ABSTRACT

Built detergent compositions comprising an organic synthetic detergent and, as a detergency builder, the biodegradable water-soluble salts of a mixture of benzene pentaconoxylic acid and benzene hexacarboxylic acid in a proportion by weight of detergent to builder in the range of 5:1 to 1:20. The water-soluble salts of benzene pentaconoxylic acid and benzene hexacarboxylic acid are present as a mixture in a ratio of from 1:10 to 2:1.
3,844,982

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BUILT DETERGENT COMPOSITION

This application is a continuation-in-part of application Ser. No. 879,612, filed Nov. 24, 1969 and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a detergent composition which contains an organic water-soluble synthetic detergent and a degreaser builder. Such compositions are generally referred to in the art as built detergent compositions. When a large proportion of the detergent builder is used in relation to the detergent, the composition is characterized as a heavy duty composition intended primarily for laundering heavily soiled fabrics which ordinarily comprise a household laundry. Detergent compositions which contain relatively lesser amounts of builder are "light-duty" compositions intended for lightly soiled fabrics and so-called fine fabrics and woolens.

2. BACKGROUND AND DESCRIPTION OF PRIOR ART

The use of detergency builders as adjuncts to organic water-soluble synthetic detergents and the property which some materials have of improving the overall detergency performance of such detergents are well known phenomena. Polyphosphates are the most commonly used builders and within this class alkali metal, e.g., sodium and potassium, polyphosphates and pyrophosphates are most preferred.

In aqueous solutions, however, polyphosphates are known to hydrolyze to pyrophosphates and orthophosphates. Pyrophosphates have a tendency to form undesirable, insoluble precipitates with water hardness minerals such as calcium and magnesium which tend to deposit on fabrics. In this respect, they are similar to other well-known precipitating builders such as carbonates, soaps and mellitic acid. This latter compound, which is an essential ingredient in this invention, is described in U.S. Pat. No. 2,264,103 issued to Nathaniel Beverly Tucker. Mellitic acid (common nomen of benzene hexacarboxylic acid) does perform satisfactorily at certain usage levels and water hardness contents. However, built detergent formulations are commonly formulated to be used over a wide part of the country and, oftentimes, over a wide part of the world. Because of this fact, a very broad range of water hardness will be encountered which in itself dictates that a built detergent composition must be effective at both extremes of water hardness contents. Detergent compositions containing a water-soluble salt of mellitic acid as the builder component perform satisfactorily from a non-precipitating standpoint at normal usage levels in areas where the water hardness content of the water is relatively low. However, where the water is relatively hard, water-insoluble calcium and magnesium salts of mellitic acid are formed which, as stated above, precipitate onto the laundry. The effect of this is that the laundry, even after receiving a rinse, retains the aforementioned precipitates and, as a consequence, has a faded appearance and a chalky feel. Usage of an unduly large amount of a mellitic acid salt-containing detergent composition can be used to obtain satisfactory cleaning, but is objectionable to the average consumer because of economical reasons.

As a result of the inability of mellitic acids salts to perform properly in hard water areas, its inclusion into a detergent composition formulated for a wide area distribution has been necessarily avoided.

In addition to the above deficiency of the polyphosphates, some concern has been expressed that certain algae in bodies of water resort to phosphorous-containing materials for nutritional value. Phosphorus-free builder compounds, though, such as mellitic acid would be free of such criticism.

SUMMARY OF THE INVENTION

It has now been discovered that a mixture of the water-soluble salts of benzene pentacarboxylic acid and benzene hexacarboxylic acid unexpectedly meets the foregoing requirements for an effective phosphorus-free substantially biodegradable detergency builder that can be effectively used in detergent compositions useful over a wide range of water hardnesses.

Accordingly, the present invention relates to built detergent compositions, consisting essentially of: (a) an organic water-soluble synthetic detergent; and (b) as a degreaser builder, the substantially biodegradable phosphorus-free water-soluble salts of a mixture of benzene pentacarboxylic acid and benzene hexacarboxylic acid in the proportion by weight of from 1:10 to 2:1, respectively, and wherein the proportion by weight of the detergent to the degreasing builder is from 5:1 to 1:20. The water-soluble cation of the poly-carboxylic acids can be alkali metal such as sodium or potassium, ammonium or substituted ammonium such as tetraalkylammonium in which the alkyl group is methyl, ethyl, propyl, or isopropyl.

SPECIFIC DESCRIPTION OF THE INVENTION

The preferred biodegradable builders are sodium or potassium salts of benzene penta-and hexacarboxylic acid.

Benzene pentacarboxylic acid, having the formula \( \text{C}_9\text{H}_6\text{O}_{10} \) and molecular weight of 298, has the following formula:

\[ \text{HOOC} \]
\[ \text{HOOC} \]
\[ \text{COOH} \]

This acid is available commercially as colorless crystals having a melting point of 228°C. Additional properties of the acid and the preparation thereof is found on page 329 of the Dictionary of Organic Compounds (Heilbron-Oxford University Press, 1965), Volume 1, (A-Chlop).

Benzene hexacarboxylic acid is commonly referred to as mellitic acid. Mellitic acid, \( \text{C}_9\text{H}_6\text{O}_{12} \), molecular weight 342.1, has the following formula:

\[ \text{HOOC} \]
\[ \text{HOOC} \]
\[ \text{COOH} \]
\[ \text{COOH} \]
\[ \text{COOH} \]
This commercially available acid has colorless needles having a melting point of 287°C, which are soluble in water or alcohol. Its aluminum salt occurs in brown coal as honesmite. This acid is further described together with properties and preparations on Page 2067 of Dictionary of Organic Compounds (Heilbron - Oxford University Press, 1965), Volume 4, (J-Phloi).

Unexpectedly it has been found that a mixture of the benzene penta- and hexachloroxylic acid salts when incor-porated into a detergent composition results in a detergent composition that is satisfactorily useful in waters possessing a broad range of water hardness contents. In particular, a detergent composition containing a mixture of the above mentioned poly carbonate acid salts performs satisfactorily in relatively hard water, while another detergent composition containing the same total amount of builder in the form of a benzene hexachloroxylic acid salt does not perform satisfactorily at the same usage level. By "not performing satisfactorily" is meant that clothing continually washed with a solely benzene hexachloroxylic acid salt built detergent composition possesses a rough chalky feel and appears to be faded. Actually the faded appearance is primarily due to the deposition of a lightly colored precipitate from the wash water onto the clothing. This precipitate persists even after rinsing with water.

For some reason not fully understood, the addition of a benzene pentachloroxylic acid salt to the benzene hexachloroxylic acid salt significantly decreases the amount of precipitate that will form from a wash solution containing the same. It has been found that a mixture of benzene pentachloroxylic acid salt to benzene hexachloroxylic acid salt of from 1:10 to 2:1 on a weight basis provides a builder mixture that when formulated into a detergent composition at a level hereinafter disclosed is eminently satisfactory for a wide range of washing conditions. A ratio below 1:10 does provide some benefit but is not significant enough to be observed by most consumers. A mixture ratio above 2:1 is avoided in part because no added advantages accrue with respect to the prevention or modification of precipitates. Additionally, the benzene hexachloroxylic acid salt is a more effective cleaning component with respect to removing soil from laundry than is the benzene pentachloroxylic acid salt. Therefore, mixture ratios above 2:1 of the benzene penta- to benzene hexachloroxylic acid salt adversely have an effect on the aforementioned cleaning power. The aforementioned mixture ratio of 1:10 to 2:1 possesses the best performance properties with respect to precipitates prevention and cleaning ability. Preferably a mixture ratio of 1:5 to 1:1 on a weight basis is used in this invention.

The organic water-soluble synthetic detergent compounds with which the biodegradable builder compounds of the present invention can be used include anionic, nonionic, zwitterionic, or amphoteric detergents or mixtures of such classes of detergents. Each of these classes is illustrated below.

A. Anionic Soap and Non-Soap Synthetic Detergents

This class of detergents includes ordinary 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 (C₈₋₁₇ 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 U.S. Pat. Nos. 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 C₁₃₄ 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 ethoxylate 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.

Anionic phosphate sulfactants 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—SO₃H, —SO₃H₂, and —CO₂H. Alkyl phosphate esters such as (R—O)₅PO₂H and ROPO₂H₂ 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 alkoxy oxide units, e.g., ethylene oxide units. Formulae for these modified phosphate anionic detergents are:

\[ \text{R—O—(C₂H₄O)₅PO₂H} \]

or

\[ \text{R—O—(C₂H₄O)₅PO₂H} \]

where R is a long chain alkyl group.
A preferred class of anionic organic detergents are the \( \beta \)-alkoxyalkane sulfonates. These compounds have the following formula:

\[
\text{OR}_2 \quad \text{H} \\
\text{R}_1 - \begin{array}{c}
\text{CH} \\
\text{CH}_2 \text{SOM}
\end{array}
\]

where \( R_1 \) is a straight chain alky1 group having from 6 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.

Specific examples of \( \beta \)-alkoxyalkane sulfonates or alternatively 2-alkyloxyalkane-1-sulfonates, utilizable herein to provide superior cleaning and whitening levels under household washing conditions include potassium \( \beta \)-methoxydecanesulfonate, sodium \( \beta \)-methoxy-tridecane sulfonate, potassium \( \beta \)-ethoxytetradecylsulfonate, sodium \( \beta \)-isopropoxyhexadecylsulfonate, lithium \( \beta \)-butoxytetradecylsulfonate, sodium \( \beta \)-methoxyoctadecylsulfonate, and ammonium \( \beta \)-propoxydodecylsulfonate. Other synthetic anionic detergents useful herein are alkyl ether sulfates. These materials have the formula \( R(O\text{C}_2\text{H}_4\text{O})_{x}\text{SOM} \) wherein \( R \) is alkyl or alkenyl or 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 of the present invention are condensation products of ethylene oxide and monohydroric 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 6, molar proportions of ethylene oxide and the resulting mixture of molecular species, having, for example, an average of 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; and sodium tallow alkyl hexaethylene 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 Pat. No. 3,332,876 to Walker (July 25, 1967) incorporated herein by reference.

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 Pat. Nos. 2,486,921; 2,486,922; and 2,396,278.

Additional examples of anionic, non-soap, synthetic detergents, which come within the terms of the present invention, are the compounds which contain two ani-
omorphic functional groups. These are referred to as di-anionic detergents. Suitable di-anionic detergents are the disulfonates, disulfonates, or mixtures thereof which may be represented by the following formulæ:

$$R(\text{SO}_3\text{H})_2M_2, \ R(\text{SO}_3\text{H})_2M, \ R(\text{SO}_3\text{H})_2(\text{SO}_4)\text{M}_2,$$

where $R$ is an acyclic aliphatic hydrocarbyl group having 15 to 20 carbon atoms and $M$ is a water-solubilizing cation, e.g., the C15 to C20 disodium 1,2-alkyl disulfates, C15 to C20 dipotassium-1,2-alkyl disulfonates or disulfates, disodium 1,9-hexadecyl sulfates, C15 to C20 disodium-1,2-alkyl disulfonates, disodium 1,9-stearyldisulfates and 6,10-octadecyldisulfates.

The aliphatic portion of the disulfonates or disulfonates is generally substantially linear, desirable, among other reasons, because it imparts desirable biodegradable properties to the detergent compound.

The water-solubilizing cations include the customary cations known in the detergent art, i.e., the alkalai metals, and the alkaline earth metals, as well as other metals in group II A, II B, III A, III B, IV A and IV B of the Periodic Table except for the exception of water-solubilizing cations are sodium or potassium. These di-anionic detergents are more fully described in British Letters Pat. No. 1,151,392 which claims priority on an application made in the U.S. (No. 564,556) on July 12, 1966.

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 U.S. Pat. Nos. 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-octadeccysulfo succinaminate; tetrasodium N-(1,2-dicarboxyethyl)-N-octadeccyl-sulfo-succinamate; di-ethyl ester of sodium sulfoacetic acid; diethyl ester of sodium sulfoacetic acid; dioxethy ester of sodium sulfoacetic acid.

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 can be produced by the sulfonation of &alpha; olefin by means of a complexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which may 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 &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 &alpha;-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 sulfonates depending upon the reaction conditions, proportions of reactants, the nature of the starting olefins and impurities in the olefin stock and side reaction during the sulfonation process.

A specific anionic detergent which has also been found excellent for use in the present invention is described more fully in the Pat. No. 3,332,880 of Phillip F. Pfau and Adriaan Kessler, issued July 25, 1967, titled Detergent Composition, the disclosure of which is herein incorporated by reference.

B. Nonionic Synthetic Detergents

Nonionic synthetic detergents may be broadly defined as compounds produced by the condensation of alkyene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or 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 insolvency, has a molecular weight of 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, disobutylene, 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 percent 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 di-isooctylphenol condensed with 15 moles of ethylene oxide.

(5) A detergent having the formula \( R^1 R^2 R^3 R^4 \rightarrow O \) (amine oxide detergent) wherein \( R^4 \) 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 \( R^4 \) 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, dimethyldodecylamine oxide, ethylmethyldodecylamine oxide, cetyltrimethylammonium oxide, cetyltrimethylammonium oxide, diethyldodecylamine oxide, diethylaminoethylamine oxide, dipropyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, bis-(2-hydroxyethyl)-3-dodecyl-1-hydroxypropylamine oxide, (2-hydroxypropyl)methyltridecylamine oxide, dimethyloleylamine oxide, dimethyl-(2-hydroxydecyl)amine oxide, and the corresponding decyl, hexadecyl and octadecyl homologs of the above compounds.

6. A detergent having the formula \( R^1 R^2 R^4 \rightarrow O \) (phosphate 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 \( R^4 \) 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 phosphate oxide detergents include: dimethyldodecylphosphate oxide, dimethyldodecylphosphate oxide, ethylmethyldodecylphosphate oxide, cetyltrimethylphosphate oxide, dimethyldodecylphosphate oxide, cetyltrimethylphosphate oxide, dimethyldodecylphosphate oxide, diethyldodecylphosphate oxide, bis-(2-hydroxyethyl)-dodecylphosphate oxide, bis-(2-hydroxypropyl)methyltridecylphosphate oxide, dimethyloleylphosphate oxide, and dimethyl-(2-hydroxydecyl)phosphate oxide and the correspond-

ing decyl, hexadecyl, and octadecyl homologs of the above compounds.

7. A detergent having the formula

\[
\begin{align*}
&O \\
&\text{R}^1 \text{R}^2 \text{R}^4 \text{R}^5 \text{R}^6 \\
&(\text{soxide detergent}) \text{ where } \text{R}^1 \text{ is an alkyl radical containing from about 10 to about 28 carbon atoms, from 0 to about 5 ether linkages and from 0 to about 2 hydroxyl substituents at least one moiety of } \text{R}^1 \text{ being an alkyl radical containing 0 ether linkages and containing from about 10 to about 18 carbon atoms, and wherein } \text{R}^2 \text{ is an alkyl radical containing from 1 to 3 carbon atoms and from one to two hydroxyl groups: octadecyl methyl sulfosuccinate, dodecyl methyl sulfosuccinate, tetracryl methyl sulfosuccinate, 3-hydroxytridecyl methyl sulfosuccinate, 3-hydroxy-4-dodecylbutyl methyl sulfosuccinate, octadecyl 2-hydroxypenyl sulfosuccinate, dodecethylethyl sulfosuccinate.}
\end{align*}
\]

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.

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-(trimethylamino)octadecanoate, disodium 3-(N-carboxymethyl)dodecylamino)-propene-1-sulfonate, disodium octadecyliminodiacetate, sodium 1-carboxymethyl-2-undecyl-imidazole, and sodium N,N-bis(2-hydroxyethyl)-2-sulfato3-dodecyloxypropylamine.

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-hexadecylammonio)-2-hydroxypropene-1-sulfonate, 3-(N,N-dimethyl-N-hexadecylammonio)-propene-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 dodecylphosphonate, ethyl 3-(N,N-dimethyl-N-dodecylammonio)propylphosphonate, 3-(P,N-dimethyl-P-dodecylphosphono)-propene-1-sulfonate, 2-(S-methyl-S-tetradecylsulfonio)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-octodecylammonio)-2-hydroxypropane-1-sulfonate. Some of these detergents are described in the following Pat. Nos: 2,129,264; 2,178,353; 2,774,786; 2,813,898; and 2,828,332.

A detergent composition prepared according to the present invention contains as essential ingredients (a) a detergent ingredient and (b) a builder ingredient. In simplest terms, a composition can contain a single detergent compound and the biodegradable builder mixture of benzene pent- and hexacarboxylic acid salts. On the other hand, it frequently is desirable to formulate a detergent composition in which the detergent ingredient consists of composition of detergent compounds selected from the foregoing classes. Thus, for example, the active ingredient can consist of a mixture of two or more anionic detergents; or a mixture of an anionic detergent and a nonionic detergent; or, by way of another example, the active detergent can be a ternary mixture of two anionic detergents and a zwitter-ionic detergent.


According to these procedures, in the process of biodegradation an organic molecule such as mellitic acid is broken down enzymatically into simpler substances. For materials containing carbon and hydrogen the theoretical ultimate end products are CO₂, water and metabolites. It is possible to measure the extent of degradation of mellitic acid by comparing the amount of oxygen utilized and the actual amount of CO₂ produced to the appropriate calculated stoichiometric values. These tests surprisingly indicated essentially complete degradation of mellitic acid.

Similarly, the same tests indicate that benzene penta-carboxylic acid is essentially completely degradable.

The present invention can find useful application by practicing a partial replacement of the biodegradable benzene penta- and hexacarboxylic acid salt mixture for traditional, commonly used detergency builders. Thus, for example, the portion of the complete detergent formulation that functions as a builder can likewise be composed of a mixture of builder compounds. For example, the substantially biodegradable builder compounds described herein can be mixed together with other water-soluble inorganic alkaline builder salts such as sodium tripolyphosphate or potassium pyrophosphate or water-soluble organic builder salts such as watersoluble salts of nitrotriacetic acid, ethylenediaminetetraacetic acid, ethane-1-hydroxy-1,1-diphosphonic acid. Still further, the builder component of a complete formulation can consist of ternary mixtures of the several types of builder compounds. In this way, it is possible to obtain a balance between the mixture of the biodegradable salts of benzene pent- and hexacarboxylic acid and such builders as sodium tripolyphosphate and the like.

Water-soluble inorganic alkaline builder salts which can be used in this invention in combination with the mixture of the biodegradable salts of benzene pent- and hexacarboxylic acid are alkaline metal carbonates, phosphates, polyphosphates, bicarbonates and silicates. Ammonium and substituted ammonium salts of these materials can also be used. Specific examples of suitable salts are sodium tripolyphosphate, sodium carbonate, sodium tetraborate, sodium and potassium pyrophosphate, sodium and ammonium bicarbonate, potassium tripolyphosphate, sodium hexametaphosphate, sodium sesquicarbonate, sodium orthophosphate and potassium bicarbonate.

Examples of suitable organic alkaline detergent builder salts are: (1) Water-soluble aminopolycarboxylates, e.g., sodium and potassium ethylenediaminetetraacetates, nitrotriacetic acid, and N-(2-hydroxyethyl)-nitrolactiactes; (2) Water-soluble salts of carboxylic acid, e.g., sodium and potassium phytates — See Pat. No. 2,739,942; (3) Water-soluble, polyphosphonates, including specifically, sodium, potassium and lithium salts of ethane-1-hydroxy-1,1-diphosphonic acid, sodium, potassium and lithium salts of methylene diphosphonic acid, sodium, potassium and lithium salts of ethylene diphosphonic acid, and sodium, potassium and lithium salts of ethane-1,1,2-triphosphonic acid. Other examples include the alkali metal salts of ethane-2-carboxy-1,1-diphosphonic acid, hydroxymethanedi-phosphonic acid, carbonyldiphosphonic acid, ethane-1-hydroxy-1,1,2-triphosphonic acid, ethane-2-hydroxy-1,1,2-triphosphonic acid, propane-1,1,2,3-tetraphosphonic acid, and propane-1,2,2,3-tetraphosphonic acid; (4) Water-soluble salts of polycarboxylate polymers and copoly- mers as described in the copending application of Francis L. Diehl, application Ser. No. 269,359, filed Apr. 1, 1963, now Pat. No. 3,308,067. Specifically, a detergent builder material comprising a water-soluble salt of a polymeric aliphatic polycarboxylic acid having the following structural relationships as to the position of the carboxylate groups and possessing the following prescribed physical characteristics: (a) a minimum molecular weight of about 350 calculated as to the acid form; (b) an equivalent weight of about 50 to about 80 calculated as to acid form; (c) at least 45 mole percent of the monomeric species having at least 2 carboxyl radicals separated from each other by not more than 2 carbon atoms; (d) the site of attachment of the polymer chain of any carboxyl-containing radical being separated by not more than 3 carbon atoms along the polymer chain from the site of attachment of the next carboxyl-containing radical. Specific examples are polymers of itaconic acid, aconitic acid, maleic acid, mesaconic acid, fumaric acid, methylene malonic acid, and citraconic acid and copolymers with themselves and other compatible monomers such as ethylene; and (5) mixtures thereof.

Mixtures of organic and/or inorganic builders can be used in combination with the builder mixture of the present invention and are generally desirable. One such auxiliary mixture of builders is disclosed in Pat. No. 3,920,121, e.g., ternary mixtures of sodium tripoly-
phosphate, sodium nitrotriacetate and trisodium ethane-1,1-dihydroxy-1,1-diphosphonate. The above described builders can also be utilized singly in this invention.

In addition, other builders can be used satisfactorily such as the water-soluble salts of citric acid, pyromelitic acid, oxydectic acid, and oxydissuccinic acid.

It is preferred to practice the present invention with compositions in which the proportion by weight of detergent to builder mixture is in the range of 2:1 to 1:10.

As a result of the present invention, it is possible to provide a complete substantially biodegradable built detergent composition by selecting a biodegradable detergent from those mentioned above and combining it with the biodegradable builder compounds of the present invention in the proportion described above. An illustrative and preferred embodiment is a biodegradable built detergent composition consisting essentially of (A) a detergent selected from alkali metal straight-chain alkyl benzene sulfonate, the alkyl group having from 8 to 24 carbon atoms, preferably 8 to 18, and an alkali metal olefin sulfonate having 8 to 24 carbon atoms, preferably 8 to 18, and (B) as a detergent builder, the biodegradable phosphorus-free water-soluble alkali metal salts of the benzene penta- and hexacarboxylic acid mixture, the proportion by weight of said detergent to said builder mixture being in the range of 5:1 to 1:20, and preferably 2:1 to 1:10. The preferred detergents are sodium β-methoxy hexadecane sulfonate, sodium salt of the sulfonation product of the condensation product of one mole of tallow alcohol with three moles of ethylene oxide, sodium decyl benzene sulfonate, sodium tridecyl benzene sulfonate, and sodium dodecene-1-sulfonate, sodium tetradecene-1-sulfonate, and sodium hexadecene-1-sulfonate. Sodium salt is the preferred salt of the benzene penta- and hexacarboxylic acids.

The built detergent compositions of the present invention can be formulated and prepared into any of the several commercially desirable solid and liquid formulations including, for example, granules, flakes, tablets, and water-based and alcohol-based liquid detergents, and the like. A special embodiment of this invention is a built liquid detergent composition containing a detergent and a builder mixture is the by weight ratio (detergent to builder mixture) of 2:1 to about 1:5; preferably 2:1 to about 1:3. Potassium salts are especially useful in liquid formulations due to the increased solubility characteristics of potassium over sodium.

The built detergent compositions of the present invention perform at their maximum level in a washing solution which has a pH in the range of from about 8 to about 12. Within this broad range, it is preferred to operate at a pH of from about 8.5 to 11. The detergent and the builder mixture can be neutralized to a degree sufficient to insure that this pH prevails in any washing solution. If desired, other alkaline materials can be added to the complete formulation to provide for any pH adjustments desired. A preferred embodiment is to have the detergent composition whether in solid or liquid form provide a pH in the aforementioned ranges at the usual recommended usage levels.

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. Tarnish inhibitors such as benzotriazole or ethylenediamine can also be added in amounts up to about 3 percent. Fluorescers, and brighteners, enzymes, 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 percent by weight of the total composition. Alkali metal, preferably potassium and sodium silicates, are preferred having a weight ratio of SiO₂ : Na₂O of from about 1:0.1 to 2:8:1. (M refers to sodium or potassium). Sodium silicate having a ratio of SiO₂ : Na₂O 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 hydro trope is desirable. Suitable hydrotopes are water-soluble alkali metal salts of toluenesulfonate, benzenesulfonate, and xylenesulfonate. Preferred hydrotopes are potassium or sodium toluenesulfonates. The hydro trope salt may be added at levels up to about 12 percent. While a hydro trope 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.

The following compositions, in which the percentages are by weight, will serve to illustrate, but not limit, the invention. Each of the compositions in the following Examples give in solution a pH within the desired range of from about 8 to about 12.

**EXAMPLE A**

A granular built detergent composition according to this invention has the following formulation:

<table>
<thead>
<tr>
<th>%</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>18%</td>
<td>Sodium alkyl benzene sulfonate in which the alkyl is a straight chain dodecyl radical</td>
</tr>
<tr>
<td>25%</td>
<td>Pentasodium salt of benzene pentacarboxylic acid</td>
</tr>
<tr>
<td>25%</td>
<td>Pentasodium salt of benzene hexacarboxylic acid</td>
</tr>
<tr>
<td>15%</td>
<td>Sodium sulfate</td>
</tr>
<tr>
<td>7%</td>
<td>Sodium silicate (ratio of SiO₂ : Na₂O of 2:1)</td>
</tr>
<tr>
<td>10%</td>
<td>Water</td>
</tr>
</tbody>
</table>

This heavily built detergent composition is especially valuable for laundering heavily soiled clothes.

The straight chain dodecyl benzene sodium sulfonate in the preceding composition can be replaced on an equal weight basis by either branched chain sodium dodecyl benzene sulfonate, sodium tallow alkyl sulfate, sodium coconut oil alkyl sulfate, sodium olefin sulfonate as described in the specification derived from alpha olefins having an average of 14 carbon atoms in the molecule, or a mixture of straight chain dodecyl benzene sodium sulfonate and sodium tallow alkyl sulfate on an equal weight basis.

**EXAMPLE B**

Another effective granular detergent composition has the following formulation:

<table>
<thead>
<tr>
<th>%</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4%</td>
<td>Straight chain sodium tridecyl benzene sulfonate</td>
</tr>
<tr>
<td>4%</td>
<td>Sodium tallow alkyl sulfate (anionic detergent)</td>
</tr>
</tbody>
</table>
In this Example, the total active detergent of 10 percent can be totally the nonionic species. In addition, the 2 percent dodecyl methyl sulfoxide can be replaced by the product of a condensation reaction between dodecyl phenol and 5 moles of ethylene oxide per mole of dodecyl phenol, or by 3-(dodecyl(dimethylammonio)-2-hydroxy propane-1-sulfonate.

The sodium salts of the builders can be added as the salt or they can be present as the free acid neutralized in situ to the salt form.

The effectiveness of the mixture of sodium salts of the benzene penta- and hexacarboxylic acids builder was demonstrated by a detergent test referred to as a fabric softness/deposition test. This test generally involves a procedure of washing laundry with the detergent composition to be tested.

The laundry pieces are washed, rinsed, graded, and the cycle is repeated several times. Grading of fabric deposition is made on a scale of 0 to 5 where 0 represents no visible precipitate deposit. Softness is also reflected in this grading in that the deposit of precipitates on the laundry samples will adversely affect its feel.

**EXAMPLE C**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentasodium salt of benzene pentacarboxylic acid</td>
<td>12.5%</td>
</tr>
<tr>
<td>Hexasodium salt of benzene hexacarboxylic acid</td>
<td>12.5%</td>
</tr>
<tr>
<td>Sodium TE₅S (sulfonation product of the condensation product of one mole of tallow alcohol with 3 moles of ethylene oxide)</td>
<td>13.8%</td>
</tr>
<tr>
<td>Sodium LAS (linear C₃₋₅ alky benzene sulfonate)</td>
<td>11.2%</td>
</tr>
<tr>
<td>Sodium silicate (SiO₂/Na₂O ratio = 2.0)</td>
<td>10.0%</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>25.0%</td>
</tr>
<tr>
<td>Balance (water)</td>
<td>15.0%</td>
</tr>
</tbody>
</table>

A commercially available automatic washer was filled with 16 gallons of water having a temperature of 100°F and hardness of 14 grains. One and one-fourth cups of the above detergent composition was next added. The contents of the washer was agitated for 30 seconds to dissolve the detergent composition. Thereafter, 2 pounds of ordinary soiled laundry plus a dark colored cotton wash cloth were added and washed for 6 minutes. The ordinary soiled laundry in addition to the wash cloth was used in this example as a source of soil and in order to give a full load. For purposes of this example, the originally soiled laundry was not evaluated at the end of the wash cycles. After a cold rinse, the originally soiled laundry and wash cloth were spun, removed, and line dried.

This procedure was repeated 9 times and then the wash cloth evaluated. No “fading effect” was noticeable, thereby indicating that enough precipitates were not deposited on the wash cloth to change the color thereof. A rating of 1 was recorded for the fabric deposition test. This compared favorably with results obtained with a commercially available laundry detergent.

**EXAMPLE D**

To show the unexpected advantage that a mixture of salts of benzene penta- and hexacarboxylic acids has over the benzene hexacarboxylic acid salt, the following detergent composition was tested under the same washing conditions as in Example C:

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium salt of benzene hexacarboxylic acid</td>
<td>25.0%</td>
</tr>
<tr>
<td>TE₅S (as in Example C)</td>
<td>13.8%</td>
</tr>
<tr>
<td>LAS (as in Example C)</td>
<td>11.2%</td>
</tr>
<tr>
<td>Sodium silicate (SiO₂/Na₂O ratio = 2.0)</td>
<td>10.0%</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>25.0%</td>
</tr>
<tr>
<td>Balance (water)</td>
<td>15.0%</td>
</tr>
</tbody>
</table>

After 10 washings the softness of the wash cloth of this example was comparable to the wash cloth washed with the composition of Example C. Softness is very difficult to measure and the full difference in softness between the mixture built composition of this invention and the mellitic acid salt-built composition could not be expected to be noticeably different after only 10 washings. However, the originally dark colored wash cloth of this example was noticeably lighter in color indicating that precipitates had been deposited. The fabric deposition rating of 4 indicated that this composition was unacceptable and measurably inferior to the formulation of this invention embodied, for example, in Example C.

Other suitable compositions of this invention are:

**EXAMPLE E**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentasodium salt of benzene pentacarboxylic acid</td>
<td>15.0%</td>
</tr>
<tr>
<td>Hexasodium salt of benzene hexacarboxylic acid</td>
<td>7.5%</td>
</tr>
<tr>
<td>3-(N,N-dimethyl-N- hexa decyl-ammonio)-2- hydroxypropane-1-sulfonate</td>
<td>45.0%</td>
</tr>
<tr>
<td>Sodium silicate (SiO₂/Na₂O ratio = 2.0)</td>
<td>10.0%</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>7.5%</td>
</tr>
<tr>
<td>Water</td>
<td>15.0%</td>
</tr>
</tbody>
</table>

**EXAMPLE F**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentasodium salt of benzene pentacarboxylic acid</td>
<td>5.0%</td>
</tr>
<tr>
<td>Hexasodium salt of benzene hexacarboxylic acid</td>
<td>50.0%</td>
</tr>
<tr>
<td>Sodium tallow soap</td>
<td>5.5%</td>
</tr>
<tr>
<td>Sodium silicate (SiO₂/Na₂O ratio = 2.0)</td>
<td>16.0%</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>13.5%</td>
</tr>
<tr>
<td>Water</td>
<td>10.0%</td>
</tr>
</tbody>
</table>

**EXAMPLE G**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentasodium salt of benzene pentacarboxylic acid</td>
<td>2.0%</td>
</tr>
<tr>
<td>Hexasodium salt of benzene hexacarboxylic acid</td>
<td>60.0%</td>
</tr>
<tr>
<td>TE₅S (as in Example C)</td>
<td>10.0%</td>
</tr>
<tr>
<td>Sodium silicate (SiO₂/Na₂O ratio = 2.0)</td>
<td>8.0%</td>
</tr>
<tr>
<td>Sodium sulfate</td>
<td>10.0%</td>
</tr>
<tr>
<td>Water</td>
<td>10.0%</td>
</tr>
</tbody>
</table>
What is claimed is:

1. A built detergent composition consisting essentially of:
   a. an organic water-soluble synthetic detergent selected from the group consisting of anionic, non-ionic, zwitterionic and ampholytic detergents, or mixtures thereof; and
   b. as a detergency builder, the biodegradable phosphorus-free, water-soluble salts of a mixture of benzene pentacarboxylic acid and benzene hexacarboxylic acid in the proportion by weight of 1:1, respectively, the cation forming the watersoluble salts of said carboxylic acids being selected from the group consisting of alkali metal, ammonium or tetraalkylammonium in which the alkyl group in methyl, ethyl, propyl or isopropyl, and wherein the proportion by weight of the detergent to the detergency builder is from 5:1 to 1:20.

* * * * *