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3,753,916

DETERGENT COMPOSITIONS CONTAINING PARTICULATE DEPOSITION ENHANCING AGENTS

John J. Parran, Jr., Springfield Township, Hamilton County, Ohio, assignor to The Procter & Gamble Company, Cincinnati, Ohio

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5 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, and is a divisional application of applicant's copending application Ser. No. 671,117, filed Sept. 27, 1967, now Pat. No. 3,580,853.

BACKGROUND OF THE INVENTION

The field of this invention 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 antidandruff 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 antidandruff 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 Reller and Jordan in U.S. Pats. 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.

2

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 molecular structure an alkyl group containing from about

8 to about 20 carbon atoms and a sulfonic acid or sulfuric acid ester radical. Such surfactants include the sodium, potassium, and triethanolamine alkyl sulfates, especially those derived by sulfation of higher alcohols produced by reduction of tallow or coconut oil glycerides; sodium or potassium alkyl benzene sulfonates, especially those of the types described by Gunther et al. in U.S. Pat. 2,477,383, granted July 26, 1949, in which the alkyl group contains from about 9 to about 15 carbon atoms; sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols obtained from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium salts of sulfuric acid esters of the reaction product of one mole of a higher alcohol (i.e., tallow or coconut oil alcohols) and about 3 moles of ethylene oxide; and the water-soluble salts of condensation products of fatty acids with sarcosine, e.g., triethanolamine N-acyl sarcosinate, the acyl radicals being derived from coconut oil fatty acids.

Preferably, anionic organic surfactants of the high sudsing type are used for the shampoo embodiments of this invention. Thus, alkyl glyceryl ether sulfonates, N-acyl sarcosinates, and alkyl ether ethylene oxide sulfates as described above are used to special advantage. These and the foregoing surfactants can be used in the form of their sodium, potassium or lower alkanolamine (e.g., mono-, di- and triethanolamine) salts.

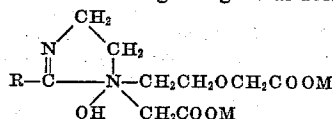
Conventional soaps are also operable anionic surfactants for the purposes of this invention. Suitable soaps include the water-soluble salts, e.g., sodium, potassium, and lower alkanolamine salts of fatty acids occurring in coconut oil, soybean oil, castor oil or tallow, or synthetically produced fatty acids may be used.

Polar nonionic surfactants can be used herein, either alone or in admixture with anionic and/or ampholytic surfactants. Surfactants of this class can serve to enhance lathering and cleaning properties of anionic detergents. By "polar nonionic surfactant" is meant a surfactant in which the hydrophilic group contains a semi-polar bond directly between two atoms, e.g., N→O, P→O, As→O, and S→O. (The arrow is the conventional representation of a semi-polar bond.) There is charge separation between the two directly bonded atoms, but the surfactant molecule bears no net charge and does not dissociate into ions.

A preferred polar nonionic surfactant for use in the present compositions is amine oxide of the general formula $R_1R_2R_3N\rightarrow O$, wherein R_1 is an alkyl, alkenyl, or monohydroxyalkyl radical having from about 10 to 16 carbon atoms, and R_2 and R_3 are each methyl, ethyl, propyl, ethanol or propanol radicals. An especially preferred amine oxide is dodecyltrimethylamine oxide.

Other operable polar nonionic surfactants are the phosphine oxides having the general formula $R_1R_2R_3P\rightarrow O$, wherein R_1 is an alkyl, alkenyl or monohydroxyalkyl radical ranging in chain length from 10 to 18 carbon atoms, and R_2 and R_3 are each alkyl or monohydroxyalkyl radicals containing from 1 to 3 carbon atoms. A preferred phosphine oxide is dodecyltrimethyl phosphine oxide.

Suitable amphoteric surfactants include the alkyl betainodipropionates, $RN(C_2H_4COOM)_2$; alkyl betainopropionates, $RN(H)C_2H_4COOM$; and long chain imidazole derivatives having the general formula:



In each of the above formulae, R is an acyclic hydrophobic group containing from about 8 to about 18 carbon atoms and M is a cation to neutralize the charge of the anion, e.g., alkali metal such as sodium and potassium and ammonium and substituted ammonium cations. Specific operable amphoteric surfactants include the di-

sodium salt of lauroyl-cycloimidinium-1-ethoxyethionic 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 alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic 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 trade name 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 nonane, for example.

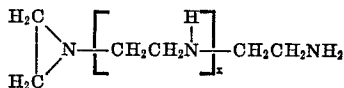
Other suitable nonionics may be derived by the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. Here again, a series of compounds may be produced, depending on the desired balance between hydrophobic and hydrophilic elements. For example, compounds (molecular weight from about 5,000 to about 11,000) of about 40% to 80% polyoxyethylene 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, 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.

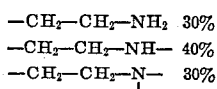
Cationic surfactants which can be used in the compositions of this invention include distearyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, coconut alkyl dimethyl benzyl ammonium chloride, dicoconut alkyl dimethyl ammonium chloride, cetyl pyridinium chloride, and cetyl trimethyl 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 alkoxyated polyethylenimine polymers. It is believed that the structural formula of the backbone of polyethylenimine is:



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:



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, Esselmann et al., granted July 16, 1940; 2,806,839, Crowther, granted Sept. 17, 1957; and 2,553,696, Wilson, granted May 21, 1951. Polyethylenimine has a cationic charge density of .004 in aqueous solution at pH 7.0.

Similarly, alkoxyated 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 1:1 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 ethoxyated 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 monoethylenically 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,

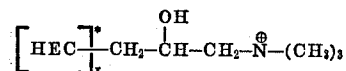
quaternized polyvinylimidazole,
quaternized poly(dimethylaminoethylmethacrylate),
quaternized poly(diethylaminoethylmethacrylate),
quaternized poly(p-dimethylaminomethylstyrene)

and others disclosed by Lang in U.S. Pat. 3,313,734, granted Apr. 11, 1967, all having molecular weights within the range from about 2,000 to 3,000,000.

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

(1) Water-soluble quaternary nitrogen-substituted cellulose ether derivatives, such as the polymer formed by

reacting a hydroxyethylcellulose (having a degree of substitution with hydroxyethyl group of 1.3) with the reaction product of 0.7 mole of epichlorohydrin and 0.7 mole of trimethylamine, per substituted anhydroglucose 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:



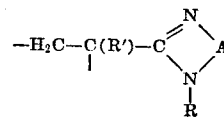
*Hydroxyethylcellulose.

Hydroxyethylcellulose is, of course, comprised of hydroxyethyl-substituted anhydroglucose units with varying degrees of hydroxyethyl 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 polymers described above are prepared include those which are water-soluble nonionic lower alkyl or hydroxyalkyl substituted. Such derivatives include methylcellulose, ethylcellulose, and hydroxyethylcellulose.

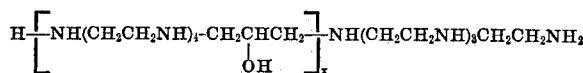
A particularly efficacious quaternary ammonium-substituted cellulose ether derivative for the purpose of this invention is available from Union Carbide under the code name JR-1L. This polymer has a molecular weight within the range from 100,000 to 1,000,000 and a cationic charge density of .005.

(2) Water-soluble linear polyamines available from The Rohm & Haas Company under the trade name "Primaflac 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



wherein A is a (C₂-C₃)-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:



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 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.

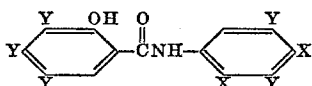
(5) Conductive Polymer #261 commercially available from The Calgon Company. This product is a water-soluble nitrogen-containing polymer having a molecular weight within the range from about 30,000 to 3,000,000 and a cationic charge density greater than .001 in aqueous solution at pH 7.0.

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.

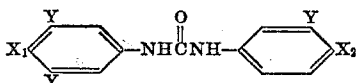
The cationic polymer can be employed herein at a concentration within the range from about 0.1% to about 10.0% by weight, preferably from about 0.25% to about 4.0% by weight.

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 antimicrobial agents, sunscreens, fabric brighteners, and various substances which creates a favorable skin feel after washing. These particulate substances depend on deposition and retention on washed surfaces to produce their intended effect.

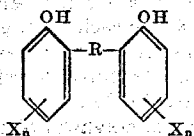
Particulate antimicrobial substances, the deposition and retention of which is enhanced by the cationic polymers described herein include, for example (a) substituted salicylanilides having the general formula:



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



wherein Y is hydrogen, halogen, or trifluoromethyl, X₁ is halogen or ethoxy, X₂ is hydrogen or halogen; (c) substituted bisphenols having the general structural formula:



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) above include

3,4',5-tribromosalicylanilide;
5-bromosalicyl-3,5-di(trifluoromethyl)anilide;
5-chlorosalicyl-3,5-di(trifluoromethyl)anilide;
3,5-dichlorosalicyl-3,4-dichloroanilide; and
5-chlorosalicyl-3-trifluoromethyl-4-chloroanilide.

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

The preferred carbanilides of (b) above include

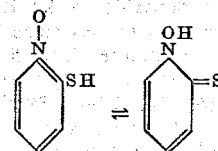
3,4,4'-trichlorocarbanilide;
3-trifluoromethyl-4,4'-dichlorocarbanilide;
3-trifluoromethyl-3',4,4'-trichlorocarbanilide;
3,3'-bis(trifluoromethyl)-4-ethoxy-4'-chlorocarbanilide; and
3,5-bis(trifluoromethyl)-4-chlorocarbanilide.

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-trichloro-2-hydroxyphenyl)methane,
bis(3,5-dichloro-2-hydroxyphenyl)sulfide,
bis(3,5,6-trichloro-2-hydroxyphenyl)sulfide, and
mixtures thereof.

Additional antimicrobial compounds suitable for use in this invention are N-trichloromethylmercapto-4-cyclohexane-1,2-dicarboximide and N-(1,1,2,2-tetrachloroethylsulfenyl)-cis-Δ⁴-cyclohexene-1,2-dicarboximide.

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



2-pyridinethiol-1-oxide 1-hydroxy-2-pyridinethione

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-pyridinethiol-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; 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 hereinbefore 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-aluminum silicate, hydroxyethylcellulose or methylcellulose; 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 suds 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 adjuvants to improve product performance or appearance. Examples of such adjuvants 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 Diehl in U.S. Pat. 3,159,581, granted Dec. 1, 1964), minor amounts of adjuvant materials which make the product more effective or more attractive. The following are mentioned by way of examples. A tarnish inhibitor such as benzotriazole or ethylenethiourea 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 $\text{SiO}_2:\text{M}_2\text{O}$ 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 $\text{SiO}_2:\text{Na}_2\text{O}$ 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 alkali 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 unfractionated 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:

	Parts by wt.
5 Sodium coconut alkyl glyceryl ether sulfonate (about 23% diglyceryl and the balance substantially monoglyceryl) -----	25.0
10 Sodium tallow alkyl glyceryl ether sulfonate (about 23% diglyceryl and the balance substantially monoglyceryl; the tallow alkyls correspond to those of substantially saturated tallow alcohols and contain approximately 2%-C ₁₄ , 32%-C ₁₆ and 66%-C ₁₈) -----	3.0
15 Sodium chloride -----	6.7
Sodium sulfate -----	3.3
Sodium N-lauroyl sarcosinate -----	3.8
N-coconut acyl sarcosine -----	1.2
Diethanolamide of coconut fatty acids -----	2.0
20 Acetylated lanolin -----	1.0
Perfume -----	0.4
Color -----	0.04
Zinc 2-pyridinethiol-1-oxide ¹ -----	2.0
25 Polyethylenimine ² /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) -----	0.5
Water -----	Balance

¹ Average particle size 2 microns.
² Molecular weight 40,000-60,000.

30 The zinc pyridinethione and ethoxylated polyethylenimine 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 antidandruff 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 greater as compared to surfaces washed with a control product without polymer.

35 Compositions identical to the composition of Example I, but containing 5 micron diameter particles of 3,4,4'-trichlorocarbanilide, 3,4',5-tribromosalicylanilide; 4,4'-dichloro-3-(trifluoromethyl)carbanilide; and bis(2-hydroxy-3,5,6-trichlorophenyl)methane, and 6.5 micron particles of N-trichloromethylmercapto-4-cyclohexene-1,2-dicarboximide and N-(1,1,2,2-tetrachloroethylsulfenyl)-cis-Δ-4-cyclohexene-1,2-dicarboximide, respectively, in place of zinc 2-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 polymer 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

40 Another antimicrobial detergent formulation in accordance with this invention is formulated as follows:

	Parts by wt.
45 Triethanolamine coconut alkyl sulfate -----	10.0
Coconut alkyl dimethyl amine oxide -----	10.0
Monoethanol amide of coconut fatty acids -----	5.0
Ethanol -----	10.0
Polyethylenimine ¹ -----	0.75
50 Cadmium 2-pyridinethiol-1-oxide (average particle size 3.0 microns) -----	0.25
Water, NaOH to adjust to pH 8.5 -----	Balance

¹ 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 2.5 centipoise (absolute viscosity) in a 1% by weight aqueous solution measured with an Ostwald Viscosimeter 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; lauroylcycloimidinium - 1 - ethoxy ethionic acid-2-ethionic acid, disodium; or dodecyl ammonioacetate, 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:

	Parts by wt.
Triethanolamine coconut alkyl sulfate -----	20.0
Monoethanol amide of coconut fatty acid -----	4.5
Magnesium aluminum silicate -----	0.9
Methylcellulose -----	0.23
Dye -----	0.008
Perfume -----	0.8
Zinc 2-pyridinethiol-1-oxide ¹ -----	1.0
Polyethylenimine ² ethylene oxide reaction product (weight ratio 4:1; molecular weight 50,000; cationic charge density .004 in aqueous solution at pH 7.0) -----	0.5
Water -----	Balance

¹ Average particle size 1.5 microns.
² Molecular weight 10,000.

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

Example	IV	V	VI	VII	VIII	IX	X	XI
Sodium coconut alkyl (ethoxy) ₂ sulfate	20				7.5			
Sodium lauroyl sarcosinate		25	5	10				
Sodium dodecyl benzene sulfonate			10					25
2-trimethylamine lauric acid			5	5			25	
Triethanolamine coconut alkyl monoglyceride sulfonate					7.5			
Potassium coconut soap					5		20	
Ethanol					10.0			5.0
Polyethylenimine ¹	2.0		2.5			0.5		1.0
Polyethylenimine 1/propylene oxide reaction product ²		1.5		2.5	0.5		2.0	
Tin 2-pyridinethiol-1-oxide (average particle size 7 microns)	1.0		0.5		2.0		0.1	
Zirconium 2-pyridinethiol-1-oxide (average particle size 4 microns)		1.0		0.5		2.5		1.5
Water								Balance

¹ (Molecular weight 10,000; cationic charge density .004 in aqueous solution at pH 7.0.)
² (Weight ratio 2:1; molecular weight 30,000; cationic charge density greater than .001 in aqueous at pH 7.0.)

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.

In Example XI, distearyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, or dicoconut alkyl dimethyl ammonium chloride can be used in place of sodium dodecyl benzene sulfonate without loss of the improved deposition and retention of zirconium 2-pyridinethiol-1-oxide particles effected by the polyethylenimine.

In Example IV, sodium coconut alkyl (ethoxy)₂ sulfate can be replaced with the condensation product of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol and having a molecular weight of 1600 or the condensation product of octyl phenol and ethylene oxide using a mole ratio of 1:15, with substantially equivalent results.

The enhanced deposition and retention of pyridinethione salts was demonstrated as follows. A control composition was formulated as in Example I, but omitting the polyethylenimine/ethylene oxide reaction product. A composition similar in formulation but containing 0.5% of polyethylenimine having a cationic charge density of .004 in aqueous solution at pH 7.0 and a molecular weight of 50,000 was prepared and designated test composition "A."

A test composition designated "B" which differed from the control composition in containing 0.5% of the polyethylenimine of composition A and 1.0% of zinc 2-pyridinethiol-1-oxide having an average particle size of 2 microns, rather than 2.0% of this latter component as in the control composition, was also prepared.

The hair of 16 female subjects was shampooed by experienced beauty shop operators who washed half of the hair and scalp of each subject with the control composition. The other half of the subject's hair and scalp was washed in the assigned test composition. The test and control compositions were used ad libitum, in quantities sufficient to provide a good lather. After lathering for 45 seconds, the hair was rinsed and the compositions were reapplied, lathered for 45 seconds and rinsed again. The hair was then dried. A sample of cornified epithelium from both the control and test halves of each subject's scalp was obtained by applying cellulose adhesive tape against the scalp. The tape was then placed on a glass slide with the adhesive in contact with the glass. The slide was examined with a polarizing microscope at approximately 400 diameters with polaroids crossed. While the cornified epithelium exhibited some degree of birefringence the highly anisotropic properties of the particulate zinc 2-pyridinethiol-1-oxide made it readily visible under such viewing conditions. The relative quantity of particulate zinc 2-pyridinethiol-1-oxide was then graded on a 0 to 4 scale, with a grade of "4" indicating heavy deposition, and "0" indicating substantially no deposition.

The following results were obtained.

TABLE 1

Composition:	Average degree of deposition
Control -----	2.3
A -----	3.4
B -----	2.6

It can be seen from the above results that deposition and retention of zinc 2-pyridinethiol-1-oxide was substantially greater from 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 1.0% 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 polyethylenimine was demonstrated as follows: The following compositions were prepared.

TABLE 2

	Parts by weight				
	Control	Composition			
		C	D	E	F
Sodium coconut alkyl glyceryl ether sulfonate ¹	25.0	25.0	25.0	25.0	25.0
Sodium tallow alkyl glyceryl ether sulfonate.....	3.0	3.0	3.0	3.0	3.0
Sodium chloride.....	6.5	6.5	6.5	6.5	6.5
Sodium sulfate.....	3.1	3.1	3.1	3.1	3.1
Sodium N-lauroyl sarcosinate.....	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 acyl diethanolamide.....	2.0	2.0	2.0	2.0	2.0
Acetylated lanolin [†]	1.0	1.0	1.0	1.0	1.0
Perfume.....	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 (average particle size 2 microns).....	2.0	1.0	0.5	1.0	0.5
Polyethylenimine/ethylene oxide reaction product ¹	0	1.0	1.0	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:

	Average degree of deposition
Composition C (8 subjects)	3.3
Control (same 8 subjects)	3.0
Composition D (8 subjects)	1.9
Control (same 8 subjects)	2.4
Composition E (4 subjects)	4.0
Control (same 4 subjects)	3.3
Composition F (8 subjects)	3.4
Control (same 8 subjects)	3.3

It can be seen that the degree of deposition attained with composition C containing only half as much zinc 2-pyridinethiol-1-oxide as the control was yet greater than the control. Composition D, which contains 1.0% polymer and only ¼ as much zinc 2-pyridinethiol-1-oxide as the control, displayed only moderately less deposition than the control. Composition E, which contains 2% polymer and only half as much zinc 2-pyridinethiol-1-oxide as the control, provides somewhat greater deposition than the control. Composition F, containing 2.0% polymer and only ¼ as much zinc 2-pyridinethiol-1-oxide as the control, provides a degree of deposition approximately equal to the control.

The degree of enhancement of particle deposition and retention in the presence of cationic polymer is also demonstrated by the Slide Particle Deposition test conducted as follows:

Dandruff scales are collected from the scalps of afflicted individuals and mounted on glass slides with a clear acrylic adhesive. The dandruff slides are covered with a clean white polyester/cotton cloth, wetted with water, and washed with a test detergent composition by brushing the cloth-covered slide with a soft toothbrush and using 20 grams of the detergent composition for 50 strokes. The slides are then rinsed for one minute with cloth in place and then for two minutes with cloth removed. 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 whole number grades before the average for that slide is taken to the nearest ¼ 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.

Polymer	Deposition		
	Test	Control	Improvement of deposition grade
EO/PEI ¹	3.08	1.92	1.16
Nalcoyte 605.....	3.08	2.00	1.08
Primafluc C-3.....	3.08	2.00	1.08
Coagulant aid 225.....	3.08	2.00	1.08
Conductive Polymer 261.....	3.08	1.75	1.33
JR-1L.....	3.08	2.00	1.08
PVI ²	3.00	2.00	1.00
DMAEMA ³	2.42	1.75	0.67
DEAEMA ⁴	2.60	1.75	0.75

¹ Ethoxylated polyethylenimine as in Example I.

² Polyvinylimidazole substantially completely quaternized with dimethyl sulfate, having a molecular weight of from 5 to 20×10⁵, and a cationic charge density of .009.

³ Poly(dimethylaminoethylmethacrylate) substantially completely quaternized with methyl phosphate, having a molecular weight between 1,000 and 5,000,000 and a cationic charge density of .006.

⁴ Poly(diethylaminoethylmethacrylate) 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 .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 toilet 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:

	Parts by wt.
Sodium alkyl glyceryl ether sulfonate ¹	8.0
Potassium alkyl sulfate ¹	20.0
Magnesium soap of 80:20 tallow:coconut fatty acids	16.7
Sodium soap of 80:20 tallow:coconut fatty acids ..	32.4
Inorganic salts (sodium and potassium chlorides and sulfates)	9.2
3,4',5-tribromosalicylanilide (average particle size 5 microns)	1.0
Cationic polymer ²	2.0
Water and miscellaneous	10.7

¹ Alkyl groups derived from middle cut of alcohols obtained by catalytic reduction of coconut alcohol which has a chain length distribution substantially as follows: 2%-C₁₀, 66%-C₁₂, 23%-C₁₄, and 9%-C₁₆.

² Quaternary ammonium-substituted hydroxyethylcellulose ether 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 epichlorohydrin and 0.7 mole of trimethylamine per substituted anhydroglucose 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.

The deposition and retention of the particulate antimicrobial agent 3,4',5-tribromosalicylanilide upon skin washed with the above composition is substantially greater 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-tribro-

mosalicylanilide with 4 micron particles of the antimicrobial agents 3,4,4'-trichlorocarbanilide; 4,4'-dichloro-3-(trifluoromethyl)carbanilide; bis(2-hydroxy-3,5,6-trichlorophenyl)methane; and a 1:1 mixture of 4,4'-dichloro-3-(trifluoromethyl)carbanilide and 3,4',5-tribromosalicylanilide, respectively, with improved deposition and retention of the antimicrobial particles being attained in each case relative to control compositions without cationic polymer.

Additional toilet detergent bars are prepared as in Example XII each containing one of the following cationic polymers in place of the quaternary ammonium-substituted cellulose ether polymer employed therein:

- (1) Nalcolyte 605, as hereinbefore defined.
- (2) Coagulant Aid 225, as hereinbefore defined.
- (3) Conductive Polymer 261, as hereinbefore defined.
- (4) Polyvinylimidazole substantially completely quaternized with dimethyl sulfate, having a molecular weight of 5,000, and a cationic charge density of .009.
- (5) Poly(dimethylaminoethylmethacrylate) substantially completely quaternized with methyl phosphate, having a molecular weight of 1,000,000, and a cationic charge density of .006.
- (6) Poly(diethylaminoethylmethacrylate) 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 retention 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 following composition:

	Parts by wt.
Sodium alkyl benzene sulfonate (the alkyl group averaging about 12 carbon atoms and being derived from polypropylene) -----	17.5
Sodium tripolyphosphate -----	49.7
Sodium sulfate -----	13.3
Silicate solids -----	7.0
3,4,4'-trichlorocarbanilide (particle size averaging 3 microns) -----	0.5
Quaternized polyvinylimidazole ¹ -----	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.

Fabrics laundered in this product retain a substantially greater quantity of 3,4,4'-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 enhanced 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 retention 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-octoxybenzophenone, 2-hydroxy-4-methoxy-2-carboxybenzophenone, and 2-hydroxy-4-methoxybenzophenone. These materials are insoluble particulate solids which are employed in bar soap formulations in concentrations ranging 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:

	Percent by wt.
5 Sodium soap of 50:50 tallow:coconut fatty acids -----	73.19
Coconut fatty acid -----	7.30
10 Cold cream -----	1.10
Inorganic salts (sodium chloride and sulfate and silicate solids) -----	0.87
Perfume -----	1.23
2-hydroxy-4-n-octoxybenzophenone (particle size 10 microns) -----	2.50
15 Cationic polymer ¹ -----	3.00
Miscellaneous -----	0.81
Water -----	10.00

¹ Same as Example XII.

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 substantially 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-dimethylaminomethylstyrene) having a molecular weight of 250,000 and a cationic charge density of .006; and JR-1L, 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 retention.

Other insoluble particulate substances which are desirably incorporated in toilet soap or detergent bars include the so-called "skin feel enhancers." Such materials are deposited as particles on the skin in the course of washing and create a favorable skin "feel" after washing. Such materials include, for example, nicotinic acid, talc and silicones, such as Dow-Corning Silicone F-157. These materials 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 bluing, e.g., ultramarine blue, deposit as particles on fabrics washed with laundry detergent 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 par-

17

ticulate bluing material and a cationic polymer in accordance with this invention is formulated as follows:

	Percent by wt.
3 - (N,N - dimethyl - N - coconutammonio)-2-hydroxy-1-sulfonate	9.00
Tergitol 12-P-12 (condensation product of 12 moles of ethylene oxide and one mole of dodecylphenol)	3.00
Tripotassium methylene diphosphonate	26.00
Sodium silicate (SiO ₂ :Na ₂ O=1.6:1)	3.00
Potassium toluenesulfonate	8.50
Sodium carboxymethylhydroxyethylcellulose	0.30
Ultramarine blue (particle size 1.8 microns)	0.15
Cationic polymer ¹	3.5
Water	Balance

¹ Poly (diethylaminoethylmethacrylate) substantially completely quarternized with dimethyl sulfate, having a molecular weight within the range from about 1,000 and 5,000,000 and a cationic charge density of .005.

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:

Example	Parts by weight			
	XVII	XVIII	XIX	XX
Sodium coconut alkyl glyceryl ether sulfonate (about 23% diglyceryl and the balance substantially monoglyceryl)	25.0	25.0	25.0	25.0
Sodium tallow alkyl glyceryl ether sulfonate (about 23% diglyceryl and the balance substantially monoglyceryl; the tallow alkyls correspond to those of substantially saturated tallow alcohols and contain approximately 2% C ₁₁ , 32% C ₁₂ , and 66% C ₁₃)	3.0	3.0	3.0	3.0
Sodium chloride	6.7	6.7	6.7	6.7
Sodium sulfate	3.3	3.3	3.3	3.3
Sodium N-lauroyl sarcosinate	3.8	3.8	3.8	3.8
N-coconut acyl sarcosine	1.2	1.2	1.2	1.2
Diethanolamide of coconut fatty acids	2.0	2.0	2.0	2.0
Acetylated lanolin	1.0	1.0	1.0	1.0
Zinc 2-pyridinethiol-1-oxide ¹	0.5			
N-trichloromethylmercapto-4-cyclohexene-1,2-dicarboximide ²		0.5	1.0	
N-(1,1,2,2-tetrachloroethylsulfenyl)-cis-Δ ⁴ -cyclohexene-1,2-dicarboximide ³				1.0
Polymer 1	1.0			
Polymer 2		1.0		
Polymer 3			2.5	
Polymer 4				4.0
Water				Balance

¹ Average particle size 2 microns.

² Average particle size 6.5 microns.

³ Average particle size 10.0 microns.

NOTE.—Polymer 1 in the above example is poly(diethylaminoethylmethacrylate) substantially completely quarternized with dimethylsulfate, having a molecular weight of 2,000,000 and a cationic charge density of .005; Polymer 2 is JR-1L; Polymer 3 is polyethylamine/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; Polymer 4 is Primafloc C-3.

Each of the above compositions provides a substantially greater degree of deposition and retention of the particulate antimicrobial agents contained therein than similar compositions formulated without these polymers.

It will be obvious to those skilled in the art that the concept of this invention is applicable to a wide variety of insoluble or sparingly soluble particulate substances in addition to those specifically described in the foregoing specification. For example, perfumes which have been adsorbed on insoluble particulate resinous substances can be deposited on skin, fabrics and other surfaces washed with detergent compositions containing same to a substantially greater degree, through the inclusion in said compositions of a cationic polymer as herein defined.

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, ampholytic, polar nonionic, nonionic, and zwitter-

18

ionic surfactants and cationic surfactants selected from the group consisting of distearyldimethylammonium chloride, stearyldimethylbenzylammonium chloride, coconutalkyldimethylbenzylammonium chloride, dicoconutalkyldimethylammonium chloride, cetylpyridinium chloride, and cetyltrimethylammonium bromide;

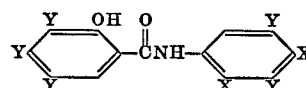
(II) from about 0.25% to about 4% of a water-soluble cationic polymer having a molecular weight within the range from about 2,000 to about 3,000,000 and a cationic charge density greater than .001, at least 30 mole percent of the molecular structure of said polymer being composed of monomers selected from the group consisting of quaternized vinylimidazole, quaternized diethylaminoethylmethacrylate, quaternized dimethylaminoethylmethacrylate, quaternized p-dimethylaminomethylstyrene monomeric units, or combinations thereof, and any balance of which is comprised of non-quaternized polymeric units derived from monoethylenically unsaturated monomeric groups;

(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:

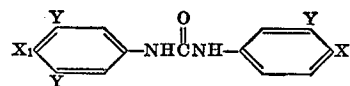
(A) antimicrobial substances selected from the group consisting of:

(1) substituted salicylanilides having the general formula:



wherein X is hydrogen or halogen, and Y is hydrogen, halogen, or trifluoromethyl;

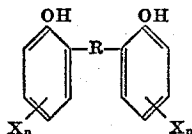
(2) substituted carbanilides having the general structural formula:



19

wherein Y is hydrogen, halogen, or trifluoromethyl, X₁ is halogen or ethoxy, X₂ is hydrogen or halogen;

- (3) substituted bisphenols having the general structural formula:



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-dicarboximide;

- (5) N - (1,1,2,2 - tetrachloroethylsulfenyl)-cis-Δ-4-cyclohexene-1,2-dicarboximide;

- (6) heavy metal salts of 2-pyridine-thiol-1-oxide selected from the group consisting of zinc, cadmium, tin, and zirconium salts; and

- (7) combinations 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.

20

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

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

4. The composition of claim 3 wherein the heavy metal salt is zinc.

5. 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 acid ester radical, and acyl sarcosinates, wherein the acyl group contains from about 10 to about 18 carbon atoms.

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MAYER WEINBLATT, Primary Examiner

P. E. WILLIS, Assistant Examiner

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,753,916 Dated August 21, 1973

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:

Col. 1, line 30, after "invention" and before "detergent" should read --- is ---.

Col. 1, line 48, "subtsances" should read --- substances ---.

Col. 4, line 65, "cahin" should read --- chain ---.

Col. 4, line 66, after "ene" and before "," should read
--- oxide ---.

Col. 5, line 21, "distribtuion" should read --- distribution ---.

Col. 5, line 74, "nitroven-substituted" should read
--- nitrogen-substituted ---.

Col. 6, line 2, "group" should read --- groups ---.

Col. 7, line 30, "creates" should read --- create ---.

Col. 8, line 66, after "form" and before "and" should read
--- ; ---.

Col. 9, line 35, "examples" should read --- example ---.

Col. 10, line 38, "asimilarly" should read --- a similarly ---.

Col. 11, line 49, after "aqueous" and before "at" should read
--- solution ---.

Signed and sealed this 7th day of May 1974.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents