DETERGENT COMPOSITIONS CONTAINING PARTICULATE DEPOSITION ENHANCING AGENTS

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No Drawing. Filed Sept. 27, 1967, Ser. No. 671,117

Int. Cl. C11D 3/22, 3/48

U.S. Cl. 252—152 10 Claims

ABSTRACT OF THE DISCLOSURE

Detergent compositions containing water-insoluble particulate substances, such as antimicrobial agents, and certain cationic polymers which serve to enhance the deposition and retention of such particulate substances on surfaces washed with the detergent composition.

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is related to the earlier-filed copending application of John J. Parran, Jr., Ser. No. 476,175, filed July 30, 1965, now abandoned.

BACKGROUND OF THE INVENTION

The field of this invention is detergent compositions including shampoos (liquid and cream), laundering, hard-surface and dishwashing detergents (granular and liquid), and personal use toilet detergent bars.

Various water-insoluble particulate substances have been incorporated in detergent products for the purpose of imparting some residual property or characteristic on surfaces washed with the products. For example, shampoo compositions containing particulate antistain agents have been developed which function by deposition and retention of the particulate agent on the hair and scalp during shampooing. Sufficient quantities of the deposited particulate agents are retained after rinsing to impart some degree of residual antimicrobial activity to the washed hair and scalp. Such antistain shampoo compositions are disclosed, for example, by Karsten, Taylor and Parran in U.S. Pat. 3,236,733, granted Feb. 22, 1966.

Particulate antimicrobial substances have also been used in various laundry detergents and personal use toilet detergent bars to impart residual antimicrobial activity on the fabrics or skin surfaces washed with same. Such products are disclosed by Keller and Jordan in U.S. Patents 3,134,711, granted May 26, 1964, and 3,256,200, granted June 14, 1966.

Various other water-insoluble or sparingly soluble particulate materials such as sunscreens, fabric brighteners, and whiteners have been employed in detergent compositions and depend for their activity on particle deposition and retention on washed surfaces.

It is apparent that an effective detergent composition, properly used, will by its very nature tend to minimize retention of particulate matter on washed surfaces. Thus, only a relatively small proportion of particles present in such detergent compositions are actually retained after rinsing of the washed surface. Since the activity of antimicrobial and other particulate agents is in part a function of the quantity of particles deposited and retained on the involved surfaces, measures which enhance deposition and/or promote retention of such particles serve to reduce the quantity of the substance in the composition required to attain a given level of activity or increase the activity attainable with a given concentration of such particles.

SUMMARY OF THE INVENTION

It has now been discovered that water-soluble cationic nitrogen-containing polymers having a molecular weight within the range from about 2,000 to about 3,000,000, and having a cationic charge density (as defined hereinafter) greater than .001 in aqueous solution, enhance the deposition and retention of water-insoluble or sparingly soluble particulate substances contained in detergent compositions on surfaces washed therewith.

Although the mechanism whereby this phenomenon occurs is not fully understood, it is believed that the polymer coats or attaches itself in some way on the involved particles imparting a net positive charge thereto which increases the affinity of the particle for the generally negatively charged washed surfaces.

It is therefore an object of this invention to provide detergent compositions which have improved capacities to impart residual activity or properties to surfaces washed therewith.

It is a further object of this invention to provide improved detergent compositions containing water-insoluble or sparingly soluble particulate substances which are deposited and retained on washed surfaces.

It is yet another object of this invention to provide a method for enhancing the deposition of particulate substances from detergent compositions and the retention of such substances on surfaces washed therewith.

These and other objects will become apparent from the following detailed description of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The detergent compositions of this invention are comprised of (1) an organic surface active agent (surfactant, i.e., detergent compound); (2) at least one water-soluble cationic nitrogen-containing polymer having a molecular weight within the range from about 2,000 to about 3,000,000 and having a cationic charge density greater than .001 in aqueous solution; and (3) a water-insoluble or sparingly soluble particulate substance capable of imparting a desired residual property to a surface to which it becomes affixed.

In its process aspect, this invention is a method for enhancing the deposition and retention of particulate substances upon surfaces washed with a detergent composition containing same, comprising uniformly admixing said particulate substances with a water-soluble cationic nitrogen-containing polymer having a molecular weight within the range from about 2,000 to about 3,000,000, and having a cationic charge density greater than .001 in aqueous solution, and incorporating said mixture in a detergent base.

The cationic charge density of a polymer as that term is used herein refers to the ratio of the number of positive charges on a monomeric unit of which the polymer is comprised to the molecular weight of said monomeric unit, i.e.,

\[
\text{cationic charge density} = \frac{\text{number of positive charges}}{\text{monomeric unit molecular weight}}
\]

The cationic charge density multiplied by the polymer molecular weight determines the number of positively charged active sites on a given polymer chain.

Organic surfactants which can be used in the compositions of this invention are anionic, ampholytic, polar nonionic, nonionic, zwitterionic or cationic. The surfactant can comprise from about 2% to about 95% by weight of the total composition. Anionic organic surfactants are generally preferred for the purposes of this invention. Suitable anionic surfactants include the water-soluble salts of organic sulfuric reaction products having in their mo-
 Specific operable amphoteric surfactants include the disodium salt of lauryl-cycloimidinium-1-ethoxy-ethionic acid - 2 - ethionic acid, dodecyl beta-alanine, and the inner salt of 2-trimethylamino lauric acid. As zwitterionics, the substituted betaines such as alkyl dimethyl ammonium acetates wherein the alkyl radical contains from about 12 to about 18 carbon atoms can also be used. Several examples of this class of zwitterionic surfactants are set forth in Canadian Pat. 696,355, granted Oct. 20, 1964.

Especially preferred shampoo compositions in accordance with this invention will contain a non-soap anionic organic surfactant at a concentration of from about 8% to about 30% by weight of the total composition.

Although nonionic and cationic surfactants are not preferred for the purposes of this invention they can nevertheless be used without substantial loss of the advantageous effects of the cationic polymers on deposition and retention of particulate matter on washed surfaces. Nonionic surfactants may be described as compounds produced by the condensation of alkylen oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic or alkyl aromatic in nature. As those skilled in the art are well aware, the length of the hydrophilic or polyoxyalkylene radical required for condensation with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. For example, a well known class of nonionics is made available on the market under the tradename of “Pluronic.” These compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule, of course, exhibits water insolubility. The molecular weight of this portion is of the order of 950 to 4,000. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole. Liquid products are obtained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Suitable nonionics also include the polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having about 6 to 12 carbon atoms, either straight chain or branch chain, in the alkyl group with ethylene oxide in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octane, or none, for example.

Other suitable nonionics may be derived by the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. Here again, a series of compounds may be produced, depending on the desired balance between hydrophobic and hydrophilic elements. For example, compounds (molecular weight from about 5,000 to about 11,000) of about 40% to 80% poloxylxylene content and resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2,500 to 3,000, are satisfactory.

Further satisfactory nonionics include the condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, either straight chain or branch chain, with ethylene oxide, an example being a coconut alcohol/ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

Cationic surfactants which can be used in the compositions of this invention include dstearyl dimethyl ammonium chloride, coconut alkyl dimethyl benzyl ammonium chloride, coconut alkyl dimethyl benzyl ammonium chlo-
ride, diaceton alkyl dimethyl ammonium chloride, cetyl pyridinium chloride, and cetyl trimethyl ammonium bromide.

As hereinbefore indicated, the compositions of this invention contain as an essential component a water-soluble cationic nitrogen-containing polymer having a molecular weight within the range from about 2,000 to about 3,000,000 and a cationic charge density greater than .001 in aqueous solution.

Operable cationic polymers for the purpose of this invention include polyethylenimine or alkoxylated polyethylenimine polymers. It is believed that the structural formula of the backbone of polyethylenimine is:

\[
\text{HN-CH}_{2}\text{-CH}(\text{CH}_{2}\text{CH}-\text{NH})_{x}\text{-CH}_{2}\text{-CH} \]

wherein \( x \) represents a whole number of sufficient magnitude to yield a polymer of molecular weight greater than about 2,000. Branch chains occur along the polymeric backbone and the relative proportions of primary, secondary and tertiary amino groups present in the polymer will vary, depending on the manner of preparation. The distribution of amino groups in a typical polyethylenimine is approximately as follows:

- \( -\text{CH}-\text{CH}-\text{NH}_{2} \) 30%
- \( -\text{CH}-\text{CH}-\text{NH} \) 40%
- \( -\text{CH}-\text{CH}-\text{N} \) 30%

The polyethylenimine is characterized herein in terms of molecular weight. Such polymers can be prepared, for example, by polymerizing ethylenimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods are described in U.S. Pat. Nos. 2,182,306, Ulrich et al., granted Dec. 5, 1939; 3,033,746, Mayle et al., granted May 8, 1962; 2,208,095, Esslemann et al., granted July 16, 1940; 2,806,839, Crowther, granted Sept. 17, 1957; and 2,535,696, Wilson, granted May 21, 1951. Polyethylenimine has a cationic charge density of .004 in aqueous solution at pH 7.0.

Similarly, alkoxylated polyethylenimine can be prepared, for example, by reacting one part by weight ethylene oxide or propylene oxide with one part by weight of polyethylenimine prepared as described above and having a molecular weight greater than about 2,000. Preferably, the weight ratio of polyethylenimine to alkylene oxide is at least about 1:1. If this ratio is less than about 1:4 the cationic charge density of the polymer in aqueous solution will not be greater than .001 as is required for the purpose of this invention. A preferred ethoxylated polyethylenimine has a molecular weight of about 80,000 to 120,000 and a cationic charge density of .004 in aqueous solution at pH 7.0.

Yet another class of water-soluble cationic nitrogen-containing polymers which can be used in the practice of this invention are those in which at least 30 mole percent of the molecular structure is composed of monomeric units containing one or more quaternary ammonium groups and any balance of which is comprised of non-quaternized polymeric units derived from monooethylenically unsaturated monomeric groups. The degree of quaternization must be sufficient to provide a cationic charge density greater than about .001. Such polymers include, for example, quaternized polyvinylmidozole, quaternized poly(dimethyaminoethyl)acrylate), quaternized poly(diallyldimethylammonium chloride) and others disclosed by Lang in U.S. Pat. 3,313,734, granted April 11, 1967, all having molecular weights within the range from about 2,000 to about 3,000,000.

Still other types of water-soluble cationic polymers useful herein are the following:

(1) Water-soluble quaternary nitrogen-substituted cellulose ethier derivatives, such as the polymer formed by reacting a hydroxyethylcellulose (having a degree of substitution with hydroxethyl groups of 1.3) with the reaction product of 0.7 mole of epichlorohydrin and 0.7 mole of trimethylamine, per substituted hydroxyglycoside unit thereof, said polymer having a cationic charge density of .002 and a molecular weight within the range from about 200,000 to 230,000. This polymer has the structural formula:

\[
\text{HEC-CH} \equiv \text{CH-CH-N} \equiv \text{N} \equiv \text{(CH}_{2}\text{O)}_{x} \equiv \text{OH}
\]

Hydroxyethylcellulose is, of course, comprised of hydroxethyl-substituted hydroxyglycoside units with varying degrees of hydroxethyl substitution. This material is prepared by reacting alkaline cellulose with ethylene oxide as is more fully described by Gloor et al., Ind. Eng. Chem., 42:2150 (1950). The extent of substitution with the quaternary nitrogen-containing group must be sufficient to provide a cationic charge density greater than .001, and the molecular weight of the substituted hydroxyethylcellulose polymer must be within the range from about 2,000 to 3,000,000.

The preferred cellulose ether derivative from which the quaternary ammonium-substituted hydroxyglycoside polymers described above are prepared include those which are water-soluble nonionic lower alkyd or hydroxyalkyl substituted. Such derivatives include methylcellulose, ethylcellulose, and hydroxyethylcellulose.

A particularly efficacious quaternary ammonium-substituted cellulose ether derivative for the purpose of this invention is available from Union Carbide under the code name JR–1L. This polymer has a molecular weight within the range from 100,000 to 1,000,000 and a cationic charge density of .005. Polymer JA–1L is a cationic cellulose ether having the structure:

\[
[R \equiv \text{CH} \equiv \text{CH} \equiv \text{C} \equiv \text{N} \equiv \text{R} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH} \equiv \text{NH} \equiv \text{R}]
\]

wherein \( R \) is a residue of an anhydroglycoside unit, wherein \( Y \) is an integer from 50 to 20,000 and wherein each \( R \) individually represents a substituent of the general formula:

\[
-(\text{C}_{3}\text{H}_{6}\text{O})_{n} \equiv \text{(CH}_{2}\text{O})_{m} \equiv \text{H}
\]

\[
\text{CH}_{2}\text{OH}
\]

\[
\text{CH}_{2}\equiv\text{CH} \equiv \text{C} \equiv \text{N} \equiv \text{R}
\]

wherein \( m \) is an integer from 0 to 10, \( n \) is an integer from 0 to 3, and \( p \) is an integer from 0 to 10. The average values per hydroxyglycoside unit are: \( n \) from 0.35 to 0.45 and the sum of \( m + p \) is from 1 to 2.

(2) Water-soluble linear polyamines available from The Rohm & Haas Company under the trade name "Primafluc C–3." This polymer has a molecular weight within the range from about 30,000 to 80,000 and a cationic charge density in aqueous solution at pH 7.0 greater than .001, and contains at least 50 mole percent of units of the formula

\[
\text{N} \equiv \text{R} \equiv \text{CH}_{2} \equiv \text{CH} \equiv \text{C} \equiv \text{N} \equiv \text{R}
\]

wherein \( A \) is a \( (C_{3}-C_{5}) \)-alkylene group having at least 2 carbon atoms extending in a chain between the adjoined N atoms, and \( R \) and \( R' \) are each hydrogen or methyl. This and related polymers operable herein as well as a method for their preparation are fully described in U.S. Pat. 3,288,707, granted Nov. 29, 1966.

(3) The water-soluble polymers of tetraethylene pentamine and epichlorohydrin commercially available from...
the Nalco Chemical Company under the trade names Nalco 600 and Nalcolyte 605. Such polymers have the formula:

\[
\text{H} \left[ \text{NH} \left( \text{CH}_2\text{CH}_2\text{NH}_2 \right) \left( \text{CH}_2\text{CH}_2\text{NH}_2 \right) \text{NH} \left( \text{CH}_2\text{CH}_2\text{NH}_2 \right) \right] \text{N} \left( \text{CH}_2\text{CH}_2\text{NH} \right) \text{NH}_2
\]

wherein \( x \) is an integer of sufficient magnitude to yield a polymer having a viscosity at 74° F. of 21 to 42 centipoise. These polymers have a molecular weight within the range from about 2,000 to 3,000,000, and a cationic charge density greater than .001 in aqueous solution at pH 7.0.

(4) Coagulant Aid #225 commercially from The Calgon Company. This product is a water-soluble nitrogen-containing polymer having a molecular weight within the range from about 30,000 to 3,000,000 and a cationic charge density greater than .001 in aqueous solution at pH 7.0. Coagulant Aid #225 is a condensation polyethylene amine extended with chlorophosphoryl and prepared as follows: A 1-liter flask was fitted with a stirrer, reflux condenser, thermometer, and an addition funnel, and 232 g. of “Amine E–100” was introduced. This is a product of Dow Chemical Company containing about 10% tetraethylene pentamine, about 40% pentaethylene hexamine, about 20% cyclized polyalkylene, polyamines, and about 10% polyalkylene polyamines having chains greater than pentaethylene (mostly hexaethylene pentamine and heptaoctylamine).

250 g. of water was added and the solution heated to reflux. To the solution was added, at a suitable rate, 60 g. of 0.6 mole, of ethylene dichloride. The addition rate of the EDC was carefully controlled so that a minimum of unreacted EDC excess was maintained. On completion of EDC addition the reaction mixture was held at 100°–110° for one hour. The reaction product at this point was a “prepolymer” as above described.

The “prepolymer” formed as above was heated to 80° C., and the addition of 37.5 g., 0.4 mole, of chlorohydrin (ECH) was begun. The temperature was allowed to rise no higher than 90° during the addition. On completion of the addition, the reaction mixture was held at 100° for 30 minutes. The resulting polymer was a 57.5% active solution with a viscosity of 2,000 cps.

(5) Coagulant Polymer #261 commercially available from The Calgon Company. This product is a water-soluble nitrogen-containing polymer having a molecular weight within the range from about 30,000 to 3,000,000 and a cationic charge density greater than .001 in aqueous solution at pH 7.0. Conductive Polymer #261 is poly(N,N-dimethyl-3,5-methylene piperdinium chloride), average molecular weight 50,000.

If the molecular weight of the cationic polymers employed herein is less than about 2,000, no substantial enhancement of particle deposition occurs. Best results are obtained with polymers having a molecular weight within the range from about 30,000 to about 1,000,000.

The cationic polymer can be employed herein at a concentration within the range from about 0.1% to about 10.0% by weight, preferably from about 0.25% to about 4.0% by weight.

Particulate substances which can be used in the detergent compositions of this invention preferably have an average particle diameter within the range from about 0.2 to about 50 microns and include water-insoluble or sparingly soluble anti-microbial agents, sunscreens, fabric brighteners, and various substances which create a favorable skin feel after washing. These particulate substances depend on deposition and retention on washed surfaces to produce their intended effect.

Particulate antimicrobial substances, the deposition and retention of which is enhanced by the cationic polymers described herein include, for example, (a) substituted salicylanilides having the general formula:

\[
Y \text{OH} \text{NH} \text{K} \text{X} \text{Y} \text{X} \text{Y}
\]

wherein \( Y \) is hydrogen, halogen, or trifluoromethyl; \( X \) is hydrogen, halogen, or trifluoromethyl; \( X_1 \) is halogen or ethoxy; \( X_2 \) is hydrogen or halogen; (c) substituted bisphenols having the general structural formula:

\[
\text{OH} \text{OE} \text{Xn} \text{Xn}
\]

wherein \( X \) is a halogen and \( n \) is an integer from 1 to 3, \( R \) is an alkylene radical having from 1 to 4 carbon atoms or divalent sulfur; and (d) mixtures of (a), (b), and (c).

The salicylanilides encompassed by (a) include 3,4',5-tribromosalicylanilide; 5 - bromosalicyl-3,5-difluoromethyl anilide; 5 - chlorosalicyl -3,5-difluoromethyl anilide; 3,5 - dichlorosalicyl-3,4-dichloroanilide; and 5-chlorosalicyl - 3 - trifluoromethyl-4-chloroanilide.

These and other salicylanilides useful herein are disclosed by Bindsley and Model in U.S. Pat. 2,703,332, granted Mar. 1, 1955.

The preferred carbanilides of (b) above include 3,4,4' -trichlorocarbanilide; 3 - trifluoromethyl-4,4'-dichlorocarbanilide; 3 - trifluoromethyl-3,4' ,4' - trichlorocarbanilide; 3,3',bis(trifluoromethyl) - 4 - ethoxy - 4' - chlorocarbanilide; and 3,5 - bis(trifluoromethyl) - 4 - chlorocarbanilide.

The compounds in (c) above in which \( R \) represents an alkylene radical are more fully described in U.S. Letters Patent 2,555,077, granted Dec. 26, 1950. The preferred compounds of the general class of (c) above are those which are symmetrical in structural configuration, such as bis(5 - chloro-2-hydroxyphenyl) methane, bis(3,5-dichloro-2-hydroxyphenyl) methane, bis(3,5 - 6 - chloro-2-hydroxyphenyl) methane, bis(3,5 - dichloro - 2-hydroxyphenyl) sulide, bis(3,5,6-trichloro-2-hydroxyphenyl) sulide, and mixtures thereof.

Additional antimicrobial compounds suitable for use in this invention are N-trichloromethylmercapto-4-cyclohexene-1,2-dicarboximide and N-(1,1,2,2-tetrachloroethylsulfenyl)-di-4-cyclohexene-1,2-dicarboximide.

Preferred antibacterial agents employed herein are salts of 2-pyridinedithiol-1-oxide which has the following structural formula in tautomeric form, the sulfur being attached to the number 2 position of the pyridine ring:

\[
\text{N} \text{SH} \quad \text{OH}
\]

2-pyridinedithiol-1-oxide

Heavy metal salts of the above compounds are sparingly soluble and have a high degree of antibacterial activity. Preferred salts include zinc, cadmium, tin and zirconium 2-pyridinedithiol-1-oxide.

Combinations of the above-described antibacterial substances can also be used to advantage. Such combinations are illustrated in U.S. Pat. 3,281,366, granted Oct. 25, 1966.

These antimicrobial compounds are used in particulate form, with average particle sizes ranging from about 0.2 to about 30 microns. The quantity of antimicrobial agent employed can range from about 0.1% to about 10% and preferably from about 0.5% to about 2.0% by weight.
Preferred antimicrobial detergent compositions in accordance with this invention especially adapted to washing hair and scalp are comprised of from about 10% to about 35% by weight of at least one non-soap anionic, polar nonionic, ampholytic or zwitterionic surfactant; from about 0.25% to about 2.0% by weight of a water-soluble cationic nitrogen-containing polymer having a cationic charge density greater than about .001 and having an average molecular weight within the range from about 30,000 to about 1,000,000; and from about 0.5% to about 2.0% by weight of a water-soluble or sparingly soluble antimicrobial substance in particulate form; and the balance substantially water.

Detergent compositions in accordance with this invention can be prepared by methods well known in the art; however, as before indicated, it has been found that especially good results are obtained when the cationic polymer and particulate substances are uniformly admixed in an initial step, with the mixture then being added to an aqueous solution or slurry of the surfactant. If the polymeric component and particulate substance are added to the surfactant separately, the degree of deposition and retention enhancement effected by the polymer will be somewhat less.

Each of the aforementioned components can be incorporated in an aqueous vehicle which may, in addition, include such materials as organic solvents, such as ethanol; thickeners, such as carboxymethylcellulose, magnesium-alumina silicate, hydroxyethylcellulose; perfumes; sequestering agents, such as tetrasodium ethylenediaminetetraacetate; and opacifiers, such as zinc stearate or magnesium stearate, which are useful in enhancing the appearance or cosmetic properties of the product.

Coconut acyl mono- or diethanol amides as sued boosters, and strongly ionizing salts such as sodium chloride and sodium sulfate may be used to advantage.

Toilet detergent or soap bars containing a cationic polymer and particulate substance according to this invention can be based on soap or non-soap synthetic detergents and can also contain a variety of adjuncts to improve product performance or appearance. Examples of such adjuncts include free fatty acids or cold cream to improve cosmetic properties, perfumes, inorganic salts to improve bar firmness, insoluble soap to improve bar texture, coloring matter and the like.

In the case of heavy-duty laundering detergents containing the cationic polymers and particulate substances in accordance with this invention, such detergents can be in granular, flake, liquid or tablet form and can contain, in addition to detergent and inorganic or organic builder compounds such as those disclosed by Dichi in U.S. Pat. 3,159,581, granted Dec. 1, 1964), minor amounts of adjunctive materials which make the product more effective or more attractive. The following are mentioned by way of example. A tarnish inhibitor such as benzo-triazole or ethylenebithiourea may also be added in amounts up to about 2%. Fluorescers, perfume and color while not essential in the compositions of the invention, can be added in amounts up to about 1%. An alkaline material or alkali, such as sodium hydroxide or potassium hydroxide, can be added in minor amounts as supplementary pH adjusters when needed. There can also be mentioned as suitable additives, brightening agents, sodium sulfate, and sodium carbonate.

Corrosion inhibitors generally are also added. Soluble silicates are highly effective inhibitors and can be added to certain formulas of this invention at levels of from about 3% to about 8%. Alkali metal, preferably potassium or sodium, silicates having a weight ratio of SiO2:Na2O of from 1.0:1 to 2.8:1 can advantageously be used. M in this ratio refers to sodium or potassium. A sodium silicate having a ratio of SiO2:Na2O of about 1.6:1 to 2.45:1 is especially preferred for economy and effectiveness.

In the embodiment of this invention which provides for a built liquid detergent, a hydrotropic agent at times is found desirable. Suitable hydrotropes are water-soluble alkalai metal salts of toluenesulfonate, benzenesulfonate, and xylenesulfonate. The preferred hydrotropes are the potassium or sodium toluenesulfonates. The hydrotrope salt can be added, if desired, at levels of 1% to about 12%. While a hydrotrope will not ordinarily be found necessary, it can be added if so desired, for any reason including the preparation of a product which retains its homogeneity at a low temperature.

The term “coconut alkyl” as used herein and in the following examples refers to alkyl groups which are derived from the middle cut of coconut alcohol having the following approximate chain length distribution: 2% C10, 66% C12, 23% C14, and 9% C16. Other compounds designated as coconut oil derived are based on unfraccionated coconut oil or its fatty acids.

The following examples are illustrative of several detergent compositions of this invention.

EXAMPLE I

A shampoo composition was prepared having the following composition:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium coconut alkyl glycerol ether sulfonate (about 23% diglycerol and the balance substantially monoglycerol)</td>
<td>25.0</td>
</tr>
<tr>
<td>Sorbitol tallow alkyl glycerol ether sulfonate (about 23% diglycerol and the balance substantially monoglycerol; the tallow alkyls correspond to those of substantially saturated tallow alcohols and contain approximately 2% C16, 32% C18 and 66% C18)</td>
<td>3.0</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>6.7</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>3.3</td>
</tr>
<tr>
<td>Sodium N-lauroyl sarcosinate</td>
<td>3.8</td>
</tr>
<tr>
<td>N-coconut acyl sarcosine</td>
<td>1.2</td>
</tr>
<tr>
<td>Diethanolamide of coconut fatty acids</td>
<td>2.0</td>
</tr>
<tr>
<td>Acetylated lanolin</td>
<td>1.0</td>
</tr>
<tr>
<td>Parfum</td>
<td>0.45</td>
</tr>
<tr>
<td>Zinc 2-pyridinethiol-1-oxide</td>
<td>2.0</td>
</tr>
<tr>
<td>Polyethyleneimine /ethylene oxide reaction product (weight ratio 1:1, molecular weight 80,000-120,000 and cationic charge density of .004 in aqueous solution at pH 7.0)</td>
<td>0.5</td>
</tr>
<tr>
<td>Water</td>
<td>Balance</td>
</tr>
</tbody>
</table>

2 Average particle size 2 microns.
3 Molecular weight 40,000-60,000.

The zinc pyridinethione and ethoxyated polyethyleneimine were uniformly admixed and added to and uniformly mixed with the balance of the components. The resulting product was a stable cream having excellent cosmetic and antandanduff properties. The degree of deposition of zinc pyridinethione from this composition was much greater than the degree of deposition attained with a similarly formulated product which contained no cationic polymer. Residual antimicrobial activity of surfaces washed with this composition is markedly better as compared to surfaces washed with a control product without polymer.

Compositions identical to the composition of Example I, but containing 5 micron diameter particles of 3,4',4'-trichlorocarbanilide; 3,4',5 - trichloromiscycloillinidine; 4',4'-dichloro - 3 - (trifuoromethyl)carbonilide; and bis(2-hydroxy - 3,5,6 - trichlorophenyl)methane, and 6.5 micron particles of N - trichloromethylmercupato - 4 - cy clohexene - 1,2 - dicarboximide and N - (1,1,2,2 - tetra chlorothiylsulfonyl) - cis - Δ - 4 - cyclohexene - 1,2 - dicarboximide, respectively, in place of zinc - pyridinethiol-1-oxide are prepared and compared with control compositions containing these same compounds without cationic polymer. The degree of deposition and retention of these compounds in the presence of the cationic poly-
mer is found to be substantially greater than is attached with the control compositions, and a corresponding increase in residual antimicrobial activity is observed on surfaces washed therewith.

**EXAMPLE II**
Another antimicrobial detergent formulation in accordance with this invention is formulated as follows:

<table>
<thead>
<tr>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethanolamine coconut alkyl sulfate</td>
</tr>
<tr>
<td>Coconut alkyl dimethyl amine oxide</td>
</tr>
<tr>
<td>Monoethanol amide of coconut fatty acids</td>
</tr>
<tr>
<td>Ethanol</td>
</tr>
<tr>
<td>Polyethenimine</td>
</tr>
<tr>
<td>Cadmium 2-pyridinedithiol-1-oxide (average particle size 3.0 microns)</td>
</tr>
</tbody>
</table>

Water, NaOH to adjust pH 8.5, balance

A water-soluble cationic polymer having a molecular weight of 50,000 to 100,000, a cationic charge density of .004 in aqueous solution at pH 7.0, and a viscosity of 3.5 centipoise (absolute viscosity) in a 1% by weight aqueous solution measured with an Ostwald viscometer at 100°F.

This composition has excellent antimicrobial properties and in usage imparts sustained antimicrobial activity to surfaces washed therewith. The amine oxide can be replaced, in whole or in part, with coconut beta-iminodipropionate, disodium lauroylglycineiminimidum - 1 - ethoxy ethionic acid-2-ethionic acid, disodium; or dodecyl amoniumacetate, with substantially equivalent results.

Further compositions in accordance with this invention are as follows.

**EXAMPLE III**
A liquid detergent composition suitable for use as an antidandruff shampoo is formulated as follows:

<table>
<thead>
<tr>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triethanolamine coconut alkyl sulfate</td>
</tr>
<tr>
<td>Monoethanol amide of coconut fatty acid</td>
</tr>
<tr>
<td>Magnesium aluminum silicate</td>
</tr>
<tr>
<td>Dye</td>
</tr>
<tr>
<td>Perfume</td>
</tr>
<tr>
<td>Zinc 2-pyridinedithiol-1-oxide</td>
</tr>
<tr>
<td>Polyethenimine</td>
</tr>
</tbody>
</table>

This composition provides a substantial degree of anti-dandruff effect when used in the customary fashion. The degree of deposition and retention of particulate zinc pyridinedithione on the hair and scalp after shampooing with this product is substantially greater than is attained with a similar composition without the polyethenimine/ethylene oxide reaction product.

Each of the above compositions impart a residual antimicrobial activity to surfaces washed therein which is substantially greater than is attainable with similar compositions without the polymeric component.

<table>
<thead>
<tr>
<th>Table 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition: Average degree of deposition</td>
</tr>
<tr>
<td>Control</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
</tr>
</tbody>
</table>
It can be seen from the above results that deposition and retention of zinc 2-pyridinethiol-1-oxide was substantially greater in a detergent composition which contained 0.5% of polyethylenimine as compared to the control composition which contained the same amount of zinc 2-pyridinethiol-1-oxide without polymer. Similarly, composition B which contained only 1% of zinc 2-pyridinethiol-1-oxide yielded a somewhat higher degree of deposition and retention than the control composition which contained twice as much of this salt, but no polymer.

In like manner the relative deposition of zinc 2-pyridinethiol-1-oxide from a detergent composition containing various concentrations of ethoxylated polyethyleneimine was demonstrated as follows: The following compositions were prepared:

| TABLE 2 |
| Parts by weight |
| Composition |
| Control | C | D | E | F |
| Sodium coconut alkyl glycerol ether sulfonate 1 | 25.0 | 25.0 | 25.0 | 25.0 | 25.0 |
| Sodium tallow alkyl glycerol ether sulfonate | 3.0 | 3.0 | 3.0 | 3.0 | 3.0 |
| Sodium chloride | 0.9 | 0.9 | 0.9 | 0.9 | 0.9 |
| Sodium laurate | 25.1 | 25.1 | 25.1 | 25.1 | 25.1 |
| Sodium 8-lauroylsarcosinate | 3.8 | 3.8 | 3.8 | 3.8 | 3.8 |
| N-coconut acyl sarcosinate | 1.2 | 1.2 | 1.2 | 1.2 | 1.2 |
| Coconut sucrose | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Acellulase | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| Phosphate | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| Color | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 |
| Zinc 2-pyridinethiol-1-oxide | 2.0 | 1.0 | 0.5 | 0.5 | 0.5 |
| Polyethyleneimine/ethylene oxide reaction product | 0.1 | 1.0 | 2.0 | 2.0 | 2.0 |
| Water | | | | | Balance |

1 Same as Example I.

Each of the compositions was tested in the manner described supra, using a test composition and control composition on each of the test subjects. The results attained were as follows:

| Polymer | Test | Control |
| Test | Control |

| Polymer | Test | Control |
| Test | Control |
| RO/PBI 1 | 2.08 | 1.92 |
| Nucleosil 100 | 2.09 | 2.00 |
| Primmata C-3 | 2.08 | 2.00 |
| Primmata A | 2.08 | 2.00 |
| Complex polymer | 1.75 | 1.06 |
| JK-19 | 2.08 | 1.90 |
| PVT | 2.09 | 2.00 |
| DMAEMA 3 | 2.42 | 1.75 |
| DRAMA 4 | 2.45 | 1.72 |

Polyethylenimines as in Example I.

Polyvinylsiloxanes substantially completely quaternized with dimethyl sulfate, having a molecular weight of about 8 to 20 X 106 and a cationic charge density of 0.009.

Poly(dimethylaminoethylmethacrylate) substantially completely quaternized with methyl phosphite, having a molecular weight between 1,000 and 5,000,000 and a cationic charge density of 0.009.

Poly(dimethylaminoethylmethacrylate) substantially completely quaternized with dimethyl sulfate, having a molecular weight within the range from about 1,000 and 5,000,000 and a cationic charge density of 0.005.

It can be seen that substantial enhancement of particle deposition and retention is effected by the inclusion of representative cationic polymers in detergent formulations containing same.

**EXAMPLE XII**

An antimicrobial milled detergent bar which also constitutes a preferred embodiment of this invention is prepared in accordance with methods well known in the art and having the following composition:

<table>
<thead>
<tr>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium alkyl glycerol ether sulfonate 1</td>
</tr>
<tr>
<td>Potassium alkyl sulfate 1</td>
</tr>
<tr>
<td>Magnesium soap of 80:20 tallow: coconut fatty acids</td>
</tr>
<tr>
<td>Sodium soap of 80:20 tallow: coconut fatty acids</td>
</tr>
<tr>
<td>Inorganic salts (sodium and potassium chlorides and sulfates)</td>
</tr>
<tr>
<td>3,4,5-trisubstituted anilide</td>
</tr>
<tr>
<td>Cationic polymer 2</td>
</tr>
<tr>
<td>Water and miscellaneous</td>
</tr>
</tbody>
</table>

1 Alkyl groups derived from middle cut alcohol obtained by catalytic reduction of coconut alcohol which has a chain length distribution substantially as follows: 2% C16, 6% C18, 23% C20, and 9% C22.
2 Quaternary ammonium-substituted hydroxyethylcellulose ether formed by reacting a hydroxyethylcellulose ether (having a degree of substitution with hydroxyethyl groups of 1.5) with the product of 0.7 mole phosphorus oxychloride and 0.7 mole of trimethylamine per starch unit thereof, said polymer having a cationic charge density of 0.002 and a molecular weight within the range from about 200,000 to 230,000.

The deposition and retention of the particulate antimicrobial agent 3,4,5-trisubstituted anilide upon skin washed with the above composition is substantially greater. The rinse water used is tap water at 37°C. with a flow rate of 4 liters per minute. The slides are then allowed to dry.

The washed slides are examined microscopically at 400 diameters magnification using cross polarized filters. Deposition is graded on a 0-4 scale, no deposition being given a 0 grade, while maximum expected deposition is given a 4 grade. Grades in between vary approximately linearly with the density of deposited particles. Several areas of each slide are given grades before the average for that slide is taken to the nearest 1/4 of a deposition grade. In each test three slides for each test material are treated in random order. All grading and washing is done on a blind basis.

Detergent compositions substantially corresponding to the composition of Example I but containing 0.5% by weight of zinc 2-pyridinethiol-1-oxide and 2.0% by weight of various cationic polymers of this invention were tested against a control composition without polymer using the method described above. The following results were obtained.
than occurs with a control composition without cationic polymer.

Toilet detergent bars identical in composition to the bar described above are prepared, replacing the 3,4,5-tribromo-
mosaiclanilide with 4 micron particles of the antimicro-
bial agents 3,4,5-trichlorocarbanilide; 4,4'-dichloro-3-
(trifluoromethyl)carbanilide; bis(2-hydroxy-3,5,6-tri-
chlorophenyl)methane; and a 1:1 mixture of 4,4'-dichloro-
3-(trifluoromethyl)carbanilide and 3,4,5-tribromosalicyl-
anilide, respectively, with improved deposition and reten-
tion of the antimicrobial particles being attained in each case relative to control compositions without cationic polymer.

Additional toilet detergent bars are prepared as in Exam-
ple XII each containing one of the following cationic polymers in place of the quaternary ammonium-substituted cellulosic ether polymer employed therein:
(1) Nalcoyte 605, as hereinbefore defined.
(2) Coagulant Aid 225, as hereinbefore defined.
(3) Conductive Polymer 261, as hereinbefore defined.
(4) Polyvinylimidazole substantially completely quarter-
nized with dimethyl sulfate, having a molecular weight of 5,000, and a cationic charge density of .009.
(5) Poly(dimethylaminoethyletheracrylate) substantially completely quaternized with methyl phosphate, having a molecular weight of 1,000,000, and a cationic charge density of .006.
(6) Poly(diethylaminoethyletheracrylate) substantially completely quaternized with dimethyl sulfate, having a molecular weight of 300,000, and a cationic charge density of .005.

Each of these toilet detergent bars provides a degree of 3,4,5-tribromosalicylanilide particle deposition and reten-
tion on skin washed therewith which is substantially greater than is attained with toilet detergent control bars without such polymers.

EXAMPLE XIII
An antimicrobial granular built laundry detergent product is prepared by conventional means, having the follow-
ing composition:

<table>
<thead>
<tr>
<th>Description</th>
<th>Parts by weight</th>
</tr>
</thead>
</table>
| Sodium alkyl benzene sulfonate (the alkyl group av-
  eraging about 12 carbon atoms and being derived    | 17.5            |
| from propylene)                                 |                 |
| Sodium tripolyphosphate                         | 49.7            |
| Sodium sulfate                                  | 13.3            |
| Silicate solids                                 | 7.0             |
| 3,4,5-trichlorocarbanilide (particle size averag-
  ing 3 microns)                                | 0.5             |
| Quaternized polyvinylimidazole                  | 1.5             |

1 Polyvinylimidazole in which 80% of the vinylimidazole units are quaternized with dimethyl sulfate, having a molecular weight of 250,000 and a cationic charge density of .007.

Fabs laundersed in this product retain a substantially greater quantity of 3,4,5-trichlorocarbanilide particles than do fabrics washed in a control product formulated as above, but without the cationic polymer.

Each of the foregoing examples describe embodiments of this invention which involve antimicrobial particulate substances. As hereinbefore disclosed, the deposition and retention of other particulate substances are also en-
hanced by the cationic polymers. The following examples are illustrative of detergent compositions in accordance with this invention containing representative particulate substances which function through deposition and reten-
tion on washed surfaces.

Toilet detergent bars desirably contain a sunscreen or ultraviolet absorber which will deposit on the skin in the course of washing therewith to provide protection against harmful sun rays. Suitable particulate ultraviolet absorbers which can be incorporated in detergent bars for this purpose include, for example, 2-hydroxy-4-n-octoxy-
benzophenone, 2-hydroxy-4-methoxybenzophenone, and 2-hydroxy-4-methoxybenzophenone. These materials are insoluble particulate solids which are em-
ployed in bar soap formulations in concentrations rang-
ing from about 1% to about 5% by weight.

EXAMPLE XIV
A toilet soap bar containing an ultraviolet absorber is formulated in accordance with this invention as follows:

<table>
<thead>
<tr>
<th>Description</th>
<th>Parts by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium soap of 50:50 tallow/coconut fatty</td>
<td>73.19</td>
</tr>
<tr>
<td>acids</td>
<td></td>
</tr>
<tr>
<td>Coconut fatty acid</td>
<td>7.30</td>
</tr>
<tr>
<td>Cold cream</td>
<td>1.10</td>
</tr>
<tr>
<td>Inorganic salts (sodium chloride and sulfate</td>
<td>0.87</td>
</tr>
<tr>
<td>and silicate solids)</td>
<td></td>
</tr>
<tr>
<td>Perfume</td>
<td>1.23</td>
</tr>
<tr>
<td>2-hydroxy-4-n-octoxybenzophenone (particle size</td>
<td>2.50</td>
</tr>
<tr>
<td>10 microns)</td>
<td></td>
</tr>
<tr>
<td>Cationic polymer</td>
<td>3.00</td>
</tr>
<tr>
<td>Miscellaneous</td>
<td>0.81</td>
</tr>
<tr>
<td>Water</td>
<td>10.00</td>
</tr>
</tbody>
</table>

When used in the customary fashion, the toilet soap bar of this example effects a substantially greater degree of deposition and retention of the particulate ultraviolet absorber (2-hydroxy-4-n-octoxybenzophenone) on the washed skin surfaces than does an identical composition without polymer.

Additional toilet soap bars are prepared as above but containing 2-hydroxy-4-methoxy-2-carboxybenzophenone and 2-hydroxy-4-methoxybenzophenone, respectively, in place of 2-hydroxy-4-n-octoxybenzophenone, with sub-
stantially equivalent results.

Toilet soap bars formulated in accordance with Example XIV are prepared containing polyvinylimidazole substantially completely quaternized with dimethyl sulfate, having a molecular weight of 200,000 and a cationic charge density of .009; quaternized poly(p-dimethyl-
aminoethylstyrene) having a molecular weight of 250,000 and a cationic charge density of .007; and JR-11, a quaternary ammonium-substituted cellulose derivative supplied by Union Carbide, having a molecular weight within the range from 100,000 to 1,000,000, and a cationic charge density of .004; respectively, in place of the cationic polymer employed in that example. The resulting products are substantially equivalent to the product of Example XIV in terms of particle deposition and reten-
tion.

Other insoluble particulate substances which are desir-
ably incorporated in toilet soap or detergent bars include the so-called "skin feel enhancers." Such materials are de-
posited as particles on the skin in the course of wash-
ing and create a favorable skin "feel" after washing. Such materials include, for example, nicotine acid, talc and silic-
ocenes, such as Dow-Corning Silicone F-157. These mate-
rials are desirably incorporated in a toilet bar formula at levels of about 10% by weight.

EXAMPLE XV
A bar soap formulation as set forth in Example XIV is prepared substituting 10.2% by weight of nicotinic acid particles (average particle size 5 microns) for the 2-hydroxy-4-n-octoxybenzophenone and coconut fatty acid. The resulting composition yields a substantially greater degree of deposition and retention of nicotinic acid particles on skin washed with the bar than is attained with a bar similarly formulated but without cationic polymer. Similar results are obtained when Dow-Corning Silicone F-157 is used in place of nicotinic acid.

Various insoluble fabric whiteners or brighteners, such as fluorescent dyes and blinings, e.g., ultramarine blue, deposit as particles on fabrics washed with laundry deter-
gent products containing same. Such materials can be
used in heavy-duty laundry detergent products in concentrations up to about 1% by weight.

**EXAMPLE XVI**

A built liquid detergent formulation containing a particulate bluing material and a cationic polymer in accordance with this invention is formulated as follows:

<table>
<thead>
<tr>
<th>Percent by weight</th>
<th>3(N,N - dimethyl-N-coconutammonio)-2-hydroxypropane-1-sulfonate</th>
<th>9.00 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tergitol 12-P-12 (condensation product of 12 moles of ethylene oxide and one mole of dodecylphenol)</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>Tripotassium methylene diphosphate</td>
<td>26.00</td>
<td></td>
</tr>
<tr>
<td>Sodium silicate (SiO2:Na2O=1:6:1)</td>
<td>3.00 15</td>
<td></td>
</tr>
<tr>
<td>Potassium tetrabutylammonium</td>
<td>8.50</td>
<td></td>
</tr>
<tr>
<td>Sodium carboxymethylhydroxyethylcellulose</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>Ultramarine blue (particle size 1.8 microns)</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Cationic polymer</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>Balance</td>
<td></td>
</tr>
</tbody>
</table>

Poly(diallyldimethylammonium) substantially completely quaternized with dimethyl sulfate, having a molecular weight within the range from about 1,000 to 3,000,000 and a cationic charge density of .000.

The above composition when used to launder white fabrics in the conventional method results in the deposition and retention of substantially greater quantities of the ultramarine blue particles on the washed fabrics than occurs when a product similarly formulated but without cationic polymer is used.

Several additional detergent compositions exemplifying the invention are prepared as follows:

<table>
<thead>
<tr>
<th>Parts by weight</th>
<th>Example</th>
<th>XVII</th>
<th>XVIII</th>
<th>XIX</th>
<th>XX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium coconut alkyl glycery ether sulfonate</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
<td>25.0</td>
</tr>
<tr>
<td>Sodium tallow alkyl glycery ether sulfonate</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Sodium chlorides</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Sodium silicates</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
<td>5.3</td>
</tr>
<tr>
<td>Sodium N-laurylsucroseinate</td>
<td>3.8</td>
<td>3.8</td>
<td>3.8</td>
<td>3.8</td>
<td>3.8</td>
</tr>
<tr>
<td>N-coconut acyl sarcosines</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Dextrinamide of coconut fatty acids</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Acetylated lanolin</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Zinc 3-pyridinecarboxylate</td>
<td>4.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-Trichloromethyl[pentane-2,2-dicarboxylic acid]</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1,1,5,5-tetrahydro-2-naphthoatesulfonate)-3-carboxyl [5]</td>
<td>0.5</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-4-choloxene-1,2-dicarboxylic acid</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymer (1)</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
</tr>
<tr>
<td>Polymer (2)</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymer (3)</td>
<td>0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polymer (4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Balance</td>
</tr>
</tbody>
</table>

What is claimed is:

1. A detergent composition consisting essentially of:

   (I) from about 2% to about 95% of an organic surfactant selected from the group consisting of anionic, amphoteric, polar nonionic, nonionic, and zwitter-ionic surfactants and cationic surfactants selected from the group consisting of distearyl(dimethylammonium chloride stearyl dimethylbenzylammonium chloride, coconutoalkyl(dimethyl)ammonium chloride, dioctyl(dimethyl)ammonium chloride, cetyldimethylammonium chloride, and cetyltrimethylammonium bromide; and
   (II) from about 0.25% to about 4% of quaternary ammonium substituted cellulose derivatives having molecular weights within the range from about 2,000 to about 3,000,000 and cationic charge densities greater than 0.001 said derivatives containing as substituents groups selected from the group consisting of lower alkyds, lower hydroxy alkyds, poly-ethylene groups containing up to twenty ethoxy units, and quaternary ammonium groups having the general formula:

   \[
   \text{CH}_2\text{C}(\text{CH}_2\text{O})_{n}\text{CH}_3
   \]

   \[
   \text{N}(\text{CH}_2\text{CH})_{m}\text{Cl}
   \]

   wherein \( m \) and \( n \) is an integer from 0 to 10, \( m \) is an integer from 1 to 3, and \( p \) is an integer from 0 to 10;

   (III) from about 0.1% to about 10% of a water-insoluble or sparingly soluble particulate substance having an average diameter within the range from 0.2 to 30 microns, selected from the group consisting of:

   (A) amphoteric substances selected from the group consisting of:

   (1) substituted salicylanilides having the general formula:

   \[
   \text{X}-\text{NH}-\text{CO}-\text{Y}
   \]

   wherein \( X \) is hydrogen or halogen, and \( Y \) is hydrogen, halogen or trifluoroethyl;
   (2) substituted carbanilides having the general structural formula:

   \[
   \text{X}-\text{NH}-\text{CO}-\text{Y}
   \]

   wherein \( X \) is hydrogen, halogen, or trifluoroethyl, \( X_1 \) is halogen or ethoxy, \( X_2 \) is hydrogen or halogen;

   (3) substituted bisphenols having the general structural formula:

   \[
   \text{OH}-\text{Y}-\text{OH}
   \]

   wherein \( X \) is a halogen and \( n \) is an integer from 1 to 3, \( R \) is an alkylene radical having from 1 to 4 carbon atoms or divalent sulfur;

   (4) \( N \)-trichloromethylmercapto-4-cyclohexene-1,2-dicarboxylic acid;
   (5) \( N \)-[1,1,2,2-tetrahydroxy sulfonate]-3,4-cyclohexene-1,2-dicarboxylic acid;
   (6) heavy metal salts of 2-pyridinitol-1-oxide selected from the group consisting of zinc, cadmium, tin, and zirconium salts; and
   (7) combination thereof;
(B) ultraviolet absorbers selected from the group consisting of 2-hydroxy-4-n-octoxybenzophenone, 2-hydroxy-4-methoxy-2′-carboxybenzophenone, and 2-hydroxy-4-methoxybenzophenone; and

(C) ultramarine blue.

2. The composition of claim 1 wherein the cationic polymer is a quaternary ammonium substituted cellulose ether derivative having the formula:

\[
\begin{array}{c}
\text{R} \\
\text{O} \\
\text{O} \\
\text{R}_\text{cell}
\end{array}
\text{Y}
\]

wherein \( R_{\text{cell}} \) is the residue of an anhydroglucose unit, \( Y \) is an integer from 50 to 20,000, and each \( R \) has the general formula:

\[
\text{CH}_2\text{CH}_2\text{CHO}^{(m)}-(\text{CH}_2\text{CHO})_n-(\text{CH}_3\text{OH})_p-\text{H}
\]

\[
\text{CH}_2\text{CH}_2\text{Cl}_n \text{Cl}_l
\]

wherein \( n \) is an integer from 0 to 10, \( n \) is an integer from 0 to 10, and \( p \) is an integer from 0 to 10.

3. The composition of claim 1 wherein the cationic polymer is a quaternary ammonium-substituted cellulose ether derivative formed by reacting a hydroxyethylcellulose ether having a degree of substitution with hydroxyethyl groups of 1.3 with the reaction product of 0.7 mole of epichlorohydrin and 0.7 mole of trimethylamine per substituted anhydroglucose unit thereof.

4. The composition of claim 1 wherein the particulate substance is an antimicrobial substance.

5. The composition of claim 4 wherein the particulate substance is a heavy metal salt of 2-pyridinemethyl-1-oxide wherein said heavy metal salt is selected from the group consisting of zinc, cadmium, tin, and zirconium salts.

6. The composition of claim 5 wherein the heavy metal salt is zinc.

7. The composition of claim 2 wherein the particulate substance is an antimicrobial substance.

8. The composition of claim 7 wherein the particulate substance is a heavy metal salt of 2-pyridinemethyl-1-oxide wherein said heavy metal is selected from the group consisting of zinc, cadmium, tin, and zirconium salts.

9. The composition of claim 8 wherein the heavy metal is zinc.

10. The composition of claim 1 wherein the detergent is a water-soluble salt of a member selected from the group consisting of higher fatty acids, anionic organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 20 carbon atoms and a sulfuric or sulfonic ester radical, and acyl sarcosinates, wherein the acyl group contains from about 10 to about 18 carbon atoms.

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Leon D. Rosdol, Primary Examiner
M. Halpern, Assistant Examiner

U.S. Cl. X.R.
UNIVERS STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,580,853
Dated May 25, 1971

Inventor(s) John J. Parran, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 47, the second "amine" should be deleted.
Column 4, lines 23 and 24, the second phrase "or alkyl aromatic" should be deleted.
Column 4, line 24, "are" should read "areart."
Column 5, line 38, "Esslemann" should read "Esslemann."
Column 6, line 5, "anhydroglucose" should read "anhydroglucose."
Column 6, line 32, "particulary" should read "particulary."
Column 6, line 37, "JA-1L" should read "JA-1L."
Column 6, line 65, "-HC-C(R')-C" should read "-HC-C(R')-C."
Column 8, line 5, "HHCNH" should read "NHCNH."
Column 12, line 26, "2-pyridine-thiol-1-oxide" should read "2-pyridinethiol-1-oxide."
Column 13, line 27, "Sodium N-lauroylsarcosinate" should read "Sodium N-lauroyl sarcosinate."
Column 13, line 55, "than" should read "as."
Column 13, line 55, after "control" should read "control." "quarter-" should read "quarter-.
Column 15, line 26, "quaternized" should read "quaternized.
Column 15, line 56, "Fabris" should read "Fabrics."
Column 16, line 28, "absorber" should read "absorber.
Column 17, line 40, "Sodium N-lauroylsarcosinate" should read "Sodium N-lauroyl sarcosinate.
Column 17, line 52, "2% C{sub 16} 32% C{sub 14}" should read "2% C{sub 16} 32% C{sub 14}"

Signed and sealed this 1st day of May 1973.

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents