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3,580,852

DETERGENT FORMULATIONS CONTAINING TETRAHYDROFURAN 2,3,4,5 - TETRACAR- BOXYLIC ACID SALTS AS BUILDERS

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10 Claims

ABSTRACT OF THE DISCLOSURE

To obviate eutrophication of water, non-phosphorus detergent builders are provided. These are the water-soluble salts of tetrahydrofuran 2,3,4,5-tetracarboxylic acid (e.g., the tetrasodium salt thereof). Conventional detergent actives may be used with these builders.

This invention relates to novel non-phosphorus builders for use with synthetic detergents and to the resultant washing compositions and their uses.

BACKGROUND

In the manufacture of detergent formulations for laundering and general purpose washing operations, it is common practice to employ detergent builders—substances used in combination with surface-active compounds to aid in cleansing the articles being washed. The polyphosphates, notably sodium tripolyphosphate and tetrasodium pyrophosphate, are the commonly used detergent builders. However, these materials possess certain shortcomings. In the first place, the polyphosphates are susceptible to hydrolysis and degradation in aqueous solutions (Canadian Pat. 737,422). In addition, the phosphorus residues resulting from the widespread use of synthetic detergent formulations containing these phosphorus-containing builders have been said to contribute to eutrophication of rivers, lakes, underground streams, and other bodies of water. ["Detergent Phosphorus Effect on Algae" by Thomas E. Maloney, Journal of the Water Pollution Control Federation, vol. 38, No. 1, pp 38-45 (January 1966)].

To appreciate the magnitude of the problem, it has been estimated that over two billion pounds of salts of condensed phosphates are used in detergents each year in the United States. The phosphorus-containing builders can therefore be properly termed ubiquitous.

The desirability of providing an efficacious detergent builder which does not suffer from the foregoing limitations is deemed to be self-evident.

Accordingly, an object of this invention is to provide efficacious detergent builder systems which are hydrolytically stable and devoid of the eutrophic characteristics exhibited by the polyphosphates and other phosphorus builders. Another object is to provide washing compositions which are devoid of phosphorus-containing builders but which possess the advantageous characteristics of washing compositions which presently contain the polyphosphate builders.

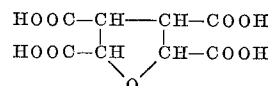
Other important objects of this invention will become

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apparent from the ensuring description and appended claims.

THE INVENTION

In accordance with this invention it has been found possible to reduce—indeed, eliminate—the phosphorus-containing builders in detergent formulations without sacrifice of cleaning power and brightness by employing as a detergent builder a water-soluble salt of tetrahydrofuran 2,3,4,5-tetracarboxylic acid. This acid has the formula:



The preferred salts are the alkali metal salts with potassium and especially sodium being particularly preferred. Other suitable salts include the ammonium and substituted ammonium salts.

The builders of this invention can be advantageously used with a wide variety of detergent actives or surfactants, including those known in the art of anionic, cationic, nonionic, amphotolytic, and zwitterionic detergents as well as any suitable mixture of such detergents. When the resultant washing compositions are used in aqueous washing systems, the cleaning power of the formulation is enhanced in much the same way as when the commonly used polyphosphate builders are employed. Yet the present builder systems are more resistant to hydrolytic degradation than the polyphosphates and do not contribute to the eutrophication problems characteristic of phosphorus-containing builders.

Accordingly, this invention provides, inter alia, a washing composition composed of an organic detergent surfactant suitable for use in water and, as a builder, a water-soluble salt of tetrahydrofuran 2,3,4,5-tetracarboxylic acid, such as the tetrasodium salt, the tetrapotassium salt, the tetralithium salt, the tetraammonium salt, or the like. Although the proportions may be varied to suit the needs of the occasion, the weight ratio of the detergent surfactant to the builder of this invention will normally fall within the range of about 1:10 to about 3:1. The preferred ratios are within the range of about 1:5 to about 3:2.

As noted above, the builder of this invention is generally employed in the form of a water-soluble salt, notably an alkali metal salt, an ammonium salt, or an alkyl ammonium salt. The alkali metal salts can involve one or a mixture of alkali metal salts although the potassium or sodium salts, especially the tetrasodium salt of tetrahydrofuran 2,3,4,5-tetracarboxylic acid, are preferred because of their relatively low cost and enhanced effectiveness. Because the detergent formulation are generally used in alkaline aqueous systems, it is entirely feasible to use in their manufacture either tetrahydrofuran 2,3,4,5-tetracarboxylic acid itself or the partially neutralized free acid. The free acid group(s) will be converted to the appropriate salt at least as soon as the formulation are put to use in an alkaline environment.

For best results, the formulations of this invention will provide in aqueous solution a pH between about 8 and about 12.

As noted above, the builders of this invention can be used with a wide variety of detergents including those classed in the art as anionic detergents, cationic detergents, nonionic detergents, ampholytic (i.e., amphoteric) detergents, and zwitterionic detergents, and any suitable mixture of two or more of these (whether from the same class or from different classes). The anionic surface-active compounds are generally described as compounds which contain hydrophilic and lyophilic groups in their molecular structure and which ionize in an aqueous medium to give anions containing the lyophilic group. Typical of these compounds are the alkali metal salts of organic sulfonates or sulfates, such as the alkali metal alkyl aryl sulfonates and the alkali metal salts of sulfates of straight chain primary alcohols. Sodium dodecylbenzene sulfonate and sodium lauryl sulfate are typical examples of these anionic surface-active compounds (anionic synthetic detergents). For a further amplification of anionic organic detergents which can be successfully built in accordance with this invention, reference should be had to U.S. Pat. No. 3,422,021, particularly the passage extending from column 11, line 47 through column 12, line 15, including the references therein cited, which passage is incorporated herein as if fully set out in this specification.

The cationic detergents are those which ionize in an aqueous medium to give cations containing the lyophilic group. Typical of these compounds are the quaternary ammonium salts which contain an alkyl group of about 12 to about 18 carbon atoms, such as lauryl benzyl dimethyl ammonium chloride. Compounds of this nature are used in detergent formulations for special purposes, e.g., sanitizing and fabric softening.

Nonionic surface-active compounds are generally described as compounds which do not ionize in water solution. Oftentimes these possess hydrophilic characteristics by virtue of the presence therein of an oxygenated chain (e.g., a polyoxyethylene chain), the lyophilic portion of the molecule being derived from fatty acids, phenols, alcohols, amides or amines. Exemplary materials are the poly-(ethylene oxide) condensates of alkyl phenols (e.g., the condensation product formed from one mole of nonyl phenol and ten moles of ethylene oxide), and the condensation products of aliphatic alcohols and ethylene oxide (e.g., the condensation product formed from 1 mole of tridecanol and 12 moles of ethylene oxide). Reference should be had to U.S. Pat. No. 3,422,021, especially the passage extending from column 12, line 16 through column 13, line 26 where a fairly extensive discussion and exemplification of nonionic synthetic detergents is set forth. Inasmuch as the nonionic synthetic detergents set forth in that passage can be successfully built in accordance with this invention, the foregoing passage is incorporated herein as if fully set out in this specification.

The ampholytic surfactants are compounds having both anionic and cationic groups in the same molecule. Exemplary of such materials are derivatives of aliphatic amines which contain a long chain of about 8 to about 18 carbon atoms and an anionic water solubilizing group, e.g., carboxysulfo, sulfo or sulfato. Examples of ampholytic detergents are sodium-3-dodecylaminopropionate, sodium-3-dodecylaminopropane sulfonate, sodium N-methyl taurate, and related substances such as higher alkyl disubstituted amino acids, betaines, thietines, sulfated long chain olefinic amines, and sulfated imidazolidine derivatives.

Zwitterionic synthetic detergents are generally regarded as derivatives of aliphatic quaternary ammonium compounds, 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 one contains an anionic water solubilizing group, e.g., carboxy, sulfo, or sulfato. Examples of compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate and 3-(N,N-di-

methyl-N-hexadecylammonio)-2-hydroxypropane-1-sulfonate. For a still further appreciation of surface-active compounds (synthetic detergents) which can be employed in the practice of this invention reference may be had, for example, to the disclosures of U.S. Pat. 2,961,409 and French Pat. 1,398,753.

The detergent builders of this invention have been found to perform exceedingly well with anionic surface-active compounds and therefore this constitutes a preferred embodiment of the invention.

Another preferred embodiment of this invention is a washing composition comprising an organic detergent surfactant, a water-soluble monovalent salt of tetrahydrofuran 2,3,4,5-tetracarboxylic acid as a builder, and about 2 to about 10 percent by weight based on the total weight of the composition of a water-soluble alkali metal silicate. The cleaning efficacy of these preferred compositions is at least comparable to commercially available household and laundry formulations. Moreover, the soluble silicates of such alkali metals as sodium and potassium serve as effective corrosion inhibitors. In accordance with this preferred embodiment it is desirable to employ one or more silicates of sodium or potassium, or both, wherein the weight ratio of $\text{SiO}_2:\text{M}_2\text{O}$ ($\text{M}=\text{Na}$ or K) is in the range of from about 1:1 to about 2.8:1. Sodium silicates wherein this ratio is in the range of about 1.6:1 to about 2.5:1 are especially useful because of their low cost and effectiveness.

Another preferred embodiment of this invention involves including with the mixture of the organic detergent surfactant and the tetrahydrofuran 2,3,4,5-tetracarboxylic acid builder (e.g., the tetrasodium salt, the tetrapotassium salt, or the mixed sodium-potassium salts thereof) an alkali metal sulfate, preferably sodium sulfate, or an alkali metal carbonate, preferably sodium carbonate, or both. Amounts up to about 60 percent by weight of the total formulation are suitable. These formulations are effective, economical mainstays of finished detergent formulations for laundry, household and/or industrial use. In the preferred compositions the amounts of alkali metal sulfates and/or alkali metal carbonate is generally from about 10 to about 50 percent by weight based on the total weight of the formulation.

Finished detergent formulations of this invention may contain minor amounts of other commonly used materials in order to enhance the effectiveness or attractiveness of the product. Exemplary of such materials are soluble sodium carboxymethyl cellulose or other soil redeposition inhibitors; benzotriazole, ethylene thiourea, or other tarnish inhibitors; perfume; fluoescers; dyes or pigments; brightening agents; enzymes; water; alcohols; other builder additives, such as the water-soluble salts of ethylenediaminetetraacetic acid, N-(2-hydroxyethyl)-ethylenediaminetriacetic acid, nitrilotriacetic acid and N-(2-hydroxyethyl)-nitrilotriacetic acid; and pH adjusters, such as sodium hydroxide and potassium hydroxide. In the built liquid detergent formulations of this invention, the use of hydro-tropic agents may be found efficacious. Suitable hydro-tropes include the water-soluble alkali metal salts of toluene sulfonic acid, benzene sulfonic acid, and xylene sulfonic acid. Potassium toluene sulfonate and sodium toluene sulfonate are preferred for this use and will normally be employed in concentrates ranging up to about 10 or 12 percent by weight based on the total composition.

It will be apparent from the foregoing that the compositions of this invention may be formulated according to any of the various commercially desirable forms. For example, the formulations of this invention may be provided in granular form, in liquid form, in tablet form, or in the form of flakes or powders.

The relative proportions and absolute quantities of the several ingredients of the finished compositions of this invention are susceptible to variation and in most cases

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will vary depending upon such factors as the nature of the particular ingredients being utilized, the end use for which the composition is intended to be put, the relative costs of the ingredients, and the like. For example, the total concentration of the detergent formulations of this invention in water will normally range below about 0.3 percent by weight although it is entirely feasible to utilize higher concentrations where the circumstances warrant or justify the use of higher concentrations. In most cases the aqueous washing solutions of this invention will contain from about 0.05 to about 0.25 weight percent of combined detergent active(s) and builder. The preferred compositions of this invention are phosphorus-free although it may be desired to include therein reduced quantities of conventional phosphorus-containing materials such as sodium tripolyphosphate, tetrasodium pyrophosphate, salts of substituted methylene diphosphonic acids, long chain tertiary phosphine oxides, or the like.

The invention is not to be limited to any particular method of mixing the builder and the detergent. The builder may be mechanically mixed in, crutched in the detergent in the form of a slurry, or dissolved in a solution of the detergent. In addition, the builder system may be admixed with the detergent in any of the forms in which the detergent is manufactured, as well as being added simultaneously or separately to an aqueous solution. In any event, the present builder system is intended to be used with the detergent at the time of application as a cleansing agent.

In order to still further illustrate the practice of this invention, the following examples are presented.

EXAMPLE I

A preferred built formulation of this invention had the following composition:

	Weight percent
Dodecylbenzene sulfonate (a typical linear alkyl benzene sulfonate) -----	20.0
Sodium silicate (ratio $\text{SiO}_2:\text{Na}_2\text{O}$ of 2.4:1) -----	6.0
Sodium carboxymethyl cellulose -----	0.6
Sodium sulfate -----	33.4
Tetrasodium salt of tetrahydrofuran 2,3,4,5-tetracarboxylic acid -----	40.0

The performance of this detergent composition was evaluated by use of the standard Launder-Ometer test. In particular, the formulation was dissolved in water to a concentration of 0.15 weight percent and the pH of the solution adjusted to 9.5 with small amounts of sodium hydroxide solution. The water had a hardness of 150 p.p.m. (Ca/Mg 3/2). Swatches of standard artificially soiled cloth were subjected to the washing procedure. The Launder-Ometer bath temperature was fixed at 120° F. and the washing span was 10 minutes. After washing, the samples were removed from the washing solution and thoroughly rinsed with pure water. After drying, the whiteness of the cloths was ascertained by use of a standard commercially available reflectance photometer. The identical procedure also was employed with a formulation identical to that described above with the exception that sodium tripolyphosphate was used in lieu of the tetrasodium salt of tetrahydrofuran 2,3,4,5-tetracarboxylic acid.

In these tests it was established that the formulation of this invention was at least as effective as the corresponding sodium tripolyphosphate formulation. In particular, the cloths washed with the formulation of this invention had a whiteness of 115 as compared to the whiteness of the same kind of soiled cloths washed in the sodium tripolyphosphate formulation (assigned the value of 100 percent).

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EXAMPLE II

Some illustrative solid heavy duty laundering formulations of this invention are as follows (percentages being weight percentages):

	Percent
Surface-active agent ¹ -----	10-25
Tetrasodium tetrahydrofuran 2,3,4,5 - tetracarboxylate -----	10-25
Sodium metasilicate (anhydrous) -----	2-10
Sodium carboxymethyl cellulose -----	1
Optical brightener (fluorescent dye) -----	0.1
Perfume -----	0.1
Sodium sulfate ² -----	Balance to 100

¹ One or a combination of the following: sodium alkyl aryl sulfonate, sodium alkyl sulfonate, sodium alkane sulfonate, sodium alkenyl sulfonate, octyl phenol ethoxylate, nonyl phenol ethoxylate, fatty alcohol ethoxylate, fatty acid amide, alkanol amide, tall oil ethoxylate.

² The sodium sulfate may be totally or partially replaced by one or more of the following: borax, soda ash, sodium bicarbonate, sodium chloride, sodium sesquicarbonate.

EXAMPLE III

Typical liquid laundering formulations of this invention are as follows (percentages being weight percentages):

	Percent
Surface-active agent (see footnote 1 above) -----	10-15
Tetrasodium tetrahydrofuran 2,3,4,5-tetracarboxylate ³ -----	10-20
Potassium metasilicate -----	2-10
Sodium carboxymethyl cellulose -----	1
Sodium benzene sulfonate ⁴ -----	5-10
Optical brightener (fluorescent dye) -----	0.1
Water -----	Balance to 100

³ The tetrasodium tetrahydrofuran 2,3,4,5-tetracarboxylate may be totally or partially replaced by tetrapotassium tetrahydrofuran 2,3,4,5-tetracarboxylate.

⁴ The sodium benzene sulfonate may be totally or partially replaced by potassium benzene sulfonate, sodium toluene sulfonate, sodium xylene sulfonate, etc.

It is not intended that this invention be unduly limited by the exemplification herein provided.

Methods for the synthesis of tetrahydrofuran 2,3,4,5-tetracarboxylic acid are known and reported in the literature. The compound is presently available as an article of commerce.

I claim:

1. A washing composition consisting essentially of an organic detergent surfactant selected from the group consisting of anionic, cationic, nonionic, ampholytic and zwitterionic surfactants and mixtures thereof, and, as a builder, a water-soluble salt of tetrahydrofuran 2,3,4,5-tetracarboxylic acid, the ratio by weight of the detergent surfactant to the builder being in the range of about 1:10 to about 3:1.

2. The composition of claim 1 wherein said water-soluble salt is a sodium salt.

3. The composition of claim 1 wherein said detergent surfactant is one or a mixture of anionic detergents.

4. The composition of claim 1 additionally containing from about 2 to about 10 percent by weight based on the total weight of the composition of a water-soluble alkali metal silicate.

5. The composition of claim 1 additionally containing up to about 60 percent by weight based on the total weight of a material selected from the group consisting of an alkali metal sulfate, an alkali metal carbonate and mixtures thereof.

6. The composition of claim 1 wherein said detergent surfactant is one or a mixture of anionic detergents, wherein said salt is the tetrasodium salt of tetrahydrofuran 2,3,4,5-tetracarboxylic acid, and wherein the composition additionally contains from about 2 to about 10 percent by weight based on the total weight of the composition of a water-soluble sodium silicate and from about 10 to

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about 50 percent by weight based on the total weight of the composition of sodium sulfate.

7. An aqueous washing medium consisting essentially of an aqueous solution having dissolved therein from about 0.05 percent to about 0.25 percent by weight of the composition of claim 1, said solution having a pH between about 8 and about 12. 5

8. A method of washing soiled fabrics which comprises contacting said fabrics with the aqueous washing medium of claim 7, rinsing said fabrics and drying the rinsed fabrics. 10

9. The composition of claim 7 wherein said detergent surfactant is one or a mixture of anionic detergents.

10. The composition of claim 7 wherein said water-soluble salt is a sodium salt of tetrahydrofuran 2,3,4,5-tetracarboxylic acid. 15

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