GERMICIDAL LIQUID LAUNDRY DETERGENT COMPOSITIONS

Liquid laundry detergent compositions provide good detergency for the cleaning of garments and textiles, as well as further providing a germicidal action to textile fabrics in a domestic laundering process. The liquid detergent compositions are aqueous compositions which comprise: A) 1 - 40 parts by weight of one or more anionic surfactant compositions selected from alkylethercarboxylates and alkylethersulfonates; B) 1 - 25 parts by weight of one or more quaternary ammonium surfactant compositions having germicidal properties; C) 3 - 50 parts by weight of one or more nonionic surfactant compositions selected from linear and secondary alcohol alkoxylates, alkylphenol ethoxylates, alkyl polyglycosides, amine oxides, alkanolamides; D) 0 - 10 parts by weight of one or more anionic co-surfactant compositions selected from alkylsulfates, alkylsulfonates, alkylethersulfonates, alkylarylsulfonates, alkylarylethersulfates present in a proportion not exceeding one half of the weight of the one or more quaternary ammonium surfactant compositions having germicidal properties; wherein the weight ratios of B:A are at 1:2 or greater, with the remaining balance to 100 parts by weight of water. Further conventional additives may be included as optional constituents. The liquid laundry detergent compositions are effective in wash bath dilutions of 1:500 and lower dilutions.
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GERMICIDAL LIQUID LAUNDRY DETERGENT COMPOSITIONS

Liquid detergent compositions for laundering of textiles and garments typically provide good detergency, good anti-soil redeposition properties, with minimal deleterious effect to textiles or garments. While such compositions are well known to provide good cleaning effects, it is also known that such liquid detergent compositions, presently being marketed as a laundry detergent compositions, do not generally provide a particularly effective sanitizing or disinfecting effect to the laundered garments or textiles. Most known art laundry detergent compositions typically fail to provide for specific protection against harmful bacteria and other microorganisms present in the garments or textiles. Accordingly, there exists a present need in the art of laundry detergent compositions for products which provide both excellent detergency and a sanitizing effect providing for a high level of protection against harmful bacteria as may normally be present in the household including gram positive and gram negative vegetative bacteria such as those belonging to the species: Salmonella, Klebsiella and Staphylococcus.

While such compositions would be desirable, these have also been difficult to produce as many effective cationic surfactant germicides, particularly certain quaternary ammonium surfactants, are known to be effective against such gram positive and gram negative vegetative bacteria but are incompatible with anionic surfactants, which are well known detergent agents.

Accordingly there remains a need in the art for improved laundry detergent compositions, particularly those which provide good cleaning as well as providing a good antibacterial effect so to effectively sanitize treated textiles or garments.

It is therefore among the objects of the invention to provide improved laundry detergent compositions in both concentrated and diluted (aqueous) form wherein said laundry detergent is characterized by good foaming, satisfactory detergents properties, and germicidal activity. Such compositions are particularly useful in the laundering of garments and/or textiles particularly when used in conjunction with commercial or residential washing machine designed for the laundering of garments and/or textiles.

According to the invention there is provided a detergent composition comprising

A) a major anionic surfactant selected from alkylether-carboxylates and alkylether sulfonates;
B) a cationic germicidal surfactant; and
C) a nonionic surfactant preferably selected from alcoholalkoxylates, alkylphenol alkoxylates, alkylpolyglycosides, amine oxides and alkanolomides, wherein the value of the cationic surfactant to the major anionic surfactant is 1:2 or greater.
In accordance with one preferred aspect of the present invention, there is provided an aqueous germicidal liquid laundry detergent composition in concentrated form, which composition comprises water, and the following constituents:

A) 1 - 40 parts by weight of one or more anionic surfactants selected from alkylethercarboxylates and alkylethersulfonate;

B) 1 - 25 parts by weight of one or more quaternary ammonium surfactant having germicidal properties;

C) 3 - 50 parts by weight of one or more nonionic surfactant selected from linear and secondary alcohol alkoxylates, alkylphenol ethoxylates, alkyl polyglycosides, amine oxides, and alkanolamides;

D) 0 - 10 parts by weight of one or more further anionic surfactant selected from alkylsulfates, alkylsulfonates, alkylene sulfonates, alkylarylsulfonates, alkylaryl ethersulfonates which are present in a proportion not to exceed one half of the weight of the one or more quaternary ammonium surfactants;

with the proviso that the weight ratios of B:A be within the weight ratio of 1:2 or greater. Where the detergent compositions desirably includes a further anionic surfactant D, it is present in amounts where the weight value of B to D is critically maintained at 2:1, or greater.

The compositions of the invention may further comprise optional constituents, many of which are well known to the art, including but are not limited to: detergency builders, chelating agents, pH adjusting agents, pH stabilizing agents (buffers), hydrotropes, optical brighteners, coloring agents, fragrances, fillers, as well as others not particularly elucidated here. These optional constituents may be added in any effective amount, but generally the total amount of such optional constituents does not exceed about 10 parts by weight of the total weight of the detergent compositions being taught herein.

Constituent (A) Particularly useful anionic surfactants which find use in the detergent compositions according to the present invention include at least one (a) alkylethercarboxylate surfactant, and/or at least one (b) alkylethersulfonate surfactant.

Useful alkylethercarboxylate surfactants include compounds according to the formula:

\[
\begin{align*}
R - O - \left( C - C - O \right)_x - R_3 & \quad M^+ \\
\end{align*}
\]

where:
R is a C₄-C₂₂ linear or branched alkyl group, preferably C₈-C₁₅ linear or branched alkyl group, and yet more preferably a C₁₂-₁₅ linear or branched alkyl group;

x is an integer from 1 to 24,

R₁, R₂ and R₃ is a group selected from H, lower alkyl radicals including methyl and ethyl radicals, carboxylate radicals including acetate and propionate radicals, succinate radicals, hydroxysuccinate radicals, or mixtures thereof wherein at least one R₁, R₂ or R₃ is a carboxylate, succinate or hydroxysuccinate radical; and,

M⁺ is a counterion including an alkali metal or ammonium counterion.

Free acid forms of the alkylethercarboxylate compounds noted above may also be used. Preferably, the alkylethercarboxylate compound is one wherein R is C₁₂-C₁₅, x is an integer from 1-10 inclusive, and R₁, R₂, and R₃ may be the same or different are preferably selected from H, and carboxylate radicals. Most preferred are alkylethercarboxylate compounds wherein R is C₁₂-C₁₅, x is an integer from 1-10 inclusive, and R₁ and R₂ are both hydrogen, and R₃ is a CH₂COO⁻ radical, and M⁺ is a counterion selected from sodium, potassium and ammonium counterions.

Such alkylethercarboxylate compounds are per se known and are available in commercial preparations wherein they are frequently provided with an aqueous carrier. Examples of such presently available commercial preparations include SURFINE WLG (Finetex Inc., Elmwood Park NJ), SANDOPAN DTC (Clariant Chem.Co., Charlotte NC) in salt forms, and in free acid forms include those marketed under the tradename NEODOX (Shell Chemical Co., Houston TX).

Alternatively, or in addition to the (a) alkylethercarboxylate surfactants noted above, there may be used one or more (b) alkylethersulfonate surfactants.

Exemplary alkylethersulfonate surfactants which may be used include those according to the formula:

\[ \text{R} \text{O}-(\text{CH₂CH₂O})_x\text{CH₃CH₂SO₃⁻ M⁺} \]

where:

R is a C₄-C₂₂ linear or branched alkyl group, preferably C₈-C₁₅ linear or branched alkyl group, and yet more preferably a C₁₂-₁₅ linear or branched alkyl group;

x is an integer from 1 to 24, and,

M⁺ is alkali metal or ammonium counterion.

Free acid forms of the alkylethersulfonate compounds noted above may also be used.
Preferably, the alkylethersulfonate compound is one wherein \( R \) is \( \text{C}_{12}-\text{C}_{15} \), \( x \) is 1-10 and \( M^+ \) is a counterion selected from sodium, potassium and ammonium counterions.

Such alkylethersulfonate compounds are known and are available in commercial preparations wherein they are frequently provided with an aqueous carrier. Examples of such commercially available preparations include AVANEL S30 and AVANEL S70 (PPG Industries, Pittsburgh PA).

In the concentrated liquid detergent compositions according to the invention, the anionic surfactant of Constituent (A) comprises from 1-40 parts by weight of the liquid detergent compositions, more preferably comprise from 5-30 parts by weight of the active constituents of the liquid detergent compositions, but most preferably comprise from 10-20 parts by weight of the active constituents of the liquid detergent compositions. Constituent (B) Cationic surfactants which exhibit germicidal activity and which may be used in the detergent compositions include certain quaternary ammonium surfactants, of which one or more such cationic surfactants may be used as the present Constituent (B). Exemplary useful quaternary ammonium compounds and salts thereof include quaternary ammonium germicides which may be characterized by the general structural formula:

\[
\begin{bmatrix}
    R_1 \\
    R_2-N^+-R_3 \\
    R_4
\end{bmatrix}
\]

where at least one or \( R_1, R_2, R_3 \) and \( R_4 \) is a hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms, and the entire cation portion of the molecule has a molecular weight of preferably at least 165. The hydrophobic radicals may be long-chain alkyl, long-chain alkoxy aryl, long-chain alkyl aryl, halogen-substituted long-chain alkyl aryl, long-chain alkyloxy alkyl, aryl alkyl, etc. The remaining radicals on the nitrogen atoms other than the hydrophobic radicals are substituents of a hydrocarbon structure usually containing a total of no more than 12 carbon atoms. The radicals \( R_1, R_2, R_3 \) and \( R_4 \) may be straight chained or may be branched, but are preferably straight chained, and may include one or more amide or ester linkages. The radical \( X^- \) may be any salt-forming anionic radical.

Exemplary quaternary ammonium salts within the above description include the alkyl ammonium halides such as cetyl trimethyl ammonium bromide, alkyl aryl ammonium halides such as octadecyl dimethyl benzyl ammonium bromide, N-alkyl pyridinium halides such as N-cetyl pyridinium bromide, and the like. Other suitable types of quaternary ammonium salts include those in which the molecule contains either amide or ester linkages such as octyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride, N-[[laurylcocoaminoformylmethyl]-pyridinium chloride, and the like. Other very effective types of quaternary ammonium compounds which are useful as
germicides include those in which the hydrophobic radical is characterized by a substituted aromatic nucleus as in the case of lauryloxyphenyltrimethyl ammonium chloride, cetylaminoxyphenyltrimethyl ammonium methosulfate, dodecylphenyltrimethyl ammonium methosulfate, dodecylbenzylintrimethyl ammonium chloride, chlorinated dodecylbenzylintrimethyl ammonium chloride, and the like.

Preferred quaternary ammonium compounds which act as germicides and which are be found useful in the practice of the present invention include those which have the structural formula:

\[
\begin{array}{c}
\text{CH}_3 \\
\text{R}_2-\text{N}^+-\text{R}_3 \\
\text{CH}_3 \\
\text{X}^-
\end{array}
\]

wherein \( R_2 \) and \( R_3 \) are the same or different \( C_8-C_{12} \) alkyl, or \( R_2 \) is \( C_{12-16} \) alkyl, \( C_8-16 \) alkylethoxy, \( C_{8-18} \) alkylphenoxyethoxy and \( R_3 \) is benzyl, and \( X \) is a halide, for example chloride, bromide or iodide or is methosulfate. The alkyl groups recited in \( R_2 \) and \( R_3 \) may be straight chained or branched, but are preferably substantially linear.

Such quaternary germicides are usually sold as mixtures of two or more different quaternaries, such as BARDAC® 205M, (presently commercially available from Lonza, Inc., Fairlawn, NJ) which is believed to be a 50% aqueous solution containing 20% by weight of an alkyl dimethyl benzylammonium chloride (50% C14, 40% C16 alkyl); 15% by weight of an octyl decyl dimethylammonium chloride; 7.5% by weight of dioctyl dimethylammonium chloride; and 7.5% by weight of didecyl dimethylammonium chloride. A further useful quaternary germicide is CYNCAL® 80% (presently commercially available from Hilton Davis Chemical Co., Cincinnati, OH) which is believed to comprise 80% by weight of an alkyl dimethyl benzylammonium chloride (50% C14, 40% C12 and 10% C16 alkyl), 10% water and 10% ethanol. Further useful quaternary germicidal agents include BTC-8358®, an alkyl benzyl dimethyl ammonium chloride (80% active) and BTC-818®, a dialkyl dimethyl ammonium chloride (both presently commercially available from the Stepan Chemical Co., Chicago, IL). Additional suitable commercially available quaternary ammonium germicides of the alkyl dimethyl benzylammonium chloride type containing the same alkyl dimethyl benzylammonium chloride mixture as that of CYNCAL® and which are generally referred to as quaternium salts include BARQUAT® MB-80, which is believed to be solution of 80% by weight solution of the quaternary, 10%wt. ethanol and 10%wt. water; BARQUAT® MB-50, believed to be 50%wt. an alkyl dimethyl benzylammonium compound, 40%wt.water and 10% ethanol; HYAMINE® 1622 believed to be an aqueous solution of benzethonium chloride, and HYAMINE® 3500, which is believed to be a 50% aqueous solution of the quaternary (presently commercially available from Lonza Inc., Fairlawn, NJ).
In the liquid laundry detergent compositions according to the invention Constituent (B) comprises from 1 - 25 parts by weight of the active constituents of the detergent compositions, more preferably comprise from 5-20 parts by weight, and most preferably comprise from 6-12 parts by weight of the active constituents of the liquid detergent compositions.

The present inventors have surprisingly found that effective germicidal efficacy of the detergent composition when diluted to form a wash bath as indicated in more detail below wherein the weight ratios of such actives of Constituent (B):Constituent (A) is at least 1:2, or greater such as 1.5:2, 2:2, 2.5:2 and even greater proportions of Constituent (B) to Constituent (A).

Constituent (C) The compositions according to the present invention further comprise one or more nonionic surfactants selected from surfactants based upon linear and secondary alcohols, alkylphenol ethoxylates, alkyl polyglycosides, amine oxides, and, alkanolamides. Such nonionic surfactants are known and are available in commercial preparations, certain such commercial preparations providing the surfactant compound in conjunction with an aqueous carrier.

Useful nonionic surfactants include the condensation products of a higher alcohol (e.g., an alkanol containing about 8 to 18 carbon atoms in a straight or branched chain configuration) condensed with about 5 to 30 moles of ethylene oxide, for example, lauryl or myristyl alcohol condensed with about 16 moles of ethylene oxide, tridecanol condensed with about 6 to moles of ethylene oxide, myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of myristyl alcohol, the condensation product of ethylene oxide with a distillation fraction of cut of coconut fatty alcohol containing a mixture of fatty alcohols with alkyl chains varying from 10 to 14 carbon atoms in length and wherein the condensate contains either about 6 moles of ethylene oxide per mole of total alcohol or about 9 moles of ethylene oxide per mole of alcohol and tallow alcohol ethoxylates containing 6 ethylene oxide to 11 ethylene oxide per mole of alcohol.

A preferred group of nonionic surfactants are those which are presently being marketed under the trade name, "NEODOL" (Shell Chemical. Co., Houston TX) These nonionic surface active agents are believed to be ethoxylated higher aliphatic, primary alcohol containing about 9-15 carbon atoms, such as C9-C11 alkanol condensed with 8 moles of ethylene oxide (NEODOL 91-8), C12-13 alkanol condensed with 6.5 moles ethylene oxide (NEODOL 23-6.5), C12-15 alkanol condensed with 12 moles ethylene oxide (NEODOL 25-12), C14-15 alkanol condensed with 13 moles ethylene oxide (NEODOL 45-13), and the like.

Additional satisfactory water soluble alcohol ethylene oxide condensates are the condensation products of a secondary aliphatic alcohol containing 8 to 18 carbon atoms in a straight or branched chain configuration condensed with 5 to 30 moles of ethylene oxide. Such nonionic surfactants are presently commercially available under the trade name "TERGITOL" (Union Carbide Corp., Danbury, CT). Specific examples of such commercially available nonionic surfactants of the
foregoing type are C_{11}-C_{15} secondary alkanols condensed with either 9 ethylene oxide (TERGITOL 15-S-9) or 12 ethylene oxide (TERGITOL 15-S-12) marketed by Union Carbide Corp., (Danbury, CT).

Other suitable nonionic surfactants include the polyethylen oxide condensates of one mole of alkyl phenol containing from about 8 to 18 carbon atoms in a straight- or branched chain alkyl group with about 5 to 30 moles of ethylene oxide. Specific examples of alkyl phenol ethoxylates include nonyl condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol, dinonyl phenol condensed with about 12 moles of ethylene oxide per mole of phenol, dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol and diisoctylphenol condensed with about 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include IGEPAL CO-630 (a nonyl phenol ethoxylate) marketed by ISP Corp. (Wayne, NJ) and TRITON X100 (an isoocyt phenol ethoxylate) marketed by Union Carbide Corp. (Danbury CT).

Alkylpolyglycosides may also be used as a nonionic surfactant in the present inventive compositions. Preferred alkylpolyglycosides include those according to the formula:

$$R_C O \longrightarrow (C_n H_{2n} O)_r -(Z)_x$$

where Z is derived from glucose, R is a hydrophobic group selected from alkyl groups, alkylphenyl groups, hydroxyalkylphenyl groups as well as mixtures thereof, wherein the alkyl groups may be straight chained or branched, which contain from about 8 to about 18 carbon atoms, n is 2 or 3, r is an integer from 0 to 10, but is preferably 0, and x is a value from about 1 to 8, preferably from about 1.5 to 5. Preferably the alkylpolyglycosides are nonionic fatty alkylpolyglucosides which contain a straight chain or branched chain C_{8}-C_{15} alkyl group, and have an average of from about 1 to about 5 glucose units per fatty alkylpolyglucoside molecule. More preferably, the nonionic fatty alkylpolyglucosides which contain straight chain or branched C_{8}-C_{15} alkyl group, and have an average of from about 1 to about 2 glucose units per fatty alkylpolyglucoside molecule.

Exemplary alkylpolyglycosides which are presently commercially available include those presently commercially available under the tradename GLUCOPON (Henkel Corp., Ambler, PA).

Also useful in the nonionic surfactant constituent of the invention are nonionic surfactant compositions based on amine oxides. One general class of useful amine oxides include alkyl di (lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or branched chain, saturated or unsaturated. The lower alkyl groups include between 1 and 7 carbon atoms. Examples include lauryl, dimethyl amine oxide, myristyl dimethyl amine oxide, and those in which the alkyl group is a mixture of different amine oxide,
dimethyl cocoamine oxide, dimethyl (hydrogenated tallow) amine oxide, and myristyl/palmityl

dimethyl amine oxide.

A further class of useful amine oxides include alkyl di (hydroxy lower alkyl) amine oxides in
which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be straight or
branched chain, saturated or unsaturated. Examples are bis(2-hydroxyethyl) cocoamine oxide, bis(2-
hydroxyethyl) tallow amine oxide, and bis(2-hydroxyethyl) stearylamine oxide.

Further useful amine oxides include those which may be characterized as alkylamidopropyl
di(lower alkyl) amine oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon
atoms, and can be straight or branched chain, saturated or unsaturated. Examples are cocoamidopropyl dimethyl amine oxide and tallowamidopropyl dimethyl amine oxide; and

Additional useful amine oxides include those which may be referred to as alkylmorpholine
oxides in which the alkyl group has about 10-20, and preferably 12-16 carbon atoms, and can be
straight or branched chain, saturated or unsaturated.

Further examples of such useful include nonionic surfactant compositions based on amine
oxides include those which are presently commercially available and include those under the trade
name AMMONYX (Stepan Co., Chicago IL).

In the concentrated liquid detergent compositions according to the invention Constituent (C)
comprises from 3 - 50 parts by weight of the actives constituent in the detergent compositions taught
herein. More preferably, the nonionic surfactant composition comprise from 5 - 30 parts by weight,
and most preferably comprise from

10 - 25 parts by weight of the actives constituent of the present inventive liquid detergent
compositions.

Further examples of these anionic, cationic and nonionic surfactant compositions recited
above are known to the art, and described in McCutcheon’s Detergents and Emulsifiers, Vol. 1,
and/or, Kirk-Othmer, Encyclopedia of Chemical Technology, noted above.

Constituent (D) While not always included in compositions according to the present
invention, the present inventors have found that a minor amount of a further anionic co-surfactant
provides further detergents action and foaming action. Such a further anionic surfactant is present in a
relatively small amount, i.e., less than 10 parts by weight based on the total weight of the liquid
detergent composition, with the further limitation that such anionic co-surfactant is present in an
amount of no more than ½ of the total weight of Constituent (B).

Anionic surfactants which are useful for use as the recited anionic co-surfactant which may
be any anionic surfactant which is determined not to undesirably detract from the efficacy of
Constituent (B) when included in a formulation within the scope of the instant invention. Known
anionic surfactants may be used, including for example, alkali metal salts or ammonium salts of
compounds selected from certain alkylsulfates, alkylsulfonates, alkylethersulfates, alkylaryl sulfonates, alkylaryl ethersulfates, and mixtures thereof.

A further class of useful anionic surfactants which find use as the co-surfactant recited herein include alkyl ethersulfates and salts thereof, especially one or more alkyl ethersulfates which may be represented by the following general formula:

$$\text{R}-(\text{CH}_2\text{CH}_2\text{O})_n\text{O}^-\text{S}^+\text{O}^-\text{X}^+$$

wherein R is a C₈ - C₁₈ alkyl group, n is an integer from 1 to 30, and X represents a counterion selected from alkaline earth metals and ammonium. Of these alkyl ethersulfates, especially preferred are those wherein R is a C₁₂-C₁₅ group, n is 4, and X is a sodium cation or an ammonium cation, i.e., NH₄⁺. Such alkyl ether sulfates may be produced by known methods, or in the alternative are presently commercially available under the trade name “STEOL” (Stepan Chem. Co., Chicago IL).

Such anionic surfactants are known and are available in commercial preparations wherein they are frequently provided in conjunction with an aqueous carrier. Further useful anionic surfactants useful as the co-surfactant include those illustrated in the Examples, below. Of course, it is to be understood that one or more anionic surfactants may be used to provide the anionic co-surfactants according to Constituent (D).

As indicated above, when present, the anionic co-surfactant according to Constituent (D) comprises from 0 - 10 parts by weight of the liquid detergent compositions of the present invention. More preferably the anionic co-surfactant comprises from 1 - 8 parts by weight, and most preferably comprise from 2 - 5 parts by weight of the liquid detergent compositions, with the proviso that the weight ratios of the cationic surfactant composition of Constituent (B): the anionic co-surfactant composition of Constituent (D) is at least 2:1, but are preferably greater, and most preferably in a ratio of at least 2.5:1.

Optionally, the compositions include up to 10% by weight of conventional laundry detergent additives as known in the art including but not limited to: builders and chelating agents, pH adjusters, stabilizers, rheology modifying agents, sequestrants, optical brighteners, solvents including alcohols such as ethanol and propylene glycol, hydrotropes such as sodium and potassium aryl sulfones and alkaryl sulfonates, coloring agents, and fragrances. Many of these are known to the art, and include those which are described in McCutcheon's Functional Materials, Vol.2, North American Edition, (1991), and each may be included at effective concentrations, with the total of such optional constituents preferably not exceeding 10% by weight of the total liquid laundry detergent composition taught herein.
For the stabilization of the inventive composition the use of pH stabilizing agents, interchangeably referred to as pH buffers, the inclusion of any pH buffering compound or pH buffer composition which is compatible with the aqueous compositions taught herein may be used, including many which are well known to the art. These include the alkali metal phosphates, polyphosphates, pyrophosphates, triphosphates, tetraphosphates, silicates, metasilicates, polysilicates, carbonates, hydroxides, and mixtures of the same. Certain salts, such as the alkaline earth phosphates, carbonates, hydroxides, can also function as buffers. It may also be suitable to use buffers such materials as aluminosilicates (zeolites), borates, aluminates and certain organic materials such as gluconates, succinates, maleates, and their alkali metal salts. Such buffers keep the pH ranges of the compositions of the present invention within acceptable limits. Other pH buffers, not particularly elucidated here may also be used. Preferably, citric acid, which is available as an anhydrous salt of an alkali metal citric acid, is added as it is readily commercially available, and effective. Citric acid is preferred as it is effective and is widely available at a low cost.

As noted above, the compositions of the invention when diluted to form a 0.20% solution in water which is equivalent to a dilution of 1 part of the inventive composition to 500 parts water, preferably deionized water, exhibit a pH in the range of 5-10, more preferably a pH in the range 7-8, and most preferably a pH of about 8. The incorporation of an effective amount of such a pH stabilizing agent provides the technical benefits of ensuring the stability of the compositions of the invention as formulated, and as used when added to an excess of water to form a cleaning composition therefrom. As is known to those skilled in the relevant art, various stains and food deposits may impart an appreciable change in the pH of water from an approximately neutral pH to that of an acidic or basic pH. The inclusion of an effective amount of a pH stabilizing agent in the compositions, when added to the excess of water will tend to return the pH of a cleaning composition to a more neutral pH. While it will be realized that the selection of the other constituents forming the inventive compositions may necessitate varying amounts of a pH buffer composition, the buffer composition generally is included in effective amounts which are conventionally determinable in order to adjust the pH of the diluted compositions to the indicated pH ranges, particularly to the preferred pH ranges indicated above.

A further optional constituent which may be desirably included in the inventive compositions include a detergency builder components, which be of the organic or inorganic type may be desirably included in the present inventive compositions. When present, the detergency builder component generally is included to comprise up to 6 parts by weight, but preferably only up to 5 parts by weight of the composition. Exemplary detergency builders include alkali metal carbonates, phosphates, polyphosphates and silicates. More specific examples include sodium tripolyphosphate, sodium carbonate, potassium carbonate, sodium polyphosphate, potassium pyrophosphate, potassium
tripolyphosphate, and sodium hexametaphosphate. Exemplary organic alkaline sequestrant builder salts include alkali metal polycarboxylates including water-soluble citrates such as calcium, sodium and potassium citrate, calcium, sodium and potassium tartrate, calcium, sodium and potassium ethylenediaminetetraacetate, calcium, sodium and potassium N-(2-hydroxyethyl)-ethylene diamine triacetates, calcium, sodium and potassium nitrilo triacetates, as well as calcium, sodium and potassium tartrate or mono- and di-succinates. These builder builders may be used individually, as a combination of two or more detergency builders, including those indicated above. Of these, especially preferred are ethylenediaminetetraacetic acid, and salts thereof particularly calcium and sodium salts thereof, and HEDTA and salts thereof. Other known art chelating agents may be used, including sodium gluconate, gluconic acid and salts thereof and sorbitol may also be used.

Further optional, but often desirable constituents include fragrances, which may be derived from natural sources or which may be synthetically produced, as well as one or more coloring agents which find use in modifying the appearance of the concentrate compositions and enhance their appearance from the perspective of a consumer or other end user.

Water forms a constituent of the concentrated liquid detergent compositions and it is preferably appropriately filtered in order to remove any undesirable impurities such as organics or inorganics, especially mineral salts which are present in hard water which may thus interfere with the operation of the invention. The amount of water added is an amount to provide the balance of the composition to provide 100 parts by weight. Generally, the water is added, generally in an amount of 40 to 95 parts by weight, so to provide the balance of the total inventive composition.

The compositions according to the present invention are particularly useful as an aqueous liquid detergent in concentrated form. The critical components of the composition are the predominant anionic surfactants according to Constituent (A), viz., the alkylethercarboxylate, and/or alkylethersulfonate and Constituent (C), viz., the one or more quaternary ammonium surfactants. We have surprisingly discovered that the critically selected anionic surfactants are compatible with quaternary ammonium germicides in the recited proportions, and thereby up to very high ratios of anionic surfactant : cationic quaternary ammonium surfactant are now obtainable in accordance with the present inventive teaching, as compared with prior art teachings relating to the compatibility between anionic and cationic surfactants. By compatibility, it is meant that these critically selected anionic surfactants do not impair the antimicrobial activity of the quaternary component to any significant degree. This is in sharp contrast to other anionic surfactants, which significantly impair the antibacterial activity of quaternaries, as has been recited in the prior art and exemplified below. The surprising discovery described in the instant invention allows the formulation of unique and useful detergent compositions which simultaneously provides excellent cleaning combined with uncompromised antibacterial protection, even in formulations with high levels of anionic surfactant.
The compositions according to the invention are prepared by dissolving the individual constituents in order to provide a liquid concentrate. In use, the concentrate is added to the wash water in an amount effective to achieve either cleaning and brightening as well as sanitization of the fabrics or garments being washed. It has been found that from approximately 1/2 to about 3/4 cup of the liquid laundry detergent concentrate compositions per wash load (domestic (U.S.A.) washing machine). Thus, based on the total wash water volume of approximately 16 gallons of water, the compositions can be used at dilutions of the concentrated composition:water from about 1:500 to 1:330, although even lower dilutions may be also used and provide such excellent cleaning and sanitization effects. Conventional washing machines may be used utilizing conventional washing cycles, particularly wherein the wash water is at a temperature in the range of 20°C - 40°C degrees, and for a bath contact time of 10-20 minutes.

**Examples:**

**Preparation of Example Formulations**

Several laundry detergent formulations according to the invention were prepared, as well as comparative examples, all of which are described in detail on Table 1, below. Examples 1 through 6 illustrate formulations which are in accordance with the present inventive teaching and exhibit ratios of the quaternary ammonium surfactant constituent (constituent B) having germicidal properties to the anionic alkylethercarboxylate and/or alkylethersulfonate surfactant constituent (constituent A) of 1:2 or greater as is disclosed in the specification above. The comparative examples, C1 through C4 describe compositions having similar constituents, which however fall outside of the ratio between constituents B:A of at least 1:2 as described above. It is to be noted that these ratios are calculated on the actives portion, or “actives” of an in individual constituent more than one of which is supplied as an aqueous composition itself, and not necessarily upon the weight percentage of a particular constituent as indicated on Table 1 below. The percentage of actives of each of the particular constituents indicated on Table 1, as well as their identity, is succinctly provided in Table 2, below.

These formulations were prepared by adding a measured amount of deionized water to a suitable glass beaker, and utilizing a magnetic stirrer, stirring the water during the addition of the further measured amounts of the remaining constituents to the water. In certain of the formulations, an amount of sodium hydroxide was added in sufficient amounts to neutralize the NEODOX 25-6, which was provided in its acid form. Afterwards, the formulations were stirred for a further 15 to 30 minutes using a magnetic stirring bar, and in each case the formulations resulted in a homogeneous liquid, suitable for use as a laundry detergent at a dilution of about 1:500 in a household washing machine.
<table>
<thead>
<tr>
<th></th>
<th>Ex.1</th>
<th>Ex.2</th>
<th>Ex.3</th>
<th>Ex.4</th>
<th>Ex.5</th>
<th>Ex.6</th>
<th>Ex.7</th>
<th>Ex.8</th>
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<td>47.02</td>
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<td>ratio of B:A</td>
<td>1.4 : 1.0: 1.0: 1.0: 1.5</td>
<td>1.6 : 1.0: 1.8 : 1.0: 1.0: 1.9</td>
<td>1.8 : 1.0: 1.0: 1.4: 1.0: 2.3</td>
<td>1.0 : 2.3</td>
<td>1.0 : 3.4</td>
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<td>ratio of B:D</td>
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<td></td>
<td></td>
<td>2.4 : 1.0: 2.28 : 1.0: 9.0 : 1.0</td>
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<td>4.0 : 1.0</td>
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**TABLE 2**

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<th>Constituent</th>
<th>Tradename:</th>
<th>Description:</th>
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<tr>
<td>A</td>
<td>SURFINE WLG</td>
<td>sodium salt of $\text{C}_{12-15}\text{-EO}_n\text{-CH}_2\text{COO}^-$ [60%wt. actives (AEC-salt form)]</td>
</tr>
<tr>
<td>A</td>
<td>NEODOX 25-6</td>
<td>$\text{C}_{12-15}\text{-EO}_n\text{-CH}_2\text{COOH}$ [88.5%wt. actives (AEC-acid form)]</td>
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<tr>
<td>A</td>
<td>AVANEL S30</td>
<td>sodium salt of $\text{C}_{12-15}\text{-EO}_3\text{-CH}_2\text{CH}_2\text{SO}_3^-$ [30%wt. actives]</td>
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<tr>
<td>A</td>
<td>AVANEL S70</td>
<td>sodium salt of $\text{C}_{12-15}\text{-EO}_7\text{-CH}_2\text{CH}_2\text{SO}_3^-$ [35%wt. actives]</td>
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<tr>
<td>D</td>
<td>BIOSOFT D40</td>
<td>sodium salt of linear alkylbenzene sulfonate [40%wt. actives]</td>
</tr>
<tr>
<td>D</td>
<td>STEOL CS-460</td>
<td>sodium lauryl-3-ethoxy sulfate [60%wt. actives]</td>
</tr>
<tr>
<td>C</td>
<td>NEODOL 25-7</td>
<td>$\text{C}_{12-15}\text{-EO}_n$ [100%wt. actives]</td>
</tr>
<tr>
<td>C</td>
<td>TERGITOL NP-9</td>
<td>nonylphenol-EO$_n$ [100%wt. actives]</td>
</tr>
<tr>
<td>C</td>
<td>AMMONYX LO</td>
<td>dodecyltrimethyl amine oxide [30%wt. actives]</td>
</tr>
<tr>
<td>C</td>
<td>APG 325 CS</td>
<td>$\text{C}_{9,11}\text{-alkylpolyglycoside}$ [50%wt. actives]</td>
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<tr>
<td>B</td>
<td>BARQUAT MB50</td>
<td>alkylidimethylbenzyl ammonium chloride [50%wt. actives]</td>
</tr>
<tr>
<td>B</td>
<td>BARQUAT 2250</td>
<td>dialkylidimethyl ammonium chloride [50%wt. actives]</td>
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<tr>
<td>--</td>
<td>sodium citrate</td>
<td>trisodium salt of citric acid - dihydrate [100%wt. actives]</td>
</tr>
<tr>
<td>--</td>
<td>NaOH</td>
<td>sodium hydroxide, aqueous [50%wt. actives]</td>
</tr>
<tr>
<td>--</td>
<td>STEPANATE SXS</td>
<td>sodium xylene sulfonate [40%wt. actives]</td>
</tr>
<tr>
<td>--</td>
<td>TINOPAL CBS-X</td>
<td>proprietary optical brightener</td>
</tr>
<tr>
<td>--</td>
<td>BLANKOPHOR TX</td>
<td>proprietary optical brightener</td>
</tr>
</tbody>
</table>

"EO" represents ethoxy
"AEC" represents alkyl ether carboxylate

**Evaluation of Antimicrobial Efficacy:**

Experimental formulations Ex.1, C1, Ex.3, C4, Ex.4 and Ex.5 were evaluated for antimicrobial efficacy at a dilution of 1:500 using a Microbial Reduction Assay against *Salmonella choleraesuis* (gram negative type pathogenic bacteria) and *Staphylococcus aureus* (gram positive type pathogenic bacteria).

The test was carried out for each of the Ex.1, C1, Ex.3, C4, Ex.4 and Ex.5 formulations at dilution of one part of a respective formulation to 499 parts of deionized water at 25°C for a 10 minute contact time. The test protocol followed for each sample was generally as follows.
1. **Inoculation of the Samples:**
   A. Inoculate 1.0 ml of the 24 hour test culture into each 9.0 ml sample tube; and test in duplicate.
   B. Subculture 1.0 ml of the sample after 10 minutes contact time with the respective diluted Example formulation.
   C. Subculture the sample into 9.0 ml of DIFCO AOAC Letheen Broth to form a “10⁻¹ Sample” dilution.

2. **Sample Dilutions and Plating**
   A. Plate the 10⁻¹, 10⁻³, and 10⁻⁵ dilutions for each sample/organism/contact time combination by the following general protocol:
      1. From the 10⁻¹ “Sample” dilution, plate 1.0 ml to form a 10⁻¹ “Sample” plate.
      2. Pipette and transfer 0.1 ml of the 10⁻¹ Sample dilution into 9.9 ml of DIFCO AOAC Letheen Broth to form a “10⁻³ Sample” dilution and form a 10⁻³ plate.
      3. Pipette and transfer 0.1 ml of 10⁻³ Sample dilution to 9.9 ml DIFCO AOAC Letheen Broth to form a “10⁻⁵ Sample” dilution and form a 10⁻⁵ plate.
   B. Pour each of the 10⁻¹ plates, 10⁻³ plate, and 10⁻⁵ plate with Tryptic Soy Agar containing polysorbate 80 and lecithin (either DIFCO or BBL).
   C. Incubate the plates for 48 hours at 35°C.

3. **Control Counts: Dilutions and Plating**
   A. Inoculate 1.0 ml of 24 hour test culture into 9.0 ml DIFCO AOAC Letheen Broth to form a “Control” dilution.
   B. Subculture 1.0 ml of the Control dilution into 9.0 ml DIFCO AOAC Letheen Broth at 10 minutes exposure; these are the “10⁻¹ Control” dilution tubes for the 10 minutes contact time controls.
   C. Plate 10⁻⁴ and 10⁻⁵ dilutions of the 10⁻¹ Control dilution for each contact time by the following protocol:
      1. Pipette 0.1 ml of the 10⁻¹ Control dilution into 9.9 ml DIFCO AOAC Letheen Broth to form a “10⁻³ Control” dilution.
      2. Plate 1.0 ml of the 10⁻³ Control dilution into 9.0 ml DIFCO AOAC Letheen Broth to form a “10⁻⁴ Control” dilution and form a “10⁻⁴ Control” plate.
3. Pipette 0.1 ml of the $10^{-3}$ Control dilution into 9.9 ml of ml DIFCO AOAC Letheen Broth to form a "$10^{-5}$ Control" dilution, and to form a "$10^{-5}$ Control" plate.

4. Pour the $10^{-4}$ and $10^{-5}$ Control plates with Tryptic Soy Agar containing polysorbate 80 and lecithin, and incubate at 35°C for 48hr.

4. **Calculation of Log$_{10}$ Reduction:**

   A. Determine the number of bacteria survivors at each contact time for both the controls and test samples of each of the plates produced in accordance with the protocols outlined for steps 1 - 3 denoted above.

   1. Count the number of colonies on the petri dish. The plate is acceptable for counting with a colony count between 25 and 250.

   2. Multiply the number of colonies by the plate dilution factor = the number of surviving bacteria/ml.

   B. Determine the numbers of Log$_{10}$ reduction in bacteria for each sample/organism/contact time combination in accordance with the following equation:

   \[
   \text{Log}_{10} \text{ (Control Count)} - \text{Log}_{10} \text{ (Survivor Count)} = \# \text{ Log}_{10} \text{ of bacteria reduction.}
   \]

   For this test with a contact time of 10 minutes, a Log$_{10}$ reduction value of 3 or greater against both organisms is acceptable for "passing" performance (i.e., broad spectrum antimicrobial activity), any lesser Log$_{10}$ reduction value indicates unacceptably poor antimicrobial efficacy. The results of this evaluation are summarized on Table 3, below.

<table>
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<tr>
<th></th>
<th>Log$_{10}$ Reduction of <em>Salmonella choleraesuis</em></th>
<th>Log$_{10}$ Reduction of <em>Staphylococcus aureus</em></th>
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<td>Ex. 6</td>
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The results reported on Table 3 clearly and distinctly point out the advantages of the formulations according to the applicant’s inventive composition inside the preferred ranges of the critical component ratios, as opposed to those which fall outside the critical component ratios. As may be seen, those formulations according to the invention surprisingly and unexpectedly provide
superior levels of antimicrobial activity as evidenced by the reported Log₁₀ reduction values >3 as noted on Table 3. This is in sharp contrast to the comparative formulations which included ratios of constituents B:A which were outside of the applicant’s preferred ranges for these constituents as discussed in more the specification above.

The results of Table 3 also illustrate the excellent germicidal efficacy of the present inventive compositions over known prior art compositions such as those described in US 4,576,529 in its Table 2 wherein germicidal efficacy was found at a maximum dilution of 1 part of composition to 333 parts water, but where most of the prior art compositions were found effective in dilutions of 1 part of composition to 200 - 250 parts water, which are dilutions far below typical dilutions used for laundry products and which could thus be disadvantageous to use from both a cost standpoint, and from a consumer acceptance standpoint. These results are in contrast to the present inventive compositions which provide excellent germicidal efficacy at typical laundry product composition dilutions, i.e., 1:500 as is demonstrated by the results on Table 3 above and thus would be expected to overcome many of the technical and consumer prejudices which might be associated with prior art compositions.

**In-use Laundry Sanitization:**

An "in-use" laundry sanitization test was performed under conditions which simulated a domestic, viz., “in-home” laundering process, in accordance with a simulated in-use test recommended by the U.S. Environmental Protection Agency (EPA) and in the EPA Product Performance Guidelines, which is a well known test method for antimicrobial laundry additives published by Petrocci and Clarke in the Journal of the Assoc. of Official Analytical Chemists, volume 52, pages 836-842 (1969), the contents of which are herein incorporated by reference. These evaluations were performed utilizing a formulation according to Example 7, which is disclosed in detail on Table 1. In summary, inoculated fabric swatches are contacted with a test detergent dilution for 10 minutes followed by neutralization and performance of plate counts for the enumeration of survivors and calculation of the percent reduction. The percent reduction in the bacteria is calculated for the swatches and wash water separately.

In this evaluation, the formulation according to Example 7 was tested for laundry sanitization against the test organism *Klebsiella pneumoniae*, a common gram negative pathogen, at a use dilution of 1:365. For comparative purposes, a sample of ULTRA LIQUID TIDE, (a presently commercially available product of the Procter and Gamble Co., Cincinnati OH) was tested at its recommended use dilution of 1:640. For control purposes, a sample of LYSOL Brand Disinfectant Fresh Scent (a product of Reckitt & Colman Inc., registered with the EPA for use as a laundry sanitizer at a dilution of 1:250) was tested at a use dilution of 1:250. The results of these tests are
summarized in Table 4, where as with the results of Table 3, the higher percent reduction reported indicates greater antimicrobial efficacy.

<table>
<thead>
<tr>
<th>TABLE 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>% reduction in 10 minutes of <em>Klebsiella pneumoniea</em></td>
</tr>
<tr>
<td>fabric swatch</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Example 7</td>
</tr>
<tr>
<td>Ultra Liquid Tide</td>
</tr>
<tr>
<td>Lysol Brand Disinfectant</td>
</tr>
</tbody>
</table>

The results in Table 4 clearly demonstrate the superior efficacy of the compositions according to Ex.7 over the currently commercially available detergent product with respect to laundry sanitization activity.

**In-use Laundry Detergency:**

This example demonstrates the utility of a composition of the instant invention for use as a laundry detergent. The formulation according to Example 8 was evaluated for laundry detergency. Cotton and 50/50 polyester/cotton blend fabric sample swatches were purchased from Test Fabrics (Middlesex NJ) and Scientific Services (Oakland NJ). The fabrics were soiled with either a standardized particulate soil, "KREFELD soil", a dust/sebume soil, an oily particulate soil, or grape juice, a stain. The soiled test fabrics were washed in a domestic washing machine using 1/2 cup of the liquid composition according to Ex. 8 to produce a 1:500 dilution in the wash bath (Sears KENMORE Model Ultra Fabric Care Heavy Duty Washing Machine (80 Series)) on a "normal" wash cycle and a "high" water setting. During this "normal" wash cycle, a warm water (105°F) wash cycle was of 10 minutes duration, followed by cold water rinse cycle. Water hardness was 150 ppm. Solids removal, viz., stain removal from the various soils was assessed quantitatively using a Hunter Lab colorimeter, which measured each of the following values: the lightness (" Lₐ " ) of the unstained swatch; the lightness of the stained and subsequently washed swatch (" Lₕ " ); redness-greenness of the unstained swatch (" aₐ " ), redness-greenness of the stained and subsequently washed swatch (" aₕ " ), yellowness-blueness of the unstained (" bₐ " ) swatch, and yellowness-blueness of the stained and subsequently washed swatch (" bₕ " ); each of these values measured as the amount of the standardized white light reflected from the fabrics. The quantitatively evaluated values were measured for the various tested fabric swatches and were used to calculate the Stain Removal Index (SRI) according to the equation:

\[
SRI = 100 - \left[(L_c - L_w)^2 + (a_c - a_w)^2 + (b_c - b_w)^2\right]^{1/2}
\]
and the results are reported on Table 5, below. The SRI value ranges from 0 to 100, with a value of 100 indicating complete soil removal.

<table>
<thead>
<tr>
<th>Stain</th>
<th>SRI values</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Cotton</td>
</tr>
<tr>
<td>KREFELD soil</td>
<td>80.41</td>
</tr>
<tr>
<td>dust/sebum</td>
<td>82.53</td>
</tr>
<tr>
<td>grape juice</td>
<td>81.59</td>
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</table>

As can be seen from the results reported on Table 5, the reported SRI values indicate excellent detergency of the formulation according to Example 8, a representative formulation according to the instant invention, under domestic laundry conditions, even at a relatively dilute ratios of 1:500 of formulation:wash bath water.
Claims:

1. An aqueous liquid laundry detergent composition having germicidal efficacy comprising:
   A) 1 - 40 parts by weight of one or more anionic surfactant compositions selected from alkylethercarboxylates and alkylethersulfonates;
   B) 1 - 25 parts by weight of one or more quaternary ammonium surfactant compositions having germicidal properties;
   C) 3 - 50 parts by weight of one or more nonionic surfactant compositions selected from linear and secondary alcohol alkoxylates, alkylphenol ethoxylates, alkyl polyglycosides, amine oxides, alkanolamides;
   D) 0 - 10 parts by weight of one or more anionic co-surfactant compositions selected from alkylsulfates, alkylsulfonates, alkylethersulfates, alkylarylsulfonates, alkylarylethersulfates present in a proportion not exceeding one half of the weight of the one or more quaternary ammonium surfactant compositions having germicidal properties; wherein the weight ratios of B:A are at 1:2 or greater, with the remaining balance to 100 parts by weight of water.

2. The aqueous liquid laundry detergent composition according to claim 1 wherein the one or more anionic surfactant compositions is an alkylethercarboxylate or salt thereof according to the formula:

   \[
   R - O - (C \equiv C - O)_x - R_3 \quad M^+ 
   \]

   where:
   - \( R \) is a C4-22 linear or branched alkyl group,
   - \( x \) is an integer from 1 to 24,
   - \( R_1, R_2 \) and \( R_3 \) is a group selected from H, lower alkyl radicals including methyl radicals and ethyl radicals, carboxylate radicals including acetate and propionate radicals, succinate radicals, hydroxysuccinate radicals, or mixtures thereof wherein at least one \( R_1, R_2 \) or \( R_3 \) is a carboxylate,
   - succinate or hydroxysuccinate radical; and,
   - \( M^+ \) is alkali metal or ammonium counterion.
3. The liquid laundry detergent composition according to claim 1 wherein the one or more anionic surfactant compositions is an alkylethersulfonate or salt thereof according to the formula:

\[
R-O-(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{CH}_2-S-O^-M^+
\]

where:
- \( R \) is a C\text{4-22} linear or branched alkyl group,
- \( x \) is an integer from 1 to 24, and,
- \( M^+ \) is alkali metal or ammonium counterion.

4. The liquid laundry detergent composition according to claim 1, 2 or 3 wherein one or more quaternary ammonium surfactant compositions having germicidal properties is one or more quaternary ammonium compounds and salts thereof according to the formula:

\[
\left[ \begin{array}{c} R_1 \\ R_2-N^-R_3 \\ R_4 \end{array} \right] X^-
\]

where:
- at least one of \( R_1, R_2, R_3 \) and \( R_4 \) is a hydrophobic, aliphatic, aryl aliphatic or aliphatic aryl radical of from 6 to 26 carbon atoms; and,
- the entire cation portion of the molecule has a molecular weight of at least 165.

5. The liquid laundry detergent composition according to any of claims 1 - 4 wherein the anionic co-surfactant is an alkylether sulfate or salt thereof according to the formula:

\[
R-(\text{CH}_2\text{CH}_2\text{O})_n-O-S-O^-X^+
\]

where:
- \( R \) is a C\text{8 - C18} alkyl group;
- \( n \) is an integer from 1 to 30; and,
- \( X \) represents an counterion selected from alkaline earth metals and ammonium.
6. Aqueous liquid laundry detergent compositions having germicidal efficacy according to any of claims 1 - 5 further comprising:
0 to 10 parts by weight based on the total weight of the aqueous detergent composition of one or more additives selected from: builders, chelating agents, pH adjusters, stabilizers, hydrotropes, rheology modifying agents, sequestrants, optical brighteners, solvents, coloring agents, and fragrances.

7. The aqueous liquid laundry detergent compositions having germicidal efficacy according to claim 1 comprising:
A) 5 - 30 parts by weight of one or more anionic surfactant compositions selected from alkylethercarboxylates and alkylethersulfonates;
B) 5 - 20 parts by weight of one or more quaternary ammonium surfactant compositions having germicidal properties;
C) 5 - 30 parts by weight of one or more nonionic surfactant compositions selected from linear and secondary alcohol alkoxylates, alkylphenol ethoxylates, alkyl polyglycosides, amine oxides, alkanolamides;
D) 1 - 8 parts by weight of one or more anionic co-surfactant compositions selected from alkylsulfates, alkylsulfonates, alkylethersulfates, alkylarylsulfonates, alkylarylethersulfates present in a proportion not exceeding one half of the weight of the one or more quaternary ammonium surfactant compositions having germicidal properties; wherein the weight ratios of B:A are at 1:2 or greater; with the remaining balance to 100 parts by weight of water.

8. Aqueous liquid laundry detergent compositions having germicidal efficacy according to claim 7 comprising:
A) 10 - 20 parts by weight of one or more anionic surfactant compositions selected from alkylethercarboxylates and alkylethersulfonates;
B) 6 - 12 parts by weight of one or more quaternary ammonium surfactant compositions having germicidal properties;
C) 10 - 25 parts by weight of one or more nonionic surfactant compositions selected from linear and secondary alcohol alkoxylates, alkylphenol ethoxylates, alkyl polyglycosides, amine oxides, alkanolamides;
D) 2 - 5 parts by weight of one or more anionic co-surfactant compositions selected from alkylsulfates, alkylsulfonates, alkylethersulfates, alkylarylsulfonates,
alkylarylethersulfates present in a proportion not exceeding one half of the weight of the one or more quaternary ammonium surfactant compositions having germicidal properties; wherein the weight ratios of B:A are at 1:2 or greater, with the remaining balance to 100 parts by weight of water.

9. Aqueous liquid laundry detergent compositions having germicidal efficacy according to claim 7 or 8 wherein the weight ratios of B:A are at least 1.5:2.

10. A process for the simultaneous laundering and sanitization of textile fabrics comprising the process step of:
laundering said textile fabrics in an aqueous wash bath which contains an aqueous liquid laundry detergent composition according to any of claims 1 - 9.

11. The process according to claim 10 wherein the liquid laundry detergent compositions are present in the aqueous bath in a weight ratio of detergent composition:water of from 1:500 - 1:330.
### A. CLASSIFICATION OF SUBJECT MATTER

| IPC 6 | C11D1/86 | C11D3/00 |

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

### B. FIELDS SEARCHED

- **Minimum documentation searched (classification system followed by classification symbols):**
  - IPC 6 C11D

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

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

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
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<td>X</td>
<td>EP 0 133 900 A (STERLING DRUG INC) 13 March 1985 see formulation C see page 13, line 13 - line 22 see claims 1-3; tables 1,2 ---</td>
<td>1,2,4,10</td>
</tr>
<tr>
<td>X</td>
<td>US 4 264 457 A (BEEKS MICHAEL J ET AL) 28 April 1981 see column 6, line 66 - line 68; claim 1 see column 3, line 41 - line 47; examples 4,6 -----</td>
<td>1,2,4,6</td>
</tr>
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### Patent family members are listed in annex.

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Date of mailing of the international search report: 04.06.97

Name and mailing address of the ISA:

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Authorized officer:

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