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3,769,223

DETERGENT FORMULATIONS

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20 Claims

ABSTRACT OF THE DISCLOSURE

To obviate eutrophication of water, non-phosphorus detergent builders and sequestering agents are provided. These are either (a) a 1-oxacyclopropane-2,3-dicarboxylic acid, (b) a water soluble salt of a 1-oxacyclopropane-2,3-dicarboxylic acid or a mixture of (a) and (b). Conventional detergent actives may be used with these builders.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 106,925, filed Jan. 15, 1971, now abandoned.

BACKGROUND OF THE INVENTION

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 a serious shortcoming. For example 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.

Further there is also at present a growing need for low cost sequestering agents efficiently operable over wide pH ranges (7–10). The use of sequestering agents to remove metal ions or to reduce metal ion concentrations is well known to the scientific community. For example, sequestering agents are used in metal cleaning processes, leather tanning, textile processes, the stabilization of dyes and vegetable oils, laundering and other washing operations, and the processing of beer. Most of the sequestering agents used today are efficient only at a high pH (9–10). In addition some of the best known sequestering agents such as sodium tripolyphosphate suffer from the eutrophication problems discussed above.

Thus, there is a need for a compound which is an effective non-phosphorus detergent builder and is also an effective sequesterant over a wide pH range. Accordingly, it is an object of this invention to provide a detergent builder system which is devoid of the eutrophic characteristics exhibited by the polyphosphates and other phosphorus builders. Further, it is an object of this invention to provide washing compositions which are devoid of phosphorus-containing builders but which possess the advantageous

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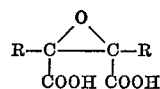
characteristics of washing compositions which presently contain the polyphosphate builders. Another object of this invention is to provide a sequestering agent which is effective over a wide pH range.

Other important objects of this invention will become apparent from the ensuing description and appended claims.

THE INVENTION

In accordance with one facet of 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 a detergent builder selected from the group consisting of (a) a 1-oxacyclopropane-2,3-dicarboxylic acid, (b) a water soluble salt of a 1-oxacyclopropane-2,3-dicarboxylic acid, and a mixture of (a) and (b).

Generally, the acids which may be used as builders in this invention have the formula:



wherein R is hydrogen or any other innocuous radical, such as a hydrocarbon group, carboxyl group, or the like. By "innocuous radical," it is meant that the radical is one which does not adversely affect the building or sequestering qualities of the compound to which it is attached. Further the radical should also not render the compound non-soluble in the medium in which it is to operate nor should the radical initiate any side reactions with components of the medium which would hamper building or sequestering action in such medium. Examples of the various 1-oxacyclopropane-2,3-dicarboxylic acids which are effective as builders in this invention are

- 1-oxacyclopropane-cis-2,3-dicarboxylic acid,
- 1-oxacyclopropane-trans-2,3-dicarboxylic acid,
- 1-oxacyclopropane-2,2,3-tricarboxylic acid,
- 1-oxacyclopropane-2,2,3,3-tetracarboxylic acid,
- 1-oxacyclopropane-2,3-dicarboxy-2-acetic acid,
- 1-oxacyclopropane-2-methyl-trans-2,3-dicarboxylic acid,
- 1-oxacyclopropane-2-cyclohexyl-cis-2,3-dicarboxylic acid,
- 1-oxacyclopropane-2,3-dimethyl-2,3-dicarboxylic acid,
- 1-oxacyclopropane-2-benzyl-cis-2,3-dicarboxylic acid,
- 1-oxacyclopropane-2-carboxymethoxy-cis-2,3-dicarboxylic acid,
- 2-benzyl-1-oxacyclopropane-2,3-dicarboxylic acid,
- 2,3-bis[1-naphthyl]-1-oxacyclopropane-2,3-dicarboxylic acid,
- 2-[4'-phenyl]-oxacyclopropane-2,3-dicarboxylic acid

and the like. Of these acids the most preferred is 1-oxacyclopropane-cis-2,3-dicarboxylic acid.

As before mentioned water soluble salts of 1-oxacyclopropane-2,3-dicarboxylic acids are also very useful detergent builders. The preferred salts are the alkali metal salts of such acids due to their relative inexpensiveness and stability. Of the alkali metal salts the sodium salts, the potassium salts and the potassium-sodium salts are preferred with the disodium salt and dipotassium salt being most preferred. A most highly preferred salt is the disodium salt of 1-oxacyclopropane-cis-2,3-dicarboxylic acid. Other salts which exhibit suitability for the purpose of this invention are ammonium salts, alkyl ammonium salts, morpholinium salts, alkanol ammonium salts and

the like. Exemplary of salts which are useful for the purposes of this invention are

disodium-1-oxacyclopropane-cis-2,3-dicarboxylic;
 1-oxacyclopropane-2,2,3-tricarboxylic acid, trisodium salt;
 1-oxacyclopropane-2,3-dimethyl-2,3-dicarboxylic acid, dipotassium salt;
 2,3-bis-[1-naphthyl]-1-oxacyclopropane-2,3-dicarboxylic acid, monorubidium monosodium salt;
 1-oxacyclopropane-2-cyclohexyl-cis-2,3-dicarboxylic acid, monolithium salt;
 1-oxacyclopropane-2,2,3,3-tetracarboxylic acid, tetrasodium salt;
 1-oxacyclopropane-cis-2,3-dicarboxy acid, diammonium salt;
 1-oxacyclopropane-2-cyclohexyl-cis-2,3-dicarboxylic acid, monoethanolamine monosodium salt, and the like.

It is to be understood that any of the above described salts may be used either singularly or in combination with each other. It is to be also understood that the salts of this invention may comprise a mixture, e.g., an alkali metal-ammonium salt, an ammonium-morpholinium salt, etc.

The builders of this invention can be advantageously used with a wide variety of detergent actives or surfactants, including those known in the art as anionic, cationic, nonionic, ampholytic, and zwitterionic detergents as well as any suitable mixture of such detergents. Those skilled in the art are thoroughly familiar with the nature of such detergent compounds and the literature is replete with illustrations and exemplifications. Typical of the literature which may be consulted in this regard are "Surface Active Agents" by Schwartz and Perry and "Surface Active Agents and Detergents" by Schwartz, Perry and Berch, the disclosure of the foregoing being incorporated herein by reference. When the builders of this invention are present in detergent formulations which are used in aqueous washing systems, the cleaning power of the formulation is enhanced in much the same way as then the commonly used polyphosphate builders are employed. Yet the present builder systems do not contribute to the eutrophication problems characteristic of phosphorus-containing builders.

Accordingly, this invention provides a detergent formulation containing an organic detergent surfactant suitable for use in water and, as a builder either a 1-oxacyclopropane-2,3-dicarboxylic acid, a water-soluble salt of such acids, or a mixture of the before mentioned acids and salts. 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 10:1 to about 1:10. A preferred range is from about 1:1 to about 1:6. The weight ratio of detergent surfactant to builder will of course be on the low side of the before mentioned range whenever utilizing a builder of high molecular weight and vice versa.

Detergent formulations containing a builder of this invention may be used in aqueous systems having a wide pH range. When it is desired to operate a system having a high pH (about 9-12), the builder salts may be used in the formulation as they render the solution basic. On the other hand when operating under acidic conditions (pH below about 6), the acidic form of the builder may be used. Of course when it is desired to operate within an intermediate range (pH of about 7), the acid and the salt may be both utilized. Another mode involves using the acid or the salt and subsequently adjusting the pH of the system by adding base or acid respectively. For example, a system having a high pH can be obtained by using the acid form of the builder and then adding a sufficiently quantity of base to achieve the desired pH. It has been found that the best building action takes place at a

pH of about 10. However, the builders of this invention are still very effective in essentially neutral systems.

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, non-ionic 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) for use in detergent formulations. The anionic surface-active compounds (which are preferred surfactants) 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 reference 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 the 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. Patent 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, thetines, sulfated long chain olefinic amines, and sulfated imidazoline 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., car-

boxy, sulfo, or sulfato. Examples of compounds falling within this definition are 3-(N,N-dimethyl-N-hexadecyl-ammonio)-propane-1-sulfonate and 3-(N,N-dimethyl-N-hexadecyl-ammonio)-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. Patent 2,961,209 and French Patent 1,298,753.

As before noted the anionic detergent surfactants are preferred and thus their use with the builders of this invention in detergent formulations is preferred.

For further disclosure of the surfactant art in general see U.S. 3,526,592 and the various U.S. patents referred to therein. Inasmuch as the surfactants set forth in these above patents are compatible with this disclosure, the foregoing patents are incorporated herein as if fully set out in the specification.

The detergent formulations may also contain from about 2 to about 10 percent by weight, based on the total weight of the formulation, a water soluble alkali metal silicate. Soluble silicates of such alkali metals as sodium and potassium serve as effective corrosion inhibitors and thus their presence yields a preferred detergent formulation. When utilizing the water-soluble alkali metal silicate, 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.

Other preferred constituents for the detergent formulations are alkali metal sulfates, 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 formulations the amount of alkali metal sulfate 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; perfume; fluorescers; dyes or pigments; brightening agents; enzymes; water; alcohols; other builder additives, such as the water-soluble salts of ethylenediaminetetracetic 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 hydrotropic agents may be found efficacious. Suitable hydrotropes 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 concentrations ranging about 2 to 10 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 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 0.25 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 0.1 to about 0.2 weight percent 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.

A further embodiment of this invention encompasses the use of either 1-oxacyclopropane-2,3-dicarboxylic acids, the water soluble salts thereof or mixtures of the salt and acid as sequestering agents.

The concentration of the above mentioned acids and salts in any given solution will of course be dependent to some extent upon the concentration of the sequesterable substances and upon that portion of the substances which are to be sequestered. Thus amounts ranging from trace quantities up to about 600 p.p.m. or more, i.e., about 10,000 p.p.m., are permissible.

A unique feature exhibited by 1-oxacyclopropane-2,3-dicarboxylic acids and its salts is that they are effective sequestrants in systems having a pH range of from about 3 to about 12. Normally though the aqueous systems in which these acids and salts will be used will have a pH of from about 7 to about 10.

A typical example of a system in which such sequestrants are very valuable is an aqueous detergent solution. In such solutions, a wide variety of detergents or surfactants, including anionic, cationic, nonionic, ampholytic, and zwitterionic detergents, as well as many suitable mixtures of such detergents may be used in conjunction with the sequestrants of this invention. The prior description of these detergents and surfactants found in this specification in conjunction with the builder action of the compounds of this invention is likewise applicable to the sequestering function of these compounds.

In washing systems the weight ratio of surfactant to sequestrant ranges from about 10:1 to about 1:10. Preferred ratios are within the range of from about 1:1 to about 1:6.

Generally speaking, when utilizing the compound(s) of this invention to sequester metallic ions in aqueous media, the metallic ions so sequestered are in great part calcium and/or magnesium as these are the metallic ions which are most prevalent in ordinary "tap" water. The salts which are most responsible for the presence of these metallic ions are calcium sulfate, calcium carbonate, magnesium carbonate, magnesium sulfate, calcium chloride, magnesium chloride, calcium nitrate, magnesium nitrate, calcium bicarbonate, magnesium bicarbonate, and the like. Other metal ions such as the ions of iron, manganese, copper, aluminum, chromium, nickel, cobalt, tin and vanadium may also be present in "tap" water and are also sequestered by the sequestrants of this invention. In special cases the various ions to be sequestered may be of different proportions than that found in "tap" water and thus it is to be understood that the sequestrants of this inven-

tion are equally efficacious in these special aqueous systems.

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
1-oxacyclopropane-cis-2,3-dicarboxylic acid -----	40.0
	100.0

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 1-oxacyclopropane-cis-2,3-dicarboxylic acid.

In these tests it was established that the formulation of this invention was essentially as effective as the corresponding sodium tripolyphosphate formulation. In particular, the cloths washed with the formulation of this invention had a whiteness of 95 ± 6 as compared to the whiteness of the same kind of solid cloths washed in the sodium tripolyphosphate formulation (assigned the value of 100 percent).

EXAMPLE II

The same procedure was followed as in Example I except that water having a hardness of 300 p.p.m. (Ca/Mg 3/2) was used. It was found that 1-oxacyclopropane-cis-2,3-dicarboxylic acid gave a whiteness of 98 percent ± 6 as compared to the assigned value of a 100 percent for sodium tripolyphosphate.

EXAMPLE III

Seven grains of calcium (calculated as calcium carbonate) were added to a gallon of water. To this solution 1-oxacyclopropane-cis-2,3-dicarboxylic acid was added so as to prepare a 0.06 percent solution of the acid. The pH was adjusted to 10 by the addition of sodium hydroxide. The residual calcium was then measured using a standardized calcium electrode. A reduction to 0.15 grain per gallon of calcium was noted indicating that 6.85 grains per gallon had been sequestered.

EXAMPLE IV

The same procedure was followed as in Example III except that the pH was adjusted to 7. Upon measurement of the remaining calcium it was found that 0.2 grain of calcium per gallon remained thus indicating that 6.8 grains of calcium per gallon were sequestered.

EXAMPLE V

The same procedure was followed as in Example III except that the acid utilized was 1-oxacyclopropane-2-carboxymethoxy-trans-2,3-dicarboxylic acid. Upon measurement of the remaining calcium it was found that 1.6

grains of calcium per gallon remained thus indicating that 5.4 grains of calcium per gallon were sequestered.

A method for the production of the above mentioned builders and sequestrants of this invention can be found in Journal of Organic Chemistry, G. B. Payne and P. H. Williams, vol. 24, p. 54, (1959).

Illustrative solid heavy duty laundering compositions of this invention are as follows (percentages being weight percentages):

	Percent
Surface-active agent (see Note 1) -----	10-25
1-oxacyclopropane-cis-2,3-dicarboxylic acid, disodium salt (see Note 3) -----	10-25
Sodium metasilicate (anhydrous) -----	2-10
Sodium carboxymethyl cellulose -----	1
Optical brightener (fluorescent dye) -----	0.1
Perfume -----	0.1
Sodium sulfate (see Note 2) -----	Balance to 100

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

	Percent
Surface-active agent (see Note 1 below) -----	10-15
1-oxacyclopropane-2,2,3-tricarboxylic acid, monopotassium salt -----	10-20
Potassium metasilicate -----	2-10
Sodium carboxymethyl cellulose -----	1
Sodium benzene sulfonate (see Note 4) -----	5-10
Optical brightener (fluorescent dye) -----	0.1
Water -----	Balance to 100

NOTES

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.

3 The 1-oxacyclopropane-cis-2,3-dicarboxylic acid, disodium salt may be totally or partially replaced by the dipotassium salt.

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

As noted above, the builders and sequestrants of this invention may be used in combination with other builders or sequestrants. Such combinations offer the opportunity for enhanced cost effectiveness or superior results, or both. Among the builders or sequestrants which may be combined with those of this invention are the water soluble salts of such acids as citric acid (e.g., trisodium citrate, tripotassium citrate, etc.), diglycolic acid (e.g., disodium diglycolate, dipotassium diglycolate, etc.), nitrilotriacetic acid (e.g., trisodium nitrilotriacetate, tripotassium nitrilotriacetate, etc.), oxydisuccinic acid (e.g., tetrasodium oxydisuccinate, tetrapotassium oxydisuccinate, etc.), and the like, as well as mixtures of two or more of such salts. If desired, the free acids (e.g., citric acid, diglycolic acid, nitrilotriacetic acid, oxydisuccinic acid, or mixtures of two or more of these acids) may be used in combination with the builders or sequestrants of this invention. Combinations in which there is no nitrogen or phosphorus containing ingredient are particularly preferred from the ecological standpoint. When using such combinations the ratios of the builders or sequestrants may be varied within relatively wide limits although generally speaking the weight ratio between the builder of this invention and the builder used therewith will fall within the range of from about 0.1:1 to about 10:1, and most preferably from about 0.25:1 to about 4:1.

The detergent formulations of this invention have utility in many cleansing operations be they household or light industrial applications. For example, they may be used in the cleaning of a non-rigid substrate such as cloth, skin or hides or in washing of rigid substrates such as dishes, floors, automobile bodies, household and industrial metal appliances, glass, etc. Other utilizations of the de-

tergent formulations of this invention will become immediately apparent to those skilled in the art.

What is claimed is:

1. A detergent formulation comprising an organic detergent surfactant suitable for use in water selected from the group consisting of anionic detergents, cationic detergents, nonionic detergents, ampholytic detergents, zwitterionic detergents, and mixtures thereof and a builder selected from the group consisting of:

- (a) a 1-oxacyclopropane-2,3-dicarboxylic acid;
- (b) a water soluble salt of a 1-oxacyclopropane-2,3-dicarboxylic acid; and
- (c) any mixture of (a) and (b),

said detergent surfactant being present in a weight ratio to said builder of from about 10:1 to about 1:10.

2. The formulation of claim 1 wherein the weight ratio of the organic detergent surfactant to the builder is in the range of from about 1:1 to about 1:6.

3. The formulation of claim 1 wherein the builder is a water soluble, alkali metal salt of 1-oxacyclopropane-2,3-dicarboxylic acid.

4. The formulation of claim 3 wherein the water soluble salt is a sodium salt, a potassium salt, or a potassium-sodium salt.

5. The formulation of claim 1 wherein the builder is 1-oxacyclopropane-cis - 2,3 - dicarboxylic acid, an alkali metal salt of 1-oxacyclopropane-cis-2,3-dicarboxylic acid or a mixture thereof.

6. The formulation of claim 5 wherein the alkali metal is sodium, potassium or a mixture thereof.

7. The formulation of claim 1 additionally containing a water soluble alkali metal silicate present in an amount of from about 2 to about 10 percent by weight, based on the total weight of the formulation.

8. The formulation of claim 1 additionally containing an alkali metal sulfate or an alkali metal carbonate, or both present in an amount of up to about 60 percent by weight, based on the total weight of the formulation.

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

10. The formulation of claim 1 wherein said detergent surfactant is one or a mixture of anionic detergents, said builder is 1-oxacyclopropane-cis-2,3-dicarboxylic acid, the disodium salt of 1-oxacyclopropane-cis-2,3-dicarboxylic acid or a mixture thereof, the formulation additionally contains from about 2 to about 10 percent by weight, based on the total weight of the formulation, of a water soluble sodium silicate and up to about 60 percent by weight, based on the total weight of the formulation, of sodium sulfate.

11. An aqueous washing system comprising water, an organic detergent surfactant selected from the group consisting of anionic detergents, cationic detergents, nonionic detergents, ampholytic detergents, zwitterionic detergents, and mixtures thereof, and a builder selected from the group consisting of

- (a) a 1-oxacyclopropane-2,3-dicarboxylic acid,
- (b) a water soluble salt of a 1-oxacyclopropane-2,3-dicarboxylic acid; and
- (c) any mixture of (a) and (b),

said detergent surfactant being present in a weight ratio to said builder of from about 10:1 to about 1:10.

12. The system of claim 11 wherein the ratio by weight of the detergent surfactant to the builder is from about 1:1 to about 1:6.

13. The system of claim 11 wherein the pH is within a range of from about 7 to about 10.

14. The system of claim 11 wherein said detergent surfactant is one or a mixture of anionic detergents.

15. The system of claim 11 wherein the builder is 1-oxacyclopropane-cis-2,3-dicarboxylic acid, the disodium salt of 1-oxacyclopropane-cis-2,3-dicarboxylic acid or a mixture thereof.

16. The method of washing articles which comprises contacting the same with the aqueous system of claim 11.

17. An aqueous solution which contains a compound selected from the group consisting of

- (a) a 1-oxacyclopropane-2,3-dicarboxylic acid,
- (b) a water soluble salt of a 1-oxacyclopropane-2,3-dicarboxylic acid; and
- (c) any mixture of (a) and (b),

in a concentration sufficient to sequester sequesterable substances which are present in the solution.

18. The aqueous solution of claim 17 wherein the sequesterable substance is selected from the group consisting of calcium ions, magnesium ions and mixtures thereof.

19. The aqueous solution of claim 17 wherein the compound is 1-oxacyclopropane-cis-2,3-dicarboxylic acid, an alkali metal salt of 1-oxacyclopropane-cis-2,3-dicarboxylic acid or a mixture thereof.

20. The aqueous solution of claim 17 wherein the solution has a pH of from about 3 to about 12.

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