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3,758,420

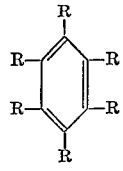
DETERGENT COMPOSITION CONTAINING A HOMOGENEOUSLY POLYFUNCTIONALLY-SUBSTITUTED AROMATIC ACID SEQUESTERING AGENT

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U.S. Cl. 252—550 2 Claims

ABSTRACT OF THE DISCLOSURE

A detergent composition is provided comprising a water-soluble organic synthetic detergent, and as a detergency aid, a sequestering agent which is a water-soluble salt of a homogeneously polyfunctionally-substituted aromatic acid compound having the formula



wherein at least three R's represent SO_3H substituents.

BACKGROUND OF THE INVENTION

Metal sequestering agents are frequently used as additives in detergent compositions of all types including household detergent compositions, e.g., laundry detergents and industrial compositions, e.g., hard-surface cleaning products. It is known, for instance, that when soaps are used in hard water, insoluble calcium and magnesium soaps are formed which detract considerably from the detergency objectives.

The surface-active and foaming properties of non-soap synthetic detergents are also adversely affected by the presence of hardness minerals, such as alkaline earth metals.

The precipitation of soap and inactivation of synthetic detergents by hardness constituents of water, especially calcium and magnesium, is a cause of considerable wastefulness in the use of such detergent ingredients. Detergent ingredients thus reacted and rendered ineffective are not available to contribute their detergency properties.

Condensed polyphosphates such as sodium tripolyphosphate and sodium pyrophosphate and nitrogen-containing compounds such as sodium nitrilotriacetate are common examples of known sequestering agents useful as ingredients in detergent compositions. As a consequence of the contribution by sequestering agents to overall improved cleaning results, such additives are referred to as "builders." In one respect, the enhanced cleaning is due to decreased adsorption of detergents and allied materials on the fabrics being washed or treated.

The phosphorus-content and nitrogen-content of such compositions may have adverse environmental effects, such as accelerated eutrophication of lakes and streams.

Eutrophication is a natural process which is vital to sustaining the life of any body of water by enabling plant organisms to grow in the water and thus provide food for fish.

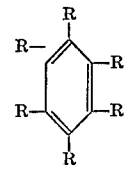
"Accelerated" or "excessive" eutrophication, however, is of timely concern. Too much plant life in lakes and streams consumes the oxygen needed by the fish and thus destroys the proper ecological balance in these bodies of water. This excessive eutrophication is caused by inordinately large amounts of nutrients going into lakes and streams. Phosphates and nitrates found in detergent

compositions are two such nutrients. These materials, however, by themselves do not cause excessive eutrophication. Other nutrients such as carbon must also be present. A combination of nutrients stimulates the growth of plant life in lakes and streams.

A primary object of the present invention is to provide phosphate- and nitrate-free detergent compositions which are effective in water solutions over a wide range of concentrations and pH's inasmuch as the conditions under which laundry is done vary widely with the individual and the locality. Another object is to provide improved heavy-duty laundry detergent compositions containing, as builders, sequestering agents selected from the novel classes of compounds described herein.

DESCRIPTION OF THE INVENTION

An improved detergent composition, according to the present invention, comprises a water-soluble organic synthetic detergent and, as a detergency aid, a sequestering agent which is a water-soluble salt of a homogeneously polyfunctionally-substituted aromatic acid compound having the formula

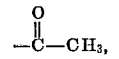


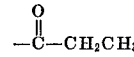
wherein each R represents
—H,
—OH,
—CH_2OH,
—CH_2CH_2OH,
—$CH_2CH_2CH_2OH$,
—$CH_2CH_2CH_2CH_2OH$,
—CH_2COOH,
—CH_2CH_2COOH,
—$CH_2CH_2CH_2COOH$,
—$CH_2CH_2CH_2CH_2COOH$,
—OCH_2COOH,
—OCH_2CH_2COOH,
—$OCH_2CH_2CH_2COOH$,
—CH_2OCH_2COOH,
—$CH_2OCH_2CH_2COOH$,
—$CH_2OCH_2CH_2CH_2COOH$,
—SO_3H,
—SCH_2COOH,
—X,
—CH_2X,
—CH_2CH_2X,
—SCH_2CH_2COOH,
—$CH(COOH)_2$,
=O

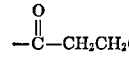
—CH_3,
—CH_2CH_3,
—$CH_2CH_2CH_3$,
—$CH_2CH_2CH_2CH_3$,
—CH_2OCH_3, or
—OR',

where X represents halogen;
wherein R' represents

—CH_2OH
—CH_2CH_2OH,
—$CH_2CH_2CH_2OH$,
—$CH_2CH_2CH_2CH_2OH$,







—CH_3,
—CH_2CH_3,
—$CH_2CH_2CH_3$,
—$CH_2CH_2CH_2CH_3$,
—CH_2OCH_3,
—$CH_2OCH_2CH_3$,
—SO_3H,
—SO_3CH_3,
—$SO_3CH_2CH_3$,

wherein at least three R substituents on the aromatic nucleus represent functional substituents and wherein all of the functional substituents from 3 to 6 inclusive in the aromatic compound are the same.

Illustrative examples of the novel class of sequestering agents of this invention are:

hexahydroxy benzene
pentahydroxy benzene
1,2,3,4-tetrahydroxy benzene
1,2,3,5-tetrahydroxy benzene
1,2,4,5-tetrahydroxy benzene
1,2,3-trihydroxy benzene
1,2,4-trihydroxy benzene
1,4,5-trihydroxy benzene
benzene-hexaacetic acid
benzene-pentaacetic acid
1,2,3,4-benzene-tetraacetic acid
1,2,3,5-benzene-tetraacetic acid
1,2,4,5-benzene-tetraacetic acid
1,2,3-benzene-triacetic acid
1,2,4-benzene-triacetic acid
1,3,5-benzene-triacetic acid
1,3,5-benzene-trisulfonic acid
hexaacetyl benzene
pentaacetyl benzene
1,2,3,4-tetraacetyl benzene
1,2,3,5-tetraacetyl benzene
1,2,4,5-tetraacetyl benzene
1,2,3-triacetyl benzene
1,2,4-triacetyl benzene
1,2,5-triacetyl benzene
hexaformyl benzene
pentaformyl benzene
1,2,3,4-tetraformyl benzene
1,2,3,5-tetraformyl benzene
1,2,4,5-tetraformyl benzene
1,2,3-triformyl benzene
1,2,4-triformyl benzene
1,3,5-triformyl benzene
hexaakis[hydroxymethyl] benzene
pentaakis[hydroxymethyl] benzene
1,2,3,4-tetraakis[hydroxymethyl] benzene
1,2,3,5-tetraakis[hydroxymethyl] benzene
1,2,4,5-tetraakis[hydroxymethyl] benzene
1,2,3-tris[hydroxymethyl] benzene
1,2,4-tris[hydroxymethyl] benzene
1,3,5-tris[hydroxymethyl] benzene
hexamethoxy benzene
pentamethoxy benzene
1,2,3,4-tetramethoxy benzene

1,2,3,5-tetramethoxy benzene
1,2,4,5-tetramethoxy benzene
1,2,3-trimethoxy benzene
1,2,4-trimethoxy benzene
1,3,5-trimethoxy benzene
hexapropoxy benzene
pentapropoxy benzene
1,2,3,4-tetraethoxy benzene
1,2,3,5-tetraethoxy benzene
1,2,4,5-tetraethoxy benzene
1,2,3-tributoxy benzene
1,2,4-tributoxy benzene
1,3,5-tributoxy benzene
hexaakis[carboxymethylether] benzene
pentaakis[carboxymethylether] benzene
1,2,3,4-tetraakis[carboxymethylether] benzene
1,2,3,5-tetraakis[carboxymethylether] benzene
1,2,4,5-tetraakis[carboxymethylether] benzene
1,2,3-tris[carboxymethylether] benzene
1,2,4-tris[carboxymethylether] benzene
1,3,5-tris[carboxymethylether] benzene
hexaakis[2-carboxyethylether] benzene
pentaakis[2-carboxyethylether] benzene
1,2,3,5-tetraakis[2-carboxyethylether] benzene
1,2,3,5-tetraakis[2-carboxyethylether] benzene
1,2,4,5-tetraakis[2-carboxyethylether] benzene
1,2,3-tris[2-carboxyethylether] benzene
1,2,4-tris[2-carboxyethylether] benzene
1,3,5-tris[2-carboxyethylether] benzene.

The process by which these sequestering agents can be prepared form no part of this invention. The discovery upon which the present invention is based is the discovery that sequestering agents coming within the class defined above and the specific examples given are effective sequestering agents which, when used in conjunction with water-soluble organic synthetic detergents, serve to significantly enhance the cleaning action of such detergents.

Of the sequesting agents described herein optimum detergency building action is achieved with those in which the functional groups are positioned near each other as illustrated for example when functional groups are attached to adjacent carbon atoms on the aromatic nucleus.

For purposes of this invention and with reference specifically to the R substituents noted above, hydrogen, the lower alkyl groups such as methyl, ethyl, propyl, butyl, isobutyl, and the halogens and halogenated-alkyl groups are non-functional substituents.

The amount of sequestering agent required to aid in the detergency varies widely depending on many circumstances including the specific sequestrant's properties, the detergent employed, the hardness content of the water, the soil load and the nature of the substrate being washed or treated, and the like. In any event, an effective or sufficient amount is used, and this implies that a sufficient amount of sequestrant is used to render the water suitable for its intended purposes. This may be juged by various means, such as soap titration, observation of the clarity of the solution, or by a practical trial of the softened water for its intended purpose. A complete softening, although sometimes desirable, is in many cases not necessary.

In preparing built laundry detergent compositions, the proportion by weight of the detergent to the sequestering agent is in the range of 20:1 to 1:20 and preferably 10:1 to 1:10. Within these ranges, compositions are represented which are lightly built or heavily built depending on the amount of sequestrant builder used.

The compositions of this invention are effective over the broad pH range of about 6 to 12, but optimum cleaning results are achieved with ordinary alkaline detergents in the range of 8 to 12 and preferably 9 to 11. The compositions can be formulated to provide a desired pH in the ranges by proper selection of appropriate salts. Thus, for example, preferred water-soluble salts for both the detergent and sequestering agent, are alkali metal salts

such as sodium, potassium, lithium and ammonium or alkyl-substituted ammonium, e.g. triethanol ammonium. Sodium and potassium are preferred water-soluble cations.

Depending on the pH of the desired solution, the salts are partially or fully neutralized.

The detergent compositions can be prepared as solid (granular, tablet, powder) or liquid (aqueous or non-aqueous-based) physical forms.

Any water-soluble organic synthetic detergent can be used in conjunction with the novel class of sequestering builder agents of this invention and have its detergency properties improved. The detergents include anionic, nonionic, ampholytic, and zwitterionic surface-ative agents, or mixtures of such materials. Each of these classes of detergents is illustrated by the following listed compounds:

(A) Anionic soap and non-soap synthetic detergents

This class of detergents includes ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkylolammonium salts of higher fatty acids containing from about 8 to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms. Suitable fatty acids can be obtained from natural sources such as, for instance, from plant or animal esters (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale and fish oils, grease, lard, and mixtures thereof). The fatty acids also can be synthetically prepared (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process). Resin acids are suitable such as rosin and those resin acids in tall oil. Naphthenic acids are also suitable. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soap.

This class of detergents also includes water-soluble salts, particularly the alkali metal salts of organic sulfuric reaction products having in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a sulfonic acid or sulfuric acid ester radical. (Included in the term alkyl is the alkyl portion of higher acyl radicals.) Examples of this group of synthetic detergents which form a part of the preferred built detergent compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8–C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, in straight chain or branched chain configuration, e.g., those of the type described in United States Letters Patents Nos. 2,220,099 and 2,477,-838 (especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl groups is about 13 carbon atoms abbreviated hereinafter as C_{13}LAS); sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty alcohol (e.g., tallow or coconut oil alcohols) and about 1 to 6 moles of ethylene oxide; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfate with about 1 to about 10 units of ethylene oxide per molecule and in which the alkyl radicals contain about 8 to about 12 carbon atoms.

Additional examples of anionic non-soap synthetic detergents which come within the terms of the present invention are the reaction product of fatty acids esterified with isethionic acid and neutrailzed with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other anionic synthetic detergents of this variety are set forth in United States Letters Patents 2,486,921; 2,486,922; and 2,396,278.

Still other anionic synthetic detergents include the class designated as succinamates. This class includes such surface active agents as disodium N-octadecylsulfo succinamate; tetrasodium N-(1,2-dicarboxyethyl)-N - octadecylsulfo-succinamate; diamyl ester of sodium sulfosuccinic acid; dihexyl ester of sodium sulfosuccinic acid; dioctyl ester of sodium sulfosuccinic acid.

Anionic phosphate surfactants are also useful in the present invention. These are surface active materials having substantial detergent capability in which the anionic solubilizing group connecting hydrophobic moieties is an oxy acid of phosphorus. The more common solubilizing groups, of course are —SO_4H, —SO_3H, and —CO_2H. Alkyl phosphate esters suca as $(R—O)_2PO_2H$ and $ROPO_3H_2$ in which R represents an alkyl chain containing from about 8 to about 20 carbon atoms are useful.

These esters can be modified by including in the molecule from one to about 40 alkylene oxide units, e.g., ethylene oxide units. Formulae for these modified phosphate anionic detergents are



or



in which R represents an alkyl group containing from about 8 to 20 carbon atoms, or an alkylphenyl group in which the alkyl group contains from about 8 to 20 carbon atoms, and M represents a soluble cation such as hydrogen, sodium, potassium, ammonium or substituted ammonium; and in which *n* is an integer from 1 to about 40.

A specific anionic detergent which has also been found excellent for use in the present invention is described more fully in the U.S. Patent 3,332,880 of Phillip F. Pflaumer and Adriaan Kessler, issued July 25, 1967, titled Detergent Composition. This detergent comprises by weight from about 30% to about 70% of Component A, from about 20% to about 70% of Component B, and from about 2% to about 15% of Component C, wherein:

(a) said Component A is a mixture of double-bond positional isomers of water soluble salts of alkene-1-sulfonic acids containing from about 10 to about 24 carbon atoms, said mixture of positional isomers including about 10% to about 25% of an alpha-beta unsaturated isomer, about 30% to about 70% of a beta-gamma unsaturated isomer, about 5% to about 25% of a gamma-delta unsaturated isomer, and about 5% to about 10% of a delta-epsilon unsaturated isomer;

(b) said Component B is a mixture of water soluble salts of bifunctionally-substituted sulfur-containing saturated aliphatic compounds containing from about 10 to about 24 carbon atoms, the functional units being hydroxy and sulfonate radicals with the sulfonate radical always being on the terminal carbon and the hydroxyl radical being attached to a carbon atom at least two carbon atoms removed from the terminal carbon atom, at least 90% of the hydroxy radical substitutions being in the 3, 4, and 5 positions; and

(c) said Component C is a mixture comprising from about 30–95% water soluble salts of alkene disulfonates containing from about 10 to about 24 carbon atoms, and from about 5% to about 70% water soluble salts of hydroxy disulfonates containing from about 10 to about 24 carbon atoms, said alkene disulfonates containing a sulfonate group attached to a terminal car-

bon atom and a second sulfonate group attached to an internal carbon atom not more than about siz carbon atoms removed from said terminal carbon atom, the alkene double bond being distributed between the terminal carbon atom and about the seventh carbon atom, said hydroxy disulfonates being saturated aliphatic compounds having a sulfonate radical attached to a terminal carbon, a second sulfonate group attached to an internal carbon atom not more than about six carbon atoms removed from said terminal carbon atom, and a hydroxy group attached to a carbon atom which is not more than about four carbon atoms removed from the site of attachment of said second sulfonate group.

(B) Nonionic synthetic detergents

Nonionic synthetic detergents may be broadly defined 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. The length of the hydrophilic or polyoxyalkylene radical which is condensed 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 nonionic synthetic detergents 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 which, of course, exhibits water insolubility, has a molecular weight of from about 1500 to 1800. The addition of polyoxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the product is retained up to the point where polyoxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic detergents include:

(1) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, diisobutylene, octene, or nonene, for example.

(2) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. For example, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5,000 to about 11,000 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 and 3,000, are satisfactory.

(3) The condensation product of aliphatic alcohols having from 8 to 22 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol-ethylene oxide condensate having from 5 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(4) Nonionic detergents include nonyl phenol condensed with either about 10 or about 30 moles of ethylene oxide per mole of phenol and the condensation products of coconut alcohol with an average of either about 5.5 or about 15 moles of ethylene oxide per mole of alcohol and the condensation product of about 15 moles of ethylene oxide with one mole of tridecanol.

Other examples include dodecylphenol condensed with 12 moles of ethylene oxide per mole of phenol; dinonylphenol condensed with 15 moles of ethylene oxide per mole of phenol; dodecyl mercaptan condensed with 10 moles of ethylene oxide per mole of mercaptan; bis-(N-2-hydroxyethyl) lauramid; nonyl phenol condensed with 20 moles of ethylene oxide per mole of nonyl phenol; myristyl alcohol condensed with 10 moles of ethylene oxide per mole of myristyl alcohol; lauramide condensed with 15 moles of ethylene oxide per mole of lauramide; and diiso-octylphenol condensed with 15 moles of ethylene oxide.

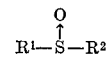
(5) A detergent having the formula $R^1R^2R^3N\rightarrow O$ (amine oxide detergent) wherein R^1 is an alkyl group containing from about 10 to about 28 carbon atoms, from 0 to about 2 hydroxy groups and from 0 to about 5 ether linkages, there being at least one moiety of R^1 which is an alkyl group containing from about 10 to about 18 carbon atoms and 0 ether linkages, and each R^2 and R^3 are selected from the group consisting of alkyl radicals and hydroxyalkyl radicals containing from 1 to about 3 carbon atoms;

Specific examples of amine oxide detergents include: dimethyldodecylamine oxide, dimethyltetradecylamine oxide, ethylmethyltetradecylamine oxide, cetyldimethylamine oxide, dimethylstearylamine oxide, cetylethylpropylamine oxide, diethyldodecylamine oxide, diethyltetradecylamine oxide, dipropyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, bis-(2-hydroxyethyl)-3 - dodecoxy - 1 - hydroxypropylamine oxide, (2-hydroxypropyl)methyltetradecylamine oxide, dimethyloleyamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, and the corresponding decyl, hexadecyl and octadecyl homologs of the above compounds.

(6) A detergent having the formula $R^1R^2R^3P\rightarrow O$ (phosphine oxide detergent) wherein R' is an alkyl group containing from about 10 to about 28 carbon atoms, from 0 to about 2 hydroxy groups and from 0 to about 5 ether linkages, there being at least one moiety of R' which is an alkyl group containing from about 10 to about 18 carbon atoms and 0 ether linkages, and each of R^2 and R^3 are selected from the group consisting of alkyl radicals and hydroxyalkyl radicals containing from 1 to about 3 carbon atoms.

Specific examples of the phosphine oxide detergents include: dimethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyltetradecylphosphine oxide, cetyldimethylphosphine oxide, dimethylstearylphosphine oxide, cetylethylpropylphosphine oxide, diethyldodecylphosphine oxide, diethyltetradecylphosphine oxide, dipropyldodecylphosphine oxide, bis-(hydroxymethyl) dodecylphosphine oxide, bis-(2-hydroxyethyl)dodecylphosphine oxide, (2 - hydroxypropyl)methyltetradecylphosphine oxide, dimethyloleylphosphine oxide, and dimethyl-(2-hydroxydodecyl)phosphine oxide and the corresponding decyl, hexadecyl, and octadecyl homologs of the above compounds.

(7) A detergent having the formula



(sulfoxide detergent) wherein R^1 is an alkyl radical containing from about 10 to about 28 carbon atoms, from 0 to about 5 ether linkages and from 0 to about 2 hydroxyl substituents at least one moiety of R^1 being an alkyl radical containing 0 ether linkages and containing from about 10 to about 18 carbon atoms, and wherein R^2 is an alkyl radical containing from 1 to 3 carbon atoms and from one to two hydroxyl groups: octadecyl methyl sulfoxide, dodecyl methyl sulfoxide, tetradecyl methyl sulfoxide, 3 - hydroxytridecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3 - hydroxy-4-dodecoxybutyl methyl sulfoxide, octadecyl 2-hydroxyethyl sulfoxide, dodecylethyl sulfoxide.

(C) Ampholytic synthetic detergents

Ampholytic synthetic detergents can be broadly described as derivatives of aliphatic or aliphatic derivatives of heterocyclic secondary and tertiary amines, in which

the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and at least one contains an anionic water-solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are

sodium 3-(dodecylamino)-propionate,
sodium 3-(dodecylamino)propane-1-sulfonate,
sodium 2-(dodecylamino)ethyl sulfate,
sodium 2-(dimethylamino)octadecanoate,
disodium 3-(N-carboxymethyl-dodecylamino)propane-1-sulfonate,
disodium 2-(oleylamino)ethyl phosphate,
disodium 3-(N-methyl-hexadecylamino)propyl-1-phosphonate,
disodium octadecyl-iminodiacetate,
sodium 1-carboxymethyl-2-undecyl-imidazole,
disodium 2-[N-(2-hydroxyethyl)octadecylamino]ethyl phospahte, and
sodium N,N-bis-(2-hydroxyethyl)-2-sulfato-3-dodecoxypropylamine.

(D) Zwitterionic synthetic detergents

Zwitterionic synthetic detergents can be broadly described as derivatives of aliphatic quaternary ammonium and phosphonium or tertiary sulfonium compounds, in which the cationic atom may be part of a heterocyclic ring, and in which the aliphatic radical may be straight chain or branched, and wherein one of the aliphatic substituents contains from about 3 to 18 carbon atoms, and at least one aliphatic substituent contains an anionic water-solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono. Examples of compounds falling within this definition are

3-(N,N-dimethyl-N-hexadecyl-ammonio)-2-hydroxypropane-1-sulfonate,
3-(N,N-dimethyl-N-hexadecylammino)-propane-1-sulfonate,
2-(N,N-dimethyl-N-dodecylammonio)acetate,
3-(N,N-dimethyl N-dodecylammonio)propionate,
2-(N,N-dimethyl-N-octadecylammonio)-ethyl sulfate,
2-(trimethylammonio)ethyl dodecyl-phosphonate,
ethyl 3-(N,N-diethyl-N-dodecylammonio)-propylphosphonate,
3-(P,P-dimethyl-P-dodecylphosphonio)-propane-1-sulfonate,
2-(S-methyl-S-tert.-hexadecyl-sulfonio)ethane-1-sulfonate,
3-(S-methyl-S-dodecylsulfonio)-propionate,
sodium 2-(N,N-dimethyl-N-dodecylammonio)ethyl phosphonate,
4-(S-methyl-S-tetradecylsulfonio)butyrate,
1-(2-hydroxyethyl)-2-undecyl-imidazolium-1-acetate,
2-(trimethylammonio)-octadecanoate, and
3-(N,N-bis-(2-hydroxyethyl)-N-octodecylammonio)-2-hydroxypropane-1-sulfonate.

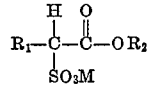
Some of these detergents are described in the following U.S. Patents: 2,129,264; 2,178,353; 2,774,786; 2,813,898; and 2,828,332.

An especially useful class of detergents which represent a preferred embodiment of the present invention when and in conjunction with the sequestering agents described above are those identified herein as "calcium insensitive" detergents. The term calcium insensitive is a functional descriptive term used to designate a class of detergents whose detergency performance properties are not as adversely effected by water hardness minerals as, for instance, soap, Besides having an inordinately high resistance to precipitation or inactivation by hard water mineral ions, these detergents are efficient in soil-removal and soil-dispersal in concentration of about 0.05% in water and, in addition, are soluble in water to at least a concentration of 0.05% at a temperature of about 80° F. to about 130° F.

Such materials include water-soluble (sodium or potassium) salts of sulfonated fatty acid esters of β-acyloxyalkane-1-sulfonic acids; β-alkyloxyalkane sulfonates; alkyl polyethylene sulfates or olefin sulfonates.

These "calcium insensitive" classes of detergents which represent a preferred embodiment of this invention are described more specifically below.

Anionic organic detergents which are calcium insensitive in the terms described above include alkali metal, ammonium and substituted-ammonium salts of esters of an α-sulfonated fatty acid in which the esters contain about 15 to about 25 carbon atoms. These detergent compounds have the following structure:



wherein R_1 is alkyl or alkenyl of about 10 to about 20 carbon atoms (forming with the two carbon atoms a fatty acid group); R_2 is alkyl of 1 to about 10 carbon atoms; and M is a salt-forming radical.

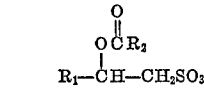
The salt-forming radical M in the hereinbefore described structural formula is a water-solubilizing cation and can be, for example, an alkali metal cation (e.g., sodium, potassium, lithium), ammonium or substituted-ammonium cation. Specific examples of substituted ammonium cations include methyl-, dimethyl-, and trimethyl- ammonium cations and quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like.

Specific examples of this class of compounds include the sodium and potassium salts of esters where R_2 is selected from methyl, ethyl, propyl, butyl, hexyl and octyl groups and the fatty acid group (R_1 plus the two carbon atoms in the structure above) is selected from lauric, myristic, palmitic, stearic, palmitoleic, oleic, linoleic acids and mixtures thereof. A preferred ester material herein is the sodium salt of the methyl ester of α-sulfonated tallow fatty acid, the term tallow indicating a carbon chain distribution approximately as follows: C_{14}—2.5%, C_{16}—28%, C_{18}—23%, palmitoleic—2%, oleic—41.5%, and linoleic—3% (the first three fatty acids listed are saturated).

Other examples of suitable salts of α-sulfonated fatty esters utilizable herein include the ammonium and tetramethylammonium salts of the hexyl, octyl, ethyl, and butyl esters of α-sulfonated tridecanoic acid; the potassium and sodium salts of the ethyl, butyl, hexyl, octyl, and decyl esters of α-sulfonated pentadecanoic acid; and the sodium and potassium salts of butyl, hexyl, octyl, and decyl esters of α-sulfonated heptadecanoic acid; and the lithium and ammonium salts of butyl, hexyl, octyl, and decyl esters of α-sulfonated nonadecanoic acid.

The salts of α-sulfonated fatty acid esters of the present invention are known compounds and are described in U.S. Pat. 3,223,645, issued Dec. 14, 1965, to Kalberg, this patent being hereby incorporated by reference.

Another specific class of suitable calcium insensitive anionic organic detergents includes salts of 2-acyloxy-alkane-1-sulfonic acids. These salts have the formula



where R_1 is alkyl of about 9 to about 23 carbon atoms (forming with the two carbon atoms in alkane group); R_2 is alkyl of 1 to about 8 carbon atoms; and M is a salt-forming radical hereinbefore described.

Specific examples of β-acyloxy-alkane-1-sulfonates, or alternatively 2-acyloxy - alkane - 1 - sulfonates, utilizable herein to provide excellent cleaning levels under house-

hold washing conditions include the sodium salt of 2-acetoxy-tridecane-1-sulfonic acid; the potassium salt of 2-propionyloxy-tetradecane-1-sulfonic acid; the lithium salt of 2-butanoyloxy-tetradecane-1-sulfonic acid; the sodium salt of 2-pentanoyloxy-pentadecane-1-sulfonic acid; the ammonium salt of 2-hexanoyloxy-hexadecane-1-sulfonic acid; the sodium salt of 2-acetoxy-hexadecane-1-sulfonic acid; the dimethylammonium salt of 2-heptanoyloxy-tridecane - 1 - sulfonic acid; the potassium salt of 2-octanoyloxy-tetradecane-1-sulfonic acid; the dimethylpiperdinium salt of 2-nonanoyloxytetradecane-1-sulfonic acid; the sodium salt of 2-acetoxyheptadecane-1-sulfonic acid; the lithium salt of 2-acetoxyoctadecane-1-sulfonic acid; the dimethylamine salt of 2-acetoxyoctadecane-1-sulfonic acid; the potassium salt of 2-acetoxy-nonadecane-1-sulfonic acid; the sodium salt of 2-acetoxy-uncosane-1-sulfonic acid; the sodium salt of 2-propionyloxy-docosane-1-sulfonic acid; and isomers thereof.

Preferred β-acyloxy-alkane-1-sulfonate salts herein are the alkali metal salts of β-acetoxy-alkane-1-sulfonic acids corresponding to the above formula wherein R_1 is an alkyl of about 14 to about 18 carbon atoms, these salts being preferred from the standpoints of their excellent cleaning properties and ready availability.

Typical examples of the above described β-acetoxy alkanesulfonates are described in the literature: Belgian Patent 650,323, issued July 9, 1963, discloses the preparation of certain 2-acyloxy alkanesulfonic acids. Similarly, U.S. Pats. 2,094,451 issued Sept. 28, 1937, to Guenther et al. and 2,086,215, issued July 6, 1937 to De Groote disclose certain salts of β-acetoxy alkanesulfonic acids. These references are hereby incorporated by reference.

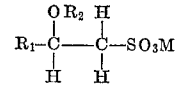
Other synthetic anionic detergents useful herein are alkyl ether sulfates. These materials have the formula $RO(C_2H_4O)_xSO_3M$ wherein R is alkyl or alkenyl of about 10 to about 20 carbon atoms, x is 1 to 30, and M is a salt-forming cation defined hereinbefore.

The alkyl ether sulfates calcium insensitive detergents of the present invention are condensation products of ethylene oxide and monohydric alcohols having about 10 to about 20 carbon atoms. Preferably, R has 14 to 18 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil or tallow, or can be synthetic. Lauryl alcohol and straight chain alcohols derived from tallow are preferred herein. Such alcohols are reacted with 1 to 30, and especially 3 to 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 3 to 6 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates of the present invention are sodium coconut alkyl ethylene glycol either sulfate; lithium tallow alkyl triethylene glycol ether sulfate; sodium tallow alkyl hexaoxyethylene sulfate; and ammonium tetradecyl octaoxyethylene sulfate.

Preferred herein for reasons of excellent cleaning properties and ready availability are the alkali metal coconut- and tallow-alkyl oxyethylene ether sulfates having an average of about 1 to about 10 oxyethylene moieties. The alkyl ether sulfates of the present invention are known compounds and are described in U.S. Pat. 3,332,876 to Walker (July 25, 1967) incorporated herein by reference.

A preferred class of calcium insensitive anionic organic detergents are the β-alkyloxy alkane sulfonates. These compounds have the following formula:



where R_1 is a straight chain alkyl group having from 10 to 20 carbon atoms, R_2 is a lower alkyl group having from 1 to 3 carbon atoms, and M is a salt-forming radical hereinbefore described.

Specific examples of β-alkyloxy alkane sulfonates or alternatively 2-alkyloxy-alkane-1-sulfonates, utilizable herein to provide superior cleaning and whitening levels under household washing conditions include

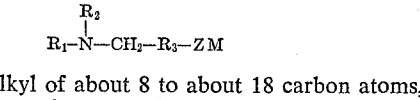
potassium β-methoxydecanesulfonate,
sodium β-methoxy-tridecanesulfonate,
potassium β-ethoxytetradecylsulfonate,
sodium β-isopropoxyhexadecylsulfonate,
lithium βt-butoxytetradecylsulfonate,
sodium β-methoxyoctadecylsulfonate, and
ammonium βn-propoxydodecylsulfonate.

Other suitable anionic detergents utilizable herein are olefin sulfonates having about 12 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which are produced by the sulfonation of α-olefin by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sultones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide may be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2, chlorinated hydrocarbon, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2, etc., when used in the gaseous form.

The α-olefins from which the olefin sulfonates are derived are mono-olefins having 12 to 24 carbon atoms, prefpreferably 14 to 16 carbon atoms. Preferably, they are straight chain olefins. Examples of suitable 1-olefins include 1-dodecene; 1-tetradecene; 1-hexadecene; 1-octadecene; 1-eicosene and 1-tetracosene.

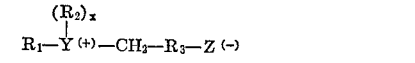
In addition to the true alkene sulfonates and a proportion of hydroxy-alkkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportions of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation.

Calcium insensitive ampholytic synthetic detergents utilizable herein have the formula



wherein R_1 is alkyl of about 8 to about 18 carbon atoms, R_2 is alkyl of 1 to about 3 carbon atoms or is hydrogen, R_3 is alkylene of 1 to about 4 carbon atoms, Z is carboxy, sulfonate, or sulfate, and M is a salt-forming cation. Examples of compounds falling within this definition are sodium 3-dodecylaminopropionate; sodium 3-dodecylaminopropane sulfonate; N-alkyltaurines such as the ones prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. Patent 3,658,072; sodium salts of N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Patent 2,438,091; and the products sold under the trade name "Miranol" and described in U.S. Patent 2,528,378.

Calcium insensitive zwitterionic synthetic detergents in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate or sulfate. A general formula for these compounds is:



wherein R_1 contains an alkyl, alkenyl, or hydroxyalkyl radical of from about 8 to about 18 carbon atoms having from 0 to about 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen and sulfur atoms; R_2 is an alkyl or monohydroxy alkyl group containing 1 to about 3 carbon atoms; x is 1 when Y is a sulfur atom and 2 when Y is a nitrogen atom, R_3 is an alkylene or hydroxy alkylene of from 1 to about 4 carbon atoms and Z is a radical se-

lected from the group consisting of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples include:

4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1-carboxylate;
5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxy-pentane-1-sulfate;
3-[P,P-diethyl-P-3,6,9-trioxatetracosanephosphonio]-2-hydroxypropane-1-phosphate;
3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropylammonio]-propane-1-phosphonate;
3-(N,N-dimethyl-N-hexadecylammonio)propane-1-sulfonate;
3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate;
4-[N,N-di(2-hydroxyethyl)-N-(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;
3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;
3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and
3-[N,N-di(3-hydroxypropyl)-N-hexadecyl ammonio]-2-hydroxypentane-1-sulfonate.

Examples of compounds falling within this definition are 3 - (N,N - dimethyl-N-hexadecylammonio)propane-1-sulfonate and 3-(N,N-dimethyl-N-tridecylammonio)-2-hydroxypropane-1-sulfonate which are especially preferred for their excellent cool water detergency characteristics.

The alkyl groups contained in said detergent surfactants can be straight or branched, preferably straight, and saturated or unsaturated as desired.

EXAMPLE

An effective granular laundry detergent composition according to this invention has the following formulation.

	Percent
Sodium alkyl benzene sulfonate in which the alkyl group is a straight chain dodecyl group	20
Sodium-1,3,5-trihydroxy-2,4,6-benzene trisulfonate sequestering agent	50
Sodium sulfate	14
Sodium silicate	6
Water	10

The sequestering agent in the preceding example can be replaced with an equal weight proportion of sodium-1,3,5-trihydroxy-2,4,6-benzene tricarboxylate, or sodium-1,3,5-trihydroxy-2,4,6-benzene triacetate and an effective composition is obtained.

In a finished detergent formulation, there can be present other materials which make the product more effective or more aesthetically attractive. The following are mentioned only by way of example. A water-soluble sodium carboxymethyl cellulose can be added in minor amounts to inhibit soil redeposition or for other reasons. Tarnish inhibitors such as benzotriazole or ethylenethiourea can also be added in amounts up to about 3%. Fluorescers, enzymes, and brighteners, perfumes, coloring agents, while not per se essential in the compositions of this invention, can be added in minor amounts. As already mentioned, an alkaline material or alkali such as sodium or potassium hydroxide can be added as supplementary pH adjusters. Other usual additives include sodium sulfate, sodium carbonate, water and the like. Corrosion inhibitors are also frequently used. Water-soluble silicates are highly effective corrosion inhibitors and can be added if desired at levels of from about 3% to about 8% by weight of the total composition. Alkali metal, preferably potassium and sodium silicates, are preferred having a weight ratio of SiO_2:M_2O of from about 1.0:1 to 2.8:1 (M refers to sodium or potassium). Sodium silicate having a ratio of SiO_2:Na_2O of from about 1.6:1 to 2.45:1 is especially preferred.

In the embodiment of this invention which provides for a built liquid detergent, a hydrotropic agent may be found desirable. Suitable hydrotropes are water-soluble alkali metal salts of toluenesulfonate, benzenesulfonate, and xylene sulfonate. Preferred hydrotropes are potassium or sodium toluenesulfonates. The hydrotropes may be added, if desired, at levels of from 0% up to about 12%. While a hydrotrope will not ordinarily be found necessary, it can be added, if so desired, for any reason such as to function as a solubilizing agent and to produce a product which retains its homogeneity at a low temperature.

SEQUESTRATION EVALUATION PROCEDURE

The sequestering properties of the novel class of sequestrants of this invention are demonstrated with the following procedure.

The evaluations are run in 200 ml. beakers at 23±3° C. with a magnetic stirrer. 50 ml. 14 grain/gal. (calculated as $CaCO_3$) $CaCl_2$ solution is poured into the beaker. The requisite amount of sequestering agent (builder) sample to give a final solution concentration of 0.06%, 0.03%, or 0.02%, is weighed or pipetted into the beaker. The sample is brought to pH 7 with KOH or HCl as needed. Distilled water is added to give a total volume of 100±3 ml. Fine adjustment is made to pH 7.00±0.05 with a Corning Model 12 meter and Corning Model 476022 glass electrode. At this point the calcium ion electrode is plugged in place of the pH electrode and the calcium ion activity is measured. The expanded scales either 0 to +100 or 0 to −100 millivolts, as necessary, are used. All readings are made with slow stirring. The resultant millivolt reading is converted into grains/gal. using a standardization curve. This amount represents residual hardness. The standards, 100, 10, 7, 5, 3, 1, 0.5 and 0.1 grains/gal. (as $CaCO_3$) $CaCl_2$ at pH 7.00 are linear with potential down to 1 grain/gal. and by 0.1 grain/gal. (1.7×10^{-5} molar) the practical limit of measurement has been reached. Day-to-day variation in potential readings is appreciable above 1 grain/gal.; it amounts to ±3 millivolts or ±10%. Below 1 grain/gal. error grows rapidly; however, precise statements of error limits are meaningless. A day-to-day variation in the behavior of even good calcium electrodes is to be expected below 1 grain/gal. At times, linearity will extend almost to 0.1 grain/gal. and then the best error limits will obtain. A further clue to superb calcium electrode performance is the rate at which it comes to its final potential. At best, this will be on the order of a second; about 10 seconds is the usual time. In summary, readings to within 10% can always be made down to 1 grain/gal. With a superb electrode, this can be extended to 0.1 grain/gal.

This procedure was used in the examples given below in which sequestering properties are given.

As noted, above, the synthesis methods for preparing the sequestering agents represents no part of this invention. While any known reactions can be used, the following examples are given to illustrate successful preparative methods. The sequestration values are given with several of the following examples.

EXAMPLE I

Preparation of 1,3,5-trihydroxy benzene

Fifty grams of water, fifty grams of NaOH and 10 grams of resorcinol were placed in nickel, 500 ml. crucible. This was heated to and held for four hours at 320° C. After cooling to room temperature, the material was removed from the crucible then neutralized with HCl. 1,3,5-trihydroxy benzene was isolated from the final reaction mass.

Calcium electrode test results for 1,3,5-trihydroxy benzene were as follows:

Weight sequestrant	pH	(Residual) [Ca+] grain/gal.
0		7
0.03	10	5.8
0.06	10	5.0

EXAMPLE II

Preparation of Na_3-1,3,5-trisulfobenzene

Three grams of phosphorous pentoxide, one mole of benzene, and 500 grams of concentrated sulfuric acid are added to a stirred reaction vessel. This mixture is heated to 290° C. and permitted to react for one hour. After cooling to room temperature the material is neutralized with NaOH. Na_3-1,3,5-trisulfobenzene is isolated from the reaction mass.

Calcium electrode test results on a sample of this material were as follows:

Weight sequestrant	pH	(Residual) [Ca+] grain/gal.
0		7
0.03	7	5.6
0.03	10	5.8
0.06	7	5.8
0.06	10	4.2

EXAMPLE III

Preparation of 1,2,4,5-tetraakis[hydroxymethyl] benzene

One mole of 1,2,4,5-tetraakis[chloromethyl]benzene is added to 500 grams of 50% $NaOH/H_2O$. From this, 1,2,4,5-tetraakis[hydroxymethyl]benzene is isolated.

Sequestering properties are demonstrated by the calcium electrode procedure described above.

EXAMPLE IV

Preparation of 1,3,5-tris[acetylether]benzene

One mole of 1,3,5-trihydroxy benzene is added to ten moles of acetylchloride. The mixture is permitted to react for 7 hours at 25° C. From the reaction mass, 1,3,5-tris[acetylether]benzene is isolated.

Sequestering properties are demonstrated by the calcium electrode procedure described above.

EXAMPLE V

Preparation of 1,2,3-tris[carboxymethyl ether]benzene

One mole of 1,2,3-trihydroxy benzene is added to five moles of chloroacetic acid. This mixture is permitted to react for 72 hours at 30° C. From the reaction mass, 1,2,3-tris[carboxymethylether]benzene is isolated.

Sequestering properties are demonstrated by the calcium electrode procedure described above.

EXAMPLE VI

Preparation of 1,2,3-trihydroxybenzene

One hundred grams of gallic acid are added to 300 grams of distilled water in an autoclave. The mixture is held at 100° C. for four hours. From the reaction mass, 1,2,3-trihydroxy benzene is isolated.

Calcium electrode test results on a sample of 1,2,3-trihydroxy benzene are as follows:

Weight	pH	[Ca+]
0		7
0.03	7	2.2
0.03	10	2.7
0.06	7	1.05
0.06	10	1.95

EXAMPLE VII

Preparation of 1-methyl-2,4,6-trisulfobenzene

One mole of the potassium salt of toluene-2,4-disulfonate are reacted with three moles of chlorosulfonic acid at 240° C. for four hours. The mixture is neutralized with KOH. From the reaction mass, tri-potassium-1-methyl-2,4,6-trisulfobenzene is isolated.

Sequestering properties are demonstrated by the calcium electrode procedure described above.

EXAMPLE VIII

Preparation of hexaakis[hydroxymethyl]benzene

One mole of hexaakis[chloromethyl]benzene is added to 600 grams of 50% $NaOH/H_2O$. The mixture is permitted to react at 25° C. for one hour. Hexaakis[hydroxymethyl]benzene is isolated from the reaction mass.

Sequestering properties are demonstrated by the calcium electrode procedure described above.

EXAMPLE IX

Preparation of 1-[chloromethyl]-2,4,5-tris[hydroxymethyl]benzene

One mole of 1,2,4,5-tetraakis[chloromethyl]benzene is added to 240 grams of 50% $NaOH/H_2O$. The material is permitted to react for three hours at 25° C. From the reaction mass, 1-[chloromethyl]-2,4,5-tris[hydroxymethyl]benzene is isolated.

Sequestering properties are demonstrated by the calcium electrode procedure described above.

EXAMPLE X

Preparation of 1,3,5-trimethoxybenzene

One mole of 1,3,5-trihydroxy benzene is added to 5 moles of methyl sulfate and 1000 grams of 50% aqueous NaOH. The materials are permitted to react for two hours at 25° C. From the reaction mass, 1,3,5-trimethoxy benzene is isolated.

Sequestering properties are demonstrated by the calcium electrode procedures described above.

EXAMPLE XI

A calcium electrode evaluation with 1,3,5-trisulfobenzene yielded the following results:

Weight sequestrant	pH	[Ca+] grain/gal. (residual)
0		7
0.03	7	5.6
0.03	10	5.8
0.06	7	5.8
0.06	10	4.2

EXAMPLE XII

A calcium electrode evaluation with hexahydroxybenzene yielded the following results:

Weight sequestrant	pH	[Ca+] grain/gal. (residual)
0		7
0.03	7	
0.03	10	
0.06	7	
0.06	10	<0.1

EXAMPLE

An effective granular laundry detergent composition according to this invention has the following formulation.

	Percent
Sodium alkyl benzene sulfonate in which the alkyl group is a straight chain dodecyl group	20
Sodium-1,3,5-trisulfobenzene	50
Sodium sulfate	14
Sodium silicate	6
Water	10

The sequestering agent in the preceding example can be replaced with an equal weight proportion of 1,3,5-trihydroxybenzene, 1,2,3-trihydroxybenzene or hexaakis (hydroxymethyl)benzene and an effective composition is obtained.

In many industrial, institutional and household processes and products, a small amount of a metal ion contamination present in water can adversely affect color, stability, appearance, quality and saleability of a product or the efficiency of a process. The role of a sequestering agent in overcoming such adverse effects of metal ions is fairly well recognized and appreciated. Accordingly, another embodiment of the present invention is to provide a process for treating aqueous solutions containing polyvalent metal ions by adding to the solution an effective amount of at least one of the novel class of sequestering agent in vorecoming such adevsrse effects of metal ions amount ranges from .25 p.p.m. to 10,000 p.p.m. of the aqueous solution. This embodiment of the present invention is based on the discovery of the sequestering properties of the sequestering agents described herein.

As indicated above, the manner of synthesizing the sequestering agents of this invention form no part of this invention. Any suitable reaction can be used. Thus, for example, sulfonations are effected by reaction of the aromatic-based material with SO_3 in such solvents as HCl, H_2SO_4, SO_2 or H_2O. Carboxy groups are formed by adding previously carboxylated materials to aromatics by oxidation of methyls or chloromethyls with H_2O_2, potassium dichromate, potassium permanganate, or nitric acid. Phenolic —OH groups are added by means of alkali fusion of aromatics or by means of acidification of hydroperoxides of isopropyl aromatics. Alcoholic —OH groups are added by reacting chloromethyl aromatics with aqueous NaOH or KOH. These procedures and the others used are adapted as needed so as to obtain the desired end product. The aforementioned processes are more fully described in Organic Chemistry by R. T. Morrison and R. N. Boyd, published by Allyn and Bacon, Inc. in 1962.

In addition, a suitable synthesis reaction for the preparation of hexahydroxybenzene is described in Ira E. Neifert and Edward Bartow, J. Am. Chem. Soc. 65, 1770–2 (1943).

What is claimed is:

1. A detergent composition consisting essentially of a water-soluble organic synthetic detergent selected from the group consisting of anionic, nonionic, ampholytic and zwitterionic surface active agents and mixtures thereof and, as a detergency aid, a sequestering agent which is a water soluble salt selected from the group consisting of alkali metal and ammonium salts of 1,3,5-benzene-trisulfonic acid and wherein the ratio of water-soluble organic synthetic detergent to sequestering agent is from 20:1 to 1:20.

2. The detergent composition of claim **1** wherein the sequestering agent is the trisodium salt of 1,3,5-benzenetrisulfonic acid.

References Cited

UNITED STATES PATENTS

3,491,154	1/1970	Priestly et al.	260—607
3,692,684	9/1972	Hentschel	252—89

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Chem. Absts.: vol. 57, p. 11079i.

MAYER WEINBLATT, Primary Examiner

P. E. WILLIS, Assistant Examiner

U.S. Cl. X.R.

252—531, 535, 539, 554, 558, Digest

PO-1050
(5/69)

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,758,420 Dated September 11, 1973

Inventor(s) Daniel S. Connor and Harry Karl Krummel

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

Col. 3, line 40, delete "1,4,5-trihydroxy benzene" and insert therefor ---1,3,5-trihydroxy benzene ---.

Col. 4, line 39, delete "sequesting" and insert therefor --- sequestering ---.

Col. 6, line 20, delete "suca" and insert therefor --- such ---.

Col. 9, line 19, delete "phospahte" and insert therefor --- phosphate ---.

Col. 9, line 39, delete "3-(N,N-dimethyl-N-hexadecylammino)- insert therefor --- 3-(N,N-dimethyl-N-hexadecylammonio)- ---.

Col. 9, line 45, delete "ethyl 3-(N,N-diethyl-N-dodecylammonio)-" and insert therefor --- ethyl 3-(N,N-dimethyl-N-dodecylammonio)- --

Col. 17, lines 17,18,19, delete "agent in vorecoming such adevsre effects of metal ions amount ranges from .25 p.p.m. to 10,000 p.p.m. of the aqueous solution." and insert therefor --- agents described and illustrated above. Ordinarily, this amount ranges from .25 p.p.m. to 10,000 p.p.m. of the aqueous solution.---.

Signed and sealed this 1st day of January 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents