	C	D
SAES	0	1	4	4
SAE	10%	10	15	5
Alcohol ethoxylate, NEODOL 25-5 or equivalent	10	10	5	20
Solvent, Shell sol 71 or 72 or equivalent	20	20	25	20
Isopropyl alcohol	12	15	15	15
Triethanolamine oleate	3	4	4	4
water	balance	balance	balance	balance

EXAMPLE 41

The following dishwash liquid formulations, including magnesium salts to improve grease removal, are made as follows:

	A	B	C	D
SAES	20	20	25	10

SAE	1	1	0	1
Mg (LAS)$_2$	10	10	0	5
Mg(AE3S)$_2$	5	4	10	15
Fatty acid diethanol amide or fatty acid monoethanol amide	5	0	5	0
Amine oxide	1	10	0	8
Ethanol and/or sodium xylene sulfonate	8	6	8	8
Water, dye, and/or perfume	balance	balance	balance	balance

EXAMPLE 42

The following hard surface cleaner formulations, either household or industrial & institutional, are made as follows:

	A	B	C	D
SAES	0	1	3	1
SAE	5	4	5	4
C-12-LAS	0	1	3	1
Pine oil	0	5	20	1
Triethanol amine	0	3	6	1
Phosphate, carbonate, and/or silicate builder	7	0	0	5
Ethanol and/or sodium xylene sulfonate	6	12	12	6
Water, dye, and/or perfume	balance	balance	balance	balance

EXAMPLE 43

The following aerosol-type prespotter formulations are made as follows:

	A	B	C	D	E
SAE	30	25	10	10	30
SAES	0	5	0	0	1
Shell sol 71 or 72 (or equivalent isoparaffinic solvent	64	50	90	89	41
Ethanol	4	10	0	0	5
water	2	10	0	1	3

EXAMPLE 44

These examples show the components used for the overall commercial laundry process. In many commercial laundry facilities, the equipment used is generally described as a large "home-type" machine: that is, mechanically and physically capable of cleaning 100 pounds or more of dry laundry. Other machines, of larger capacity, have the capability to add ingredients as needed, as the washing process proceeds, and these formulations would represent the total ingredients added during the entire process.

The following commercial laundry-with phosphate builder formulations are made as follows:

	A	B	C	D	E
SAE	10	15	20	5	0
SAES	5	0	5	5	5
LAS	3	1	0	1	5
Sodium tripolyphosphate	20	10	5	3	20
Sodium Carbonate and/or NaOH	35	30	30	35	30
Sodium perborate, monohydrate	20	0	5	10	1
Sodium silicate	5	1	10	5	5
Minors*	Up to 5	Up to 5	Up to 5	Up to 5	Up to 5
Sodium sulfate or sodium chloride as filler	To 100 %	To 100 %	To 100	To 100	To 100

*Minors = fabric whitening agent, enzymes, carboxymethylcellulose, bleach activator, etc, as required

EXAMPLE 45

These examples show the components used for the overall commercial laundry process. In many commercial laundry facilities, the equipment used is generally described as a large "home-type" machine: that is, mechanically and physically capable of cleaning 100 pounds or more of dry laundry. Other machines, of larger capacity, have the capability to add ingredients as needed, as the washing process proceeds, and these formulations would represent the total ingredients added during the entire process.

The following commercial laundry —no phosphate formulations are made as follows:

	A	B	C	D	E
SAE	10	15	20	5	0
SAES	5	0	5	5	5
LAS	3	1	0	1	5
Zeolita 4 or equivalent	20	10	5	20	20
Sodium Carbonate and/or NaOH	35	30	30	35	30
Sodium perborate, monohydrate	20	0	5	10	1
Sodium silicate	5	1	10	5	5
Minors*	Up to 5	Up to 5	Up to 5	Up to 5	Up to 5
Sodium sulfate or sodium chloride as filler	To 100	To 100	To 100	To 100	To 100

*Minors = fabric whitening agent, enzymes, carboxymethylcellulose, bleach activator, etc, as required

EXAMPLE 46

The following carpet and upholstery cleaner (shampoo) formulations are made as follows:

	A	B	C	D	E
SAE	5	4	1	0	5
SAES	0	1	15	15	5
Sodium	2	5	10	1	3

trpolyphosphate					
Isopropyl alcohol	4	5	1	1	6
Dye, perfume, fluorescent whitening agent	As desired	As desired	As desired	As desired	As desired
Water	To 100 %	To 100%	To 100%	To 100%	To 100%

EXAMPLE 47

Phosphate ester(s)—synthesis and use

Phosphate esters are produced by reacting alcohol ethoxylates, alkyl-phenol ethoxylates or SAE with PCl_3 or P_2O_5. These are surfactants where in general a single alkyl group has reacted with the phosphorus source. A typical structure would be $ROP(OH)_2$, and then this ester is generally neutralized with NaOH or KOH.

While phosphate esters have utility across all liquid formulations as both a surfactant and hydrotrope, these compounds are more generally used in industrial liquid formulations.

Two such formulation types are:

Bottle Wash Liquid

	A	B	C	D	E
SAE	1	1	5	2	1
SAES	0	1	1	2	1
NaOH	10	10	15	10	15
Organic builder, sodium citrate or sodium gluconate	2	4	6	8	4
Phosphate ester, SAE type	5	10	1	3	20
Dye and perfume, as desired	1	1	1	1	1
Water	To 100 %	To 100 %	To 100 %	To 100 %	To 100 %

Hard Surface Cleaner

	A	B	C	D	E
SAE	5	1	8	10	6
SAES	5	8	1	10	6
Trisodium phosphate	1	2	3	5	10
Ethylene glycol, monobutyl ether*	7	6	2	10	5
Sodium metasilicate, pentahydrate	3	2	1	5	1
KOH	2	1	3	5	1
Phosphate ester, SAE type	5	10	1	15	8
Water, dye, and perfume	To 100 %	To 100 %	To 100 %	To 100 %	To 100 %

*Butyl OXITOL from Dow or equivalent solvent

EXAMPLE 48

The following shampoo formulations with optional ingredients are made as follows:

	A	B	C	D	E
SAES and / or alcohol sulfate or alcohol ethoxysulfate	5	10	15	3	25
Foam booster*	2	4	10	3	15
**Cetyl alcohol or equivalent	1	0.5	1.5	2	0
Cocoamidopropyl betaine***	5	10	1	0	15
Ethanol****	3	5	7	0	2
Preservatives, dye, perfume, as desired	1	1	1	1	1
*****PEG diester, if desired	0.5	1	0	2	0
Water and salts	To 100 %	To 100 %	To 100 %	To 100 %	To 100 %

*Foam boosters are typically fatty ester mono- or di-ethanol amides, such as NINOL 49CE from Stepan. Easily thickened formulations, such as E, may use an amine oxide as both a foam booster and for enhanced mildness. A lauryldimethylamine oxide, such as Ammonyx from Stepan, is suitable.

**Small amounts of long-chain alcohols enhance foaming. Mixtures of cetyl and stearyl alcohol, along with NEODOL ® 67 alcohol, are useful.

***Betaines or equivalent compounds such as Sulfo-betaines, or other “mild” surfactants, including alpha-olefin sulfonate, are used to enhance the perception of mildness in the overall formulation.

****Ethanol is relatively inexpensive, and is viewed as synergistic with perfumes.

*****A polyethylene glycol diester, such as Kessco PEG distearate from Stepan, is added at a low level if an opaque shampoo is desired.

CLAIMS

1. A method of treating a hydrocarbon containing formation, comprising:

(a) providing a composition to at least a portion of the hydrocarbon containing formation, wherein the composition comprises a secondary alcohol derivative; and

(b) allowing the composition to interact with hydrocarbons in the hydrocarbon containing formation.

2. The method of claim 1 wherein the secondary alcohol derivative is selected from the group consisting of secondary alcohol ethoxylates, secondary alcohol ethoxysulfates, secondary alcohol ethoxycarboxylates, and mixtures of any of these components.

3. A composition produced from a hydrocarbon containing formation, comprising hydrocarbons from a hydrocarbon containing formation and a secondary alcohol derivative.

4. The composition of claim 3 wherein the secondary alcohol derivative is selected from the group consisting of secondary alcohol ethoxylates, secondary alcohol ethoxysulfates, secondary alcohol ethoxycarboxylates, and mixtures of any of these components.

5. A personal care composition comprising

(a) a secondary alcohol derivative; and

(b) a cosmetically-acceptable vehicle.

6. The personal care composition of claim 5 wherein the secondary alcohol derivative is selected from the group consisting of secondary alcohol ethoxylates, secondary

alcohol ethoxysulfates, secondary alcohol ethoxycarboxylates, and mixtures of any of these components.

7. A personal care composition comprising
   (a) a secondary alcohol derivative;
   (b) at least one sunscreen; and
   (c) a cosmetically-acceptable vehicle.

8. The personal care composition of claim 7 wherein the secondary alcohol derivative is selected from the group consisting of secondary alcohol ethoxylates, secondary alcohol ethoxysulfates, secondary alcohol ethoxycarboxylates, and mixtures of any of these components.

9. A shampoo composition comprising
   (a) a secondary alcohol derivative;
   (b) at least one co-surfactant; and
   (c) water.

10. The shampoo composition of claim 9 wherein the secondary alcohol derivative is selected from the group consisting of secondary alcohol ethoxylates, secondary alcohol ethoxysulfates, secondary alcohol ethoxycarboxylates, and mixtures of any of these components.

11. A detergent composition comprising
   (a) a secondary alcohol derivative; and
   (b) at least one co-surfactant.

12. The detergent composition of claim 11 wherein the secondary alcohol derivative is selected from the group consisting of secondary alcohol ethoxylates, secondary

alcohol ethoxysulfates, secondary alcohol ethoxycarboxylates, and mixtures of any of these components.