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3,812,044

## DETERGENT COMPOSITION CONTAINING A POLYFUNCTIONALLY-SUBSTITUTED ARO- MATIC ACID SEQUESTERING AGENT

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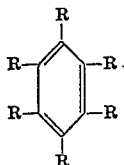
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2 Claims 10

### 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 polyfunctionally-substituted aromatic acid compound having the formula



wherein at least two R's are different functional groups of the type described.

### 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 effected 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 stream 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 de-

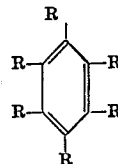
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tergent compositions are two such nutrients. These materials, however, by themselves do not cause excessive eutrophication. Other nutrients such as carbon must also be present. A combination of nutrients stimulates the growth of plant life in lakes 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 polyfunctionally-substituted aromatic acid compound having the formula



wherein each R represents

- H,
- OH,
- CH<sub>2</sub>OH,
- CH<sub>2</sub>CH<sub>2</sub>OH,
- CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH,
- CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH,
- COOH,
- CH<sub>2</sub>COOH,
- CH<sub>2</sub>CH<sub>2</sub>COOH,
- CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH,
- CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH,
- OCH<sub>2</sub>COOH,
- OCH<sub>2</sub>CH<sub>2</sub>COOH,
- OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH,
- CH<sub>2</sub>OCH<sub>2</sub>COOH,
- CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>COOH,
- CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>COOH,
- SO<sub>3</sub>H,
- SCH<sub>2</sub>COOH,
- X,
- CH<sub>2</sub>X,
- CH<sub>2</sub>CH<sub>2</sub>X,
- SCH<sub>2</sub>CH<sub>2</sub>COOH,
- CH(COOH)<sub>2</sub>'
- =O
- $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{H} \end{array}$
- $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{COOH} \end{array}$
- $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{CH}_3 \end{array}$
- CH<sub>3</sub>,
- CH<sub>2</sub>CH<sub>3</sub>,
- CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>,
- CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>,
- CH<sub>2</sub>OCH<sub>3</sub>, or
- OR',

wherein X represents halogen;

wherein R' represents

—SO<sub>3</sub>H,  
—SO<sub>3</sub>CH<sub>3</sub>,  
—SO<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>,  
—CH<sub>2</sub>OH,  
—CH<sub>2</sub>CH<sub>2</sub>OH,  
—CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH,  
—CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH,

$\text{O}$   
||  
—C—CH<sub>3</sub>,

$\text{O}$   
||  
—C—CH<sub>2</sub>CH<sub>3</sub>,

$\text{O}$   
||  
—C—CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>,

—CH<sub>3</sub>,  
—CH<sub>2</sub>CH<sub>3</sub>,  
—CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>,  
—CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>,  
—CH<sub>3</sub>OCH<sub>3</sub>,  
—CH<sub>3</sub>OCH<sub>2</sub>CH<sub>3</sub>,

and wherein at least two R substituents on the aromatic nucleus are different functional groups.

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

1,3,5-trihydroxy-2,4,6-benzene trisulfonic acid  
1,4-disulfo-2,3,5,6-tetracarboxybenzene,  
1,4-dihydroxy-2,3,5,6-tetracarboxybenzene,  
1,3,5-trihydroxy-2,4,6-benzenetricarboxylic acid  
1,3-disulfo-2,4,5,6-tetracarboxybenzene  
1,3-dihydroxy-2,4,5,6-tetracarboxybenzene  
1,3,5-tris[carboxymethylether]-2,4,6-trisulfobenzene  
1,3,5-tris[carboxymethylether]-2,4,6-tricarboxybenzene  
1,3,5-tris[2-carboxyethylether]-2,4,6-trisulfobenzene  
1,3,5-tris[2-carboxyethylether]-2,4,6-tricarboxybenzene  
1,3,5-trihydroxy-2,4,6-benzenetricarboxylic acid  
1,3,5-trisulfo-2,4,6-benzenetricarboxylic acid  
1,3,5-triacetal-2,4,6-trihydroxybenzene  
2,3,4,5,6-pentacarboxybenzyl alcohol  
2,4-disulfo-3,5,6-tricarboxybenzyl alcohol  
4-sulfo-2,3,5,6-tetracarboxybenzyl alcohol  
1,4-methoxy-2,3,5,6-tetracarboxybenzene  
1,4-bis(hydroxymethyl)-2,3,5,6-tetracarboxybenzene  
1,3-dihydroxy-5-[carboxymethylether]benzene  
1-carboxy-2-hydroxy-3,5-disulfobenzene  
1,2,4,5-tetraakis[hydroxymethyl]-3-sulfobenzene  
1-hydroxy-2,6-disulfo-4-carboxybenzene  
1,3-dihydroxy-5-[acetyloxy]benzene  
1-methyl-2,3,4,5,6-pentacarboxybenzene  
2,3,4,5,6-pentacarboxybenzaldehyde  
1-sulfo-2,3,4,5,6-pentacarboxybenzene  
1,4-dimethyl-2,3,5,6-tetracarboxybenzene  
1,3,5-trihydroxy-2,4,6-benzenetrimethylsulfonate  
2,3,4,5,6-pentacarboxybenzylsulfuric acid  
2,3,4,5,6-pentacarboxybenzylsulfonic acid  
2,3,4,5,6-pentacarboxybenzyl-carboxymethyl-ether  
2,3,4,5,6-pentacarboxybenzyl-2-carboxyethyl-ether  
1,3-disulfo-2,4,5-tricarboxybenzene  
1-sulfo-2,3,5,6-tetracarboxybenzene  
1,5-disulfo-2,3,4-trihydroxybenzene  
1,3,5-trihydroxy-2,4-disulfobenzene  
1,3,5-trisulfo-2,4-dihydroxybenzene  
1-hydroxy-2,3,5,6-tetracarboxybenzene  
2,4-dihydroxy-1,3,5-tricarboxybenzene  
2,3,4-trihydroxy-1,5-dicarboxybenzene  
1,3,5-trihydroxy-2,4-dicarboxybenzene  
1,3,5-tris[carboxymethylether]-2,4-dicarboxybenzene  
1,3,5-tris[2-carboxyethylether]-2,4-dicarboxybenzene  
2,4-bis[carboxymethylether]-1,3,5-tricarboxybenzene  
2,4-bis[2-carboxyethylether]-1,3,5-tricarboxybenzene  
2,3,5,6-tetracarboxybenzyl-carboxymethyl-ether  
2,3,5,6-tetracarboxybenzyl-2-carboxyethyl-ether  
5-sulfo-1,2,4-tricarboxybenzene

2,3-dihydroxy-1,4-benzenediacetic acid  
1,3-dihydroxy-2,4-disulfobenzene  
1,2-dihydroxy-3,5-disulfobenzene  
2,4,6-tricarboxybenzyl-carboxymethyl-ether  
5 1-sulfo-2,4,6-tricarboxybenzene  
2,4,6-tricarboxybenzyl-2-carboxyethyl-ether  
1-hydroxy-2,4-disulfo-6-carboxybenzene  
1,3-disulfo-2,5-dicarboxybenzene  
1-hydroxy-2,4,6-tricarboxybenzene  
10 1,3,5-trihydroxy-2-carboxybenzene  
1,3,5-trisulfo-2-carboxybenzene  
1,2,3-trihydroxy-5-carboxybenzene  
1,3,5-trisulfo-2-hydroxybenzene  
1,3,5-tris[carboxyethylether]-2-carboxybenzene  
1,3,5-tris[2-carboxyethylether]-2-carboxybenzene  
15 2-[2-carboxyethylether]-1,3,5-tricarboxybenzene  
2-[carboxymethylether]-1,3,5-tricarboxybenzene  
1,2-dihydroxy-3-sulfo-5-carboxybenzene  
1-sulfo-2,4,5-tricarboxybenzene  
20 1,4-dihydroxy-2,5-disulfobenzene  
2,4-disulfo-1,5-dihydroxybenzene  
1,4-dihydroxy-2,5-benzenediacetic acid  
4,6-dicarboxy-1,3-dihydroxybenzene  
1,4-bis[carboxymethylether]-2,5-dicarboxybenzene  
25 1,4-bis[2-carboxyethylether]-2,5-disulfobenzene  
1,4-bis[carboxymethylether]-2,5-disulfobenzene  
2,4,5-tricarboxybenzyl-carboxymethyl-ether  
1-carboxy-2-hydroxy-4-sulfo-5-benzenediacetic acid  
1,4-dihydroxy-2,5-dicarboxybenzene  
30 1,3-dihydroxy-2-carboxybenzene  
1-sulfo-2-hydroxy-3-carboxybenzene  
1,3-bis[carboxymethylether]-2-carboxybenzene  
1,3-bis[2-carboxyethylether]-2-carboxybenzene  
1,3-dihydroxybenzyl-carboxymethyl-ether  
35 1,3-dihydroxybenzyl-2-carboxyethyl-ether  
1-hydroxy-4-sulfo-2-carboxybenzene  
2,4-disulfo-1-hydroxybenzene  
1-[carboxymethylether]-2,4-disulfobenzene  
1-[2-carboxyethylether]-2,4-disulfobenzene  
40 1-hydroxy-2-carboxybenzene  
1-[2-carboxyethylether]-2-carboxybenzene  
1-[carboxymethylether]-2-carboxybenzene  
1-hydroxy-4-benzenesulfonic acid  
1-hydroxy-2-benzene sulfonic acid  
45 1-[carboxymethylether]-4-benzene sulfonic acid  
1-[2-carboxyethylether]-4-benzene sulfonic acid  
1-[carboxymethylether]-2-benzene sulfonic acid  
1-[2-carboxyethylether]-2-benzene sulfonic acid  
1,5-dicarboxy-2,4-bis[carboxyformyl]benzene.

50 The process by which these sequestering agents can be prepared from 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 sequestering 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 sequestering agent's properties, the detergent employed, the hardness content of the water, the oil 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 sequestering agent is used to render the water

suitable for its intended purpose. This may be judged 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, non-ionic, ampholytic, and zwitterionic surface-active 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 resin 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 ( $C_8$ - $C_{13}$  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 Numbers 2,220,099 and 2,477,383

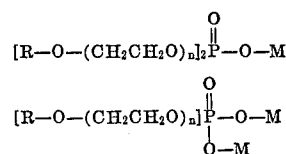
(especially valuable are linear straight chain alkyl benzene sulfonates in which the average of the alkyl groups is about 13 carbon atoms abbreviated hereinafter as  $C_{13}$ LAS); sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; 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 neutralized 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  $-SO_3H$ ,  $-SO_3Na$ , and  $-CO_2H$ . Alkyl phosphate esters such as  $(R-O)_2PO_3H$  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



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. Pat. 3,332,880 of Phillip F. Pflaumer and Adrian 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 carbon atom and a second sulfonate group attached to an internal carbon atom not more than about six 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) lauramide; 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 di-isooctylphenol 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:

dimethyltetradecylamine oxide,  
ethylmethyltetradecylamine oxide,  
cetyldimethylamine oxide,  
dimethylstearylamine oxide,  
cetyl ethylpropylamine oxide,  
diethyl dodecylamine oxide,  
diethyl tetradecylamine oxide,  
dipropyl dodecylamine oxide,  
bis-(2-hydroxyethyl) dodecylamine oxide,  
bis-(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropylamine oxide,  
(2-hydroxypropyl) methyl tetradecylamine oxide,  
dimethyloleylamine 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  $R^1$  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 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,  
cetyl ethylpropylphosphine oxide,

diethyldodecylphosphine oxide,  
diethyltetradecylphosphine oxide,  
dipropyldodecylphosphine oxide,  
bis-(hydroxymethyl)dodecylphosphine oxide,  
bis-(2-hydroxyethyl)dodecylphosphine oxide,  
(2-hydroxypropyl)methyltetradecylphosphine oxide,  
dimethylolelphosphine 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  $\text{R}^1$  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  $\text{R}^1$  being an alkyl radical containing 0 ether linkages and containing from about 10 to about 18 carbon atoms, and wherein  $\text{R}^2$  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., carboxyl, 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-methylhexadecylamino)propyl-1-phosphonate,  
disodium octadecyl-iminodiacetate,  
sodium 1-carboxymethyl-2-undecylimidazole,  
disodium 2-[N-(2-hydroxyethyl)octadecylamino] ethyl phosphate, 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-hexadecylammonio)-propane-1-sulfonate,  
2-(N,N-dimethyl-N-dodecylammonio)acetate,  
2-(N,N-dimethyl-N-dodecylammonio)propionate,  
2-(N,N-dimethyl-N-octadecylammonio)-ethyl sulfate,  
2-(trimethylammonio)ethyl dodecylphosphonate,

ethyl 3-(N,N-dimethyl-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-undecylimidazolium-1-acetate,  
2-(trimethylammonio)octadecanoate, and  
3-(N,N-bis-(2-hydroxyethyl)-N-octadecylammonio)-2-hydroxypropane-1-sulfonate.

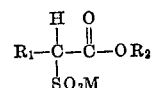
Some of these detergents are described in the following U.S. Patents: 2,129,264; 2,178,353; 2,774,786; 2,813,898; and 2,828,332.

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  $\beta$ -acyloxyalkane-1-sulfonic acids;  $\beta$ -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  $\alpha$ -sulfonated fatty acid in which the esters contain about 15 to about 25 carbon atoms. These detergent compounds have the following structure:



wherein  $\text{R}_1$  is alkyl or alkenyl of about 10 to about 20 carbon atoms (forming with the two carbon atoms a fatty acid group);  $\text{R}_2$  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 piperidinium cations and those derived from alkylamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like.

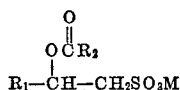
Specific examples of this class of compounds include the sodium and potassium salts of esters where  $\text{R}_2$  is selected from methyl, ethyl, propyl, butyl, hexyl and octyl groups and the fatty acid group ( $\text{R}_1$  plus the two carbon atoms in the structure above) is selected from lauric, myristic, palmitic, stearic, palmitoleic, oleic, linoleic acids and mixtures thereof. A preferred ester material herein is the sodium salt of the methyl ester of  $\alpha$ -sulfonated tallow fatty acid, the term tallow indicating a carbon chain distribution approximately as follows:  $\text{C}_{14}$ —2.5%,  $\text{C}_{16}$ —28%,  $\text{C}_{18}$ —23%, palmitoleic—2%, oleic—41.5%,

and linoleic—3% (the first three fatty acids listed are saturated).

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

The salts of  $\alpha$ -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  $\text{R}_1$  is alkyl of about 9 to about 23 carbon atoms (forming with the two carbon atoms an alkaline group);  $\text{R}_2$  is alkyl of 1 to about 8 carbon atoms; and M is a salt-forming radical hereinbefore described.

Specific examples of  $\beta$ -acyloxy-alkane-1-sulfonates, or alternatively 2-acyloxy-alkane-1-sulfonates, utilizable herein to provide excellent cleaning levels under household 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 dimethylpiperidinium salt of 2-nonanoyloxy-tetradecane-1-sulfonic acid; the sodium salt of 2-acetoxy-heptadecane-1-sulfonic acid; the lithium salt of 2-acetoxy-octadecane-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  $\beta$ -acyloxy-alkane-1-sulfonate salts herein are the alkali metal salts of  $\beta$ -acetoxy-alkane-1-sulfonic acids corresponding to the above formula wherein  $\text{R}_1$  is an alkyl of about 14 to about 18 carbon atoms, these salts being preferred from the standpoints of the excellent cleaning properties and ready availability.

Typical examples of the above described  $\beta$ -acetoxy alkanesulfonates are described in the literature: Belgian Pat. 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 DeGroote disclose certain salts of  $\beta$ -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  $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$  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.

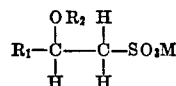
The alkyl ether sulfates calcium insensitive detergents of the present invention are condensation products of ethylene oxide and monohydride alcohols having about 10 to about 20 carbon atoms. Preferably, R has 14 to 18 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil or tallow, 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 ether 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  $\beta$ -alkyloxy alkane sulfonates. These compounds have the following formula:



where  $\text{R}_1$  is a straight chain alkyl group having from 10 to 20 carbon atoms,  $\text{R}_2$  is a lower alkyl group having from 1 to 3 carbon atoms, and M is a salt-forming radical hereinbefore described.

Specific examples of  $\beta$ -alkoxy alkane sulfonates or alternatively 2-alkoxy-alkane-1-sulfones, utilizable herein to provide superior cleaning and whitening levels under household washing conditions include

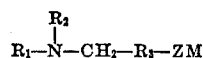
potassium  $\beta$ -ethoxytetradecylsulfonate, sodium  $\beta$ -methoxy-tridecanesulfonate, potassium  $\beta$ -ethoxytetradecylsulfonate, sodium  $\beta$ -isopropoxyhexadecylsulfonate, lithium  $\beta$ -t-butoxytetradecylsulfonate, sodium  $\beta$ -methoxyoctadecylsulfonate, and ammonium  $\beta$ -n-propoxydodecylsulfonate.

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  $\alpha$ -olefin by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones 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  $\text{SO}_2$ , chlorinated hydrocarbon, etc., when used in the liquid form, or by air, nitrogen, gaseous  $\text{SO}_2$ , etc., when used in the gaseous form.

The  $\alpha$ -olefins from which the olefin sulfonates are derived are mono-olefins having 12 to 24 carbon atoms, preferably 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-alkanesulfonates, 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

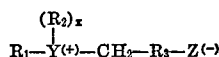


wherein  $\text{R}_1$  is alkyl of about 8 to about 18 carbon atoms,  $\text{R}_2$  is alkyl of 1 to about 3 carbon atoms or is hydrogen,  $\text{R}_3$  is alkylene of 1 to about 4 carbon atoms, Z is carboxy,



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. Pat. 3,658,072; sodium salts of N-higher alkyl aspartic acids such as those produced according to the teaching of U.S. Pat. 2,438,091; and the products sold under the trade name "Miranol" and described in U.S. Pat. 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 selected 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-hydroxypentane-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-hexadecylammonio]-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.

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 hydrotrope 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.

#### 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.

#### 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  $23 \pm 3^\circ C$ . with a magnetic stirrer. 50 ml. 14 gram/gal. (calculated as  $CaCO_3$ )  $CaCl_2$  solution is poured into the breaker. 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  $100 \pm 3$  ml. Fine adjustment is made to pH  $7.00 \pm 0.05$  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  $\pm 100$  or 0 to  $\pm 100$  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. ( $1.7 \times 10^{-5}$  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  $\pm 3$  millivolts or  $\pm 10\%$ . 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.

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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 represent 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 $\text{Na}_3$ -1,3,5-trihydroxy-2,4,6-benzene trisulfonate

Two hundred grams of 1,3,5-trihydroxy benzene dihydrate were added to a stirred four-neck flask cooled by an ice bath to 0° C. Two kilograms of chlorosulfonic acid were then carefully added over a period of twenty-five minutes. After standing for an hour, the reaction mass was filtered through a fritted glass funnel and washed with 6 liters of dichloromethane. This acid batch was then added to a second similar batch and allowed to stand in a desiccator over sulfuric acid for two days at reduced pressure. Part of the dried solid was suspended in dichloromethane and neutralized with 50% NaOH/H<sub>2</sub>O. After the solvent was pulled off by heating at 30° C. under reduced pressure, the product,  $\text{Na}_3$ -1,3,5-trihydroxy-2,4,6-benzene trisulfonate, was freeze dried.

A calcium electrode test yielded the following results:

	pH	[Ca <sup>2+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	3.8
0.03	10	0.9
0.03	7	0.6
0.06	10	<0.1

A calcium electrode test was then performed on this product with the following results:

	pH	[Ca <sup>2+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	5.4
0.025	10	4.0
0.03	7	2.0
0.06	10	1.0

#### EXAMPLE II

##### Preparation of $\text{Na}_3$ -1,3,5-trihydroxy-2,4,6-benzene tricarboxylate

One hundred grams of  $\text{Na}_3$ -1,3,5-trihydroxy-2,4,6-benzene trisulfonate, as from the first example, 600 mls. of distilled water, 100 grams of sodium acetate and a few drops of acetic acid are added to a stirred reaction vessel. To this, 100 grams of bromine, is added dropwise. This mixture is agitated and held at 0° C. for two hours. The precipitate, 1,3,5 - trihydroxy - 2,4,6 - tribromobenzene, is then filtered out and freeze dried. Thirty grams of this dried material are slurried into 200 mls. of ethyl ether. Fifty mls. of this slurry, 15 grams of magnesium turnings, and 200 mls. of ethyl ether are charged into a three-neck reaction vessel and heated to reflux. After adding one gram of iodine crystals, the remainder of the slurry is added slowly. An additional gram of iodine crystals is added when about half of the slurry has been added to the reaction mass. The mixture is agitated at reflux for six hours then allowed to stand for two days. After separation all residual magnesium turnings, the remaining material is placed in an agitated reaction flask and 2 pounds of Dry Ice are added slowly. The slurry is then filtered and the 1,3,5-trihydroxy-2,4,6-benzene tricarboxylic acid is neutralized with 10% NaOH to yield  $\text{Na}_3$ -1,3,5-trihydroxy-

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droxy-2,4,6-benzene tricarboxylate. In the calcium electrode test described above, this compound has demonstrable sequestering properties.

#### EXAMPLE III

##### Preparation of $\text{Na}_3$ -2,4,6-trisulfo phenol

Twenty-five grams of chemically pure phenol were dissolved in 600 ml. of dichloromethane in a three-neck 2000 ml. reaction vessel. To this 200 grams of chlorosulfonic acid were added. The reaction mass was heated until the solvent had evaporated and then material reached 140° C. This temperature was held for 30 minutes. The sample was then cooled in a Dry Ice/acetone bath and neutralized with 380 grams of a 21% NaOH aqueous solution. The product,  $\text{Na}_3$ -3,4,6-trisulfo phenol, was filtered and washed with distilled water, then dried at 110° C. in an oven.

A calcium electrode test was then performed on this product with the following results:

	pH	[Ca <sup>2+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	5
0.03	10	4
0.03	7	3.6
0.06	10	1.7

#### EXAMPLE IV

##### Preparation of $\text{Na}_2$ (1,5-disulfo-2,3,4-trihydroxy benzene)

Thirty-five gram of 1,2,3-trihydroxy benzene were added with 300 ml. of dichloromethane to a stirred 2000 ml. reaction vessel. The vessel was held in an ice bath at 0° C. 175 grams of chlorosulfonic acid were added dropwise to this over a period of twenty minutes. The sample was neutralized with 200 grams of a 25% NaOH aqueous solution. The resulting product,  $\text{Na}_2$ (1,5-disulfo-2,3,4-trihydroxy benzene), was filtered and dried in an oven at 110° C.

A calcium electrode test was performed on this salt and on the starting material, 1,3,5-trihydroxy benzene, with the following results:

	Weight <sup>1</sup>	pH	[Ca <sup>2+</sup> ] (residual)
45 Salt	0	7	7
	0.03	7	5
	0.03	10	2.7
	0.06	7	4
	0.06	10	0.25
50 Trihydroxy benzene	0.03	7	2.2
	0.03	10	2.7
	0.06	7	1.05
	0.06	10	1.95

<sup>1</sup>Sequestering agent.

#### EXAMPLE V

##### Preparation of $\text{Na}_3$ (1-carboxy-2-hydroxy-3,5-disulfo benzene)

Forty grams of sodium salicylate and 500 ml. of dichloromethane were added to a stirred 3000 ml. reaction flask cooled by an ice bath to 0° C. To this, 175 grams of chlorosulfonic acid were added slowly. After standing at 0° C. for 30 minutes, the material was neutralized with 140 grams of a 28% NaOH aqueous solution. The resulting product,  $\text{Na}_3$ -1-carboxy-2-hydroxy-3,5-disulfo benzene, was filtered and dried in an oven at 110° C.

A calcium electrode test was performed and yielded the following results:

	pH	Residual [Ca <sup>2+</sup> ] grain/gal.
Weight sequestrant:		
0	7	7
0.03	7	5
0.03	10	4.8
0.06	7	5
0.06	10	4.0



## 17 EXAMPLE VI

### Preparation of Na<sub>3</sub>-1-hydroxy-2,6-disulfo-4-carboxybenzene

Into a three liter stirred reaction flask, 15 grams of p-hydroxy benzoic acid, 20 grams phosphorous pentoxide, and 300 mls. of chloroform were added. To this, 300 grams of 30% oleum were added slowly. This reaction mass was heated to 100° C. and held there while being agitated for 30 minutes. The reaction vessel was then placed in an ice bath to cool the mixture to 0° C. 300 grams of concentrated hydrochloric acid were added. The precipitate was filtered out and neutralized with 80 grams of 50% NaOH/H<sub>2</sub>O. The Na<sub>3</sub>-1-hydroxy-2,6-disulfo-4-carboxybenzene was dried for two days in an oven at 105° C.

The results of a calcium electrode test performed on this sample are as follows:

	pH	Residual [Ca <sup>2+</sup> ] grain/gal.
Weight sequestrant:		
0.....		7
0.03.....	7	5
0.03.....	10	4.8
0.06.....	7	5
0.06.....	10	4.0

## EXAMPLE VII

### Preparation of Na<sub>3</sub>-1,3,5-trisulfo-2,4-dihydroxy benzene

200 mls. of chloroform, 10 grams of resorcinol, and 300 mls. of chlorosulfonic acid were added to a stirred reaction vessel cooled with a Dry Ice/ethanol bath. After charging the material, the reaction mass was heated to 100° C. and held there for 30 minutes. The reaction vessel was then placed in an ice/water bath and 75 mls. of concentrated hydrochloric acid were added to the mixture. The precipitate was filtered out and neutralized with 50% NaOH to give Na<sub>3</sub>-1,3,5-trisulfo-2,4-dihydroxybenzene.

The results of a calcium electrode test on this are as follows:

	pH	Residual [Ca <sup>2+</sup> ] grain/gal.
Weight sequestrant:		
0.....		7
0.03.....	7	5.2
0.03.....	10	3.7
0.06.....	7	4.2
0.06.....	10	1.7

## EXAMPLE VIII

### Preparation of Na<sub>2</sub>-1,3-dihydroxy-4,6-disulfobenzene

Ten grams of resorcinol and ½ pint of carbon disulfide were added to a stirred reaction flask being held in an ice/water bath. Fifty grams of chlorosulfonic acid were added slowly. The mixture was allowed to react for one hour while being stirred continuously. The sample was then neutralized with 35 grams of 50% NaOH/H<sub>2</sub>O.

Calcium electrode test results for this, Na<sub>2</sub>-1,3-dihydroxy-4,6-disulfobenzene, are as follows:

	pH	[Ca <sup>2+</sup> ]
Weight:		
0.....		7
0.06.....	10	1.6

## EXAMPLE IX

### Preparation of Na<sub>2</sub>-1,2,3,5-trihydroxy-2,4-disulfobenzene

Ten grams of 1,3,5-trihydroxy benzene dihydrate and 200 mls. of chloroform were added to a stirred reaction vessel being held at 0° C. 110 grams of chlorosulfonic acid were added dropwise to this. This mixture was heated to 110° C. and allowed to react at this temperature for one hour. This reaction mass was then neutralized with 80 grams of 50 NaOH/H<sub>2</sub>O. The Na<sub>2</sub>-1,3,5-trihydroxy-2,4-disulfobenzene was dried at 100° C.

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Calcium electrode test results are as follows:

	pH	Residual [Ca <sup>2+</sup> ] grain/gal.
Weight sequestrant:		
0.....		7
0.03.....	10	3.5
0.06.....	7	2.5
0.06.....	10	2.7

## EXAMPLE X

### Preparation of 1,3,5-trihydroxy-2,4,6-triacetyl benzene

Three moles of carbon sulfoxide in an ethereal solution are added to three moles of methylmagnesium iodide at -10° C. The reaction mass is permitted to react for four hours. 1,3,5-trihydroxy-2,4,6-triacetylbenzene is isolated in ten percent yield.

Sequestering properties are demonstrated by the calcium electrode test described herein above.

## EXAMPLE XI

### Preparation of Na<sub>3</sub>-1-sulfo-2-methyl-4,5-dicarboxybenzene

120 grams of 1,2,4-trimethylbenzene were added to 200 grams of concentrated sulfuric acid. The material was allowed to react for two hours to form 1,3,4-trimethyl-5-sulfobenzene. Twenty grams of this were then added 41 grams of 30% hydrogenperoxide and allowed to react at 100° C. for two hours. The product was filtered and neutralized with 1 N NaOH to give Na<sub>3</sub>-1-sulfo-2-methyl-4,5-dicarboxy benzene.

Calcium electrode test results for this were:

	pH	[Ca <sup>2+</sup> ] (residual)
Weight sequestrant:		
0.....		7
0.03.....	7	4.8
0.03.....	10	4.5
0.06.....	7	4.3
0.06.....	10	3.7

## EXAMPLE XII

### Preparation of Na<sub>2</sub>-2,3-dihydroxy-1,4-benzene diacetate

Ten grams of 2,3-dihydroxy-1,4-benzene diacetic acid were neutralized with ten grams of 50% NaOH/H<sub>2</sub>O. The product was dried in an oven at 110° C.

Calcium electrode test results for Na<sub>2</sub>-2,3-dihydroxy-1,4-benzene diacetate are as follows:

	pH	[Ca <sup>2+</sup> ] (residual)
0.....		7
0.03.....	7	4.7
0.03.....	10	4.0
0.06.....	7	2.2
0.06.....	10	1.45

## EXAMPLE XIII

### Preparation of 1,3-dihydroxy-5[acetyl ether] benzene

One mole of 1,3,5-trihydroxy benzene is added to one mole of acetylchloride. The mixture is permitted to react at 30° C. for 24 hours. From the reaction mass, 1,3-dihydroxy-5-[acetyl ether] benzene is separated.

Sequestering properties are demonstrated by the calcium electrode test described herein.

## EXAMPLE XIV

### Preparation of 1,3-dihydroxy-5-[carboxymethyl ether] benzene

One mole of 1,3,5-trihydroxy benzene is added to one mole of chloroacetic acid. The mixture is permitted to react for 24 hours at 30° C. From this reaction mass, 1,3-dihydroxy-5-[carboxymethyl ether] benzene is isolated.

Sequestering properties are demonstrated by the calcium electrode test described herein.

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### EXAMPLE XV

Preparation of Na-1,2,4,5-tetraakis[hydroxymethyl]-3-sulfobenzene

One mole of 1,2,4,5-tetraakis[chloromethyl] benzene is added to 200 grams of concentrated sulfuric acid. The mixture is permitted to react for 2 hours at 25° C.

Six moles of NaOH is 50% aqueous solution is added to the reaction mass. The desired product, Na-1,2,4,5-tetraakis[hydroxymethyl]-3-sulfobenzene, is isolated from the reaction mass.

Sequestering properties are demonstrated by the calcium electrode test described herein.

### EXAMPLE XVI

A calcium electrode evaluation with 2,3,4-trihydroxy-1,5-disulfobenzene yielded the following results:

	pH	[Ca <sup>+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	7
0.03	7	5
0.03	10	2.7
0.06	7	4
0.06	10	0.25

### EXAMPLE XVII

A calcium electrode evaluation with 1-sulfo-2, 3,5,6-tetracarboxybenzene yielded the following results:

	pH	[Ca <sup>+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	7
0.03	7	5
0.03	10	4.5
0.06	7	3.6
0.06	10	2.95

### EXAMPLE XVIII

A calcium electrode evaluation with 1-sulfo-2,4,6-tricarboxybenzene yielded the following results:

	pH	[Ca <sup>+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	7
0.03	7	5.8
0.03	10	5.0
0.06	7	4.6
0.06	10	3.8

### EXAMPLE XIX

A calcium electrode evaluation with 1-hydroxy-2,4-disulfobenzene yielded the following results:

	pH	[Ca <sup>+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	7
0.03	7	5
0.03	10	5
0.06	7	4.7
0.06	10	4.2

### EXAMPLE XX

A calcium electrode evaluation with 1,3,5-trihydroxy-2-carboxybenzene yielded the following results:

	pH	[Ca <sup>+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	7
0.03	10	4.4
0.06	7	3.5
0.06	10	2.3

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### EXAMPLE XXI

A calcium electrode evaluation with 1,2,3-trihydroxy-5-carboxybenzene yielded the following results:

	pH	[Ca <sup>+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	7
0.03	7	4.5
0.03	10	2.8
0.06	7	1.1
0.06	10	0.6

### EXAMPLE XXII

A calcium electrode evaluation with Na(1-hydroxy-2-carboxybenzene) yielded the following results:

	pH	[Ca <sup>+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	7
0.03	7	5.2
0.03	10	6
0.06	7	5.8
0.06	10	5.5

### EXAMPLE XXIII

A calcium electrode evaluation with 1,4-dihydroxy-2,5-disulfobenzene yielded the following results:

	pH	[Ca <sup>+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	7
0.03	7	5.2
0.03	10	4.5
0.06	7	6.0
0.06	10	2.6

### EXAMPLE XXIV

A calcium electrode evaluation with 1-hydroxy-2,4,6-tricarboxybenzene yielded the following results:

	pH	[Ca <sup>+</sup> ] grain/gal. (residual)
Weight sequestrant:		
0	7	7
0.03	7	5
0.03	10	5
0.06	7	5.3
0.06	10	4.7

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 affects 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 agents described and illustrated above. Ordinarily, this 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<sub>3</sub> in such solvents as HCl, H<sub>2</sub>SO<sub>4</sub>, SO<sub>2</sub> or H<sub>2</sub>O. Carboxy groups are formed by adding previously carboxylated materials to aromatics by oxidation of methyls or chloromethyls with H<sub>2</sub>O<sub>2</sub>, 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, 3,6-dihydroxybenzene-1,2,4,5-tetracarboxylic acid and related compounds can be prepared by the procedure described in detail in *J. U. Nef Annalen der Chemie* 237, 1-35 (1887).

A similar synthetic route is described in *H. von Pechmann & Ludwig Wolmann, Berichte der Deutschen Chemischen Gesellschaft* 30, 2569-71 (1898).

Other sequestering agents which come within the novel class of the sequestering agents of this invention such as phenol-2,4,6-trisulfonic acid can be prepared according to the procedure described in *Senhofer, Ann* 170, 110.

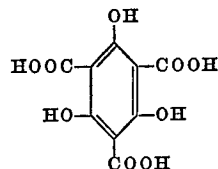
A suitable reaction synthesis for the preparation of 1,3,5-trihydroxy-2,4,6-benzene trisulfonic acid is described in *Pollak, Gebauer-Füllnegg Monats helfe für Chemie* 47, 544-552.

The foregoing description and examples describe and illustrate certain operable hard preferred embodiments of the present invention. It is not intended that the invention should be so limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of this invention.

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 salts and ammonium salts of a polyfunctionally-substituted aromatic compound having the formula



and wherein the proportion by weight of the organic synthetic detergent to the sequestering agent is in the range of 20:1 to 1:20.

2. A detergent composition of claim 1 wherein the sequestering agent is the trisodium salt of 1,3,5-trihydroxy-2,4,6-benzene tricarboxylic acid.

#### References Cited

##### UNITED STATES PATENTS

2,264,103	11/1941	Tucker	210-23
3,692,684	9/1972	Hentschel	252-89

##### OTHER REFERENCES

Martell et al.: "Chem. of the Metal Chelate Compounds," Chap. 4 (Influence of the Structure of the Chelating Agent); copyright 1952 (3rd printing), Prentice-Hall, Inc., N.J., p. 136.

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U. S. C. X.R.

252-545, 546, 547, 550, 551, 555, 558

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,812,044 Dated May 21, 1974

Inventor(s) Daniel S. Connor & 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. 4, line 14, delete "1,3,5-tris[carboxyethylether]-2-carboxybenzene" and insert therefor --1,3,5-tris[carboxymethyl-ether]-2-carboxybenzene --.

Col. 4, line 72, delete "oil" and insert therefor -- soil --.

Col. 5, line 18, delete "appropriates" and insert therefor -- appropriate --.

Col. 8, line 40, after "detergents include:" insert -- dimethyldodecylamine oxide --.

Col. 9, line 36, delete "carboxyl" and insert therefor -- carboxy --.

Col. 9, line 73, delete "2" and insert therefor -- 3 --.

Col. 11, line 26, delete "alkaline" and insert therefor -- alkane --.

Col. 11, line 71, delete "monohydride" and insert therefor -- monohydric --.

Col. 12, line 30, delete "sulfones" and insert therefor -- sulfonates --.

Col. 12, line 33, delete "ethoxytetradecylsulfonate" and insert therefor -- methoxydecanesulfonate --.

Col. 14, line 48, delete "breaker" and insert therefor -- beaker --.

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Page 2

Patent No. 3,812,044

Dated May 21, 1974

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

Page 2

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

Col. 15, line 22, delete "fritted" and insert therefor  
-- ritted --.

Col. 15, line 41, delete "thef ollowing" and insert therefor  
-- the following --.

Col. 16, line 11, delete "them aterial" and insert therefor  
-- the material --.

Col. 16, line 21, delete "[Ca<sup>+</sup>]" and insert therefor  
-- [Ca<sup>+</sup>] --.

Col. 17, line 66, delete "Na<sub>2</sub>-1,2,3,5-" and insert therefor  
-- Na<sub>2</sub>-1,3,5- --.

Col. 17, line 74, delete "50" and insert therefor -- 50% --.

Col. 18, line 12, delete "sulfoxide" and insert therefor  
-- suboxide --.

Col. 18, line 51, insert "Weight sequestrant:" over first  
column of figures.

Col. 21, line 24, delete "hard" and insert therefor -- and --.

Signed and sealed this 12th day of November 1974.

(SEAL)

Attest:

McCOY M. GIBSON JR.  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents