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EUROPEAN PATENT APPLICATION

⑳ Application number : **91305579.4**

㉑ Int. Cl.⁵ : **C11D 3/20, C11D 3/26,
C11D 3/10**

㉒ Date of filing : **20.06.91**

㉓ Priority : **22.06.90 US 542228**

㉔ Date of publication of application :
02.01.92 Bulletin 92/01

㉕ Designated Contracting States :
AT BE CH DE DK ES FR GR IT LI NL SE

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㉙ **Composition and method for fabric encrustation prevention.**

㉚ Cleaning composition and method comprising in a first embodiment an alkali metal carbonate builder and a fabric encrustation prevention system comprising a sub-stoichiometric level of a polyamino polycarboxylic acid or water-soluble salts thereof which acts to inhibit and prevent the deposition of insoluble precipitates containing water hardness ions on fabrics ; in a second embodiment the cleaning composition includes a deterative surfactant for laundry applications ; in either embodiment the following adjuncts may be included : co-builders, alkali metal silicates, bleaching species, enzymes, fragrances, dyes, brighteners and others.

This invention relates to compositions and methods for preventing fabric encrustation by decreasing or suppressing the formation of encrustation residue when using detergent applications and formulations during fabric washing operations with "hard water." In particular, this invention relates to the use of polyamino polycarboxylic acids to prevent growth or deposition of insoluble compounds on fabric surfaces during washing operations.

5 The invention is primarily concerned with inhibition and prevention of the formation and deposition of insoluble compounds on fabric.

The growth of insoluble compounds on fabric surface (fabric encrustation) from repeated washing with non-phosphate detergents in "hard water" is a negative effect in which the appearance and feel of the fabric is affected. The fabric acquires a rough feel and colored garments have a faded appearance.

10 The insoluble compounds primarily are calcium and magnesium carbonate precipitates caused when hard water containing calcium and magnesium ions react with builders, such as sodium carbonate, typically used in non-phosphate detergents. Therefore, the prevention of encrustation or the deposition of insoluble compounds formed during the washing process with "hard water" is strongly desired. Phosphonates and polyacrylates have been shown to be effective in detergent applications for the prevention of encrustation. Phosphonates can function as crystal growth inhibitors which prevents the growth of insoluble calcium and magnesium compounds at substoichiometric concentrations. Polyacrylates can function as sequestering and dispersing agents, as well as crystal growth inhibitors. Some drawbacks associated with phosphonates and polyacrylates is that phosphonates can contribute to eutrophication and polyacrylates are not biodegradable.

15 Heavy-duty laundry detergents typically contain two major ingredients, surfactant and builder, and a number of other ingredients essential to an acceptable product. Although of lesser importance to detergency, these additional ingredients impart certain desirable functions to the total formulated detergent. These miscellaneous ingredients include anti-corrosion agents, anti-soil redeposition agents, fluorescent whitening agents, bleaches, enzymes, perfume and the like. The two major components most essential to detergency are surfactant and builder.

20 The surfactant provides deterative action to the detergent. This is based on their fundamental characteristic to absorb or concentrate at the soil/ fiber/water interfaces. The detergent builder functions primarily to prevent divalent calcium and magnesium water-hardness-causing-ions from interfering with the surfactant action. The builder also may provide alkalinity and thus improve fatty acid saponification, buffering capacity, prevent flocculation, maintain ionic strength, extract metals from soils and remove alkaline-earth metal ions from the washing solutions. Phosphates are extremely effective builders; however, they are in disfavor due to their eutrophication effect on lakes and streams. Many states in the United States have enacted legislation limiting phosphate content. Such legislation to reduce phosphate content has led to a variety of non-phosphate builders, either proposed and/ or employed. Examples include silicates, zeolites, carbonates and polycarboxylates, citrates, EDTA and sodium nitrilotriacetate (NTA). Such alternatives are themselves subject to various limitations. Silicates are not preferred because they are not entirely water-soluble and they can therefore deposit onto fabrics, and also can form precipitates with the hardness ions. Zeolites are generally effective co-builders, but not as the sole builder. Polycarboxylate builders are costly.

25 High levels of alkali-metal carbonates have been found to be a cost effective non-phosphate builder, particularly in applications where a high pH is required, e.g., for oily soil removal. A drawback associated with such high carbonate levels is that calcium and magnesium ions present in the washing water readily form precipitates with the carbonates, and such precipitates deposit and/or form on the fabrics. These precipitates leave the fabrics with a rough feel and faded appearance. Various approaches have been employed in the art to combat the formation of calcium or magnesium precipitates, including the addition of seed crystals, crystal growth inhibitors and non-precipitation sequestrants. Non-precipitation sequestering and complexing agents tend to be expensive due to the stoichiometric levels needed, adding significantly to the overall formula cost.

30 British Patent Specification No. 66492 describes compositions containing related compounds, such as the polyamino polycarboxylic acid type or water-soluble salt thereof, having the property of stabilizing peroxy bleach compounds.

35 British Patent Specification No. 1383741 relates to using the compound 1,3-diamino-propan-2-ol-N,N,N',N'-tetraacetic acid or water-soluble salt thereof as a stabilizer against degradation of peroxy compounds.

40 U.S. Pat. 2,130,505 relates to various polyaminocarboxylic acids and the process for making the same. This patent mentions the use of said compounds for avoiding and rendering harmless the precipitates of water-insoluble metal salts, particularly formed from the ions which cause hard water. This patent does not teach or suggest the use of these compounds at substoichiometric levels in carbonate base detergent formulations for the prevention of fabric encrustation. This application is very ambiguous in that use levels are not given.

45 U.S. Pat. 2,396,938 relates to treatment of boilers and various parts thereof for removing coatings of scale and preventing further scale formation in boilers by the use of stoichiometric levels of various alkaline,

polyamine, tetra or higher acetic acid compounds.

U.S. Pat. 2,407,645 relates to polycarboxylic amino acids and the process for producing said acids and alkali metal salts thereof. The compounds of U.S. Pat. 2,407,645 are disclosed as useful in water softening compositions and, when mixed with soap, as washing agents.

5 U. S. Pat. 4, 352,751 relates to various diamine triacetic acids useful in the formation of fluorescent chelates of rare earth metal ions which can be employed in fluoroassay techniques.

Japanese Patent Specification 55/133498 relates to water-soluble deodorizing-detergent prepared by dissolving N-long chain acylamino acid salts and others in mineral water. These compositions are useful as detergents for use in washing of dishes and exhibit deodorizing and washing effects, as well as protective effects
10 on human skin.

Japanese Patent Specification 60/11998 relates to peroxide bleaching compositions containing chelating agents in the form of N,N-bis-(hydroxyethyl)imino, acetic acid and/or N-hydroxyethylimino, diacetic acid. These latter compounds are found useful as bleaching agents having superior bleaching effects in eliminating yellowing, striping, decolorization and the like.

15 Japanese Patent Specification 30/51500 relates to mild neutral detergent compositions for bathrooms and the like, containing surfactant detergency-improving potassium or ammonium salts of aminocarboxylic acids and glycol solvent. The three components act synergistically on metal salts of fatty acids, causing rapid decomposition. The compounds also prevent the attachment of dirt to items washed therewith.

In view of the art cited, there remains a need for compositions and methods for effectively preventing fabric encrustation in detergent applications and formulations. The prior art relates only to the use of various compounds and compositions in stabilizing the degradation of peroxy compounds; reducing hardness of water; removing scale from boilers and boiler tubes; chelating of rare metal ions capable of forming fluorescent chelates; and further employment in fluoroassay techniques.

The present application relates to the method for using polyamino polycarboxylic acid compounds as effective fabri cencrustation preventatives in detergent applications and formulations. The prior art relates only to the use of polyamino polycarboxylic acids to reduce hardness of water, or as a stabilizer against degradation of peroxy bleaching compounds. Clearly, the addition of polyamino polycarboxylic acid compounds into detergent compositions in order to decrease and/ or suppress the formation of encrustation residue in fabrics from hard water minerals due to the presence of the sodium carbonate builder in the detergent formulation is not
25 contemplated by the prior art.

A leading inorganic replacement for phosphate builders is sodium carbonate. However, high carbonate content non-phosphate builders produce the problem of "hard water" precipitates from the calcium and magnesium ions present in the "hard water." The growth or deposition of the precipitates on the fabrics during washing application make carbonate-based detergents, otherwise, not preferred.

30 It is therefore an object of the present invention to provide a cleaning composition which does not utilize phosphate builders.

It is another object of the present invention to provide a high carbonate cleaning composition which results in reduced levels of calcium and magnesium salt deposition on fabrics.

40 It is another object of the present invention to provide a largely biodegradable compound which prevents carbonate salt precipitation and/or controls encrustation.

It is another object of the present invention to provide a cleaning composition which provides good stain and soil removal performance.

It is another object of the present invention to provide a cleaning composition and method for the reduction of fabric encrustation which does not contribute to eutrophication.

45 It is yet another object of the present invention to provide a cleaning composition and method for the reduction of fabric encrustation when using high carbonate or non-phosphate detergent formulations.

It has now been found that by using the compositions and method in accordance with the present invention, fabric encrustation can be reduced or eliminated when using high carbonate, or non-phosphate detergents with water containing calcium and/or magnesium ions. The compositions and method are characterized by utilizing polyamino polycarboxylic acid and derivatives thereof. More preferably, this invention relates to the use of polyamino polycarboxylic acids and water-soluble salts thereof, especially 1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid in the detergent compositions and methods utilizing said compositions.

50 More particularly, this invention relates to the use of detergent compositions which contain 1, 3-diamino-2-hydroxypropane N, N, N', N'-tetraacetic acid or a water-soluble salt thereof with monovalent cations in a concentration of from about 1 percent to about 20 percent by weight; with a preferred range of about 2 to about 12 percent; more preferably from about 1 percent to about 5 percent.

Alkali metal salts, particularly sodium salts, potassium salts or ammonium salts, can be used as water-soluble salts of polyamino polycarboxylic acids having monovalent cations. Ammonium ions also can be regarded

as monovalent cations for the purpose of the present invention. It is noted that for the purpose of the present invention the acid forms of the polyamino polycarboxylic acid are equivalent to the salt forms except where the acid has limited solubility. It is also noted that except where explicitly stated or implied from the context, the acid and salt forms are used interchangeably. It is further noted, that if the polyamino polycarboxylic derivative is added as a water-soluble salt, the required weight percentage range will be higher than that of the acid, due to the presence of the counter ion.

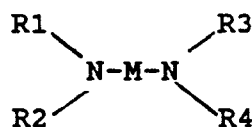
Therefore, in one embodiment, the present invention can be described as a cleaning detergent composition comprising (a) an alkali-metal carbonate builder; and (b) a fabric encrustation prohibiting amount of a polyamino poly-carboxylic acid or salt thereof.

Alkali-metal carbonate. The alkali metal carbonate is the primary and may be the only builder material of the composition of the present invention. As used herein, the primary builder is defined as that builder which, in total amount, has the higher capacity for hardness ions (e.g., calcium (+2) and magnesium (+2)). The term "co-builder" will refer to any remaining builder which has the lesser capacity for such ions. Alkali metal carbonates, sesquicarbonates and bicarbonates are suitable primary builders; however, the preferred builders are sodium and/ or potassium carbonates. A building effective amount of carbonate is present in the compositions herein, which is defined as that amount of alkali metal carbonates, as the primary builder, which would precipitate in the presence of hardness ions, in solution, during a wash period at 50°C and 250 ppm hardness. Such precipitation is determined by an increase in solution turbidity as indicated by an abrupt change in percent transmittance versus time defined hereinafter. Generally, in terms of weight percent, and assuming 68 liters of wash water and about 100 g of composition, at least about 20 to about 80 percent, preferably about 30 to about 70 percent, most preferably 50 percent carbonate is employed. As used herein, unless otherwise stated, all percentages are weight percentages of actives of the total composition. Higher levels of carbonate will function, however, at levels greater than about 80 percent there is insufficient room for the other ingredients which contribute to the overall effectiveness of the composition. The carbonate acts as the builder to remove divalent metal ions such as calcium, and additionally provides alkalinity and aids in soil removal. At the high levels disclosed herein, the alkali metal carbonate provides good cleaning performance and in situations requiring a high pH, such as oily soils, the carbonate builder may be superior to other builders.

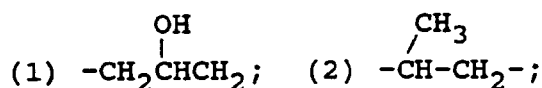
Polyamino Polycarboxylic Acid Encrustation Preventative System

The preventative system comprises substoichiometric levels of a polyamino polycarboxylic acid or water-soluble salt thereof (hereinafter referred to as "PAPCA"), which act to inhibit and prevent fabric encrustation. For purposes herein, substoichiometric levels of the polyamino polycarboxylic acid are defined to mean levels which are insufficient to prevent the precipitation of calcium and magnesium carbonate by sequestering water hardness ions. For example, such levels generally comprise less than about 30 percent, more preferably less than about 20 percent, of the total building capacity.

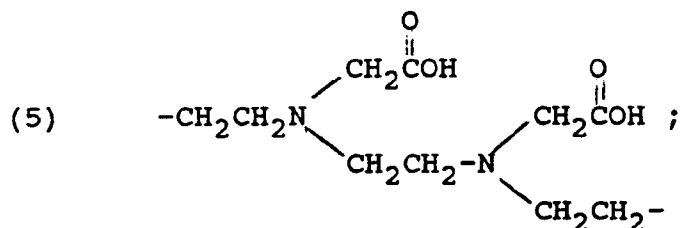
By the term "polyamino polycarboxylic acid" it is meant a compound having at least 2 amino groups and at least 2 carboxyl groups therein. The polyamino polycarboxylic acid compounds of this invention relate to the following general formula



wherein M is selected from the group consisting of:

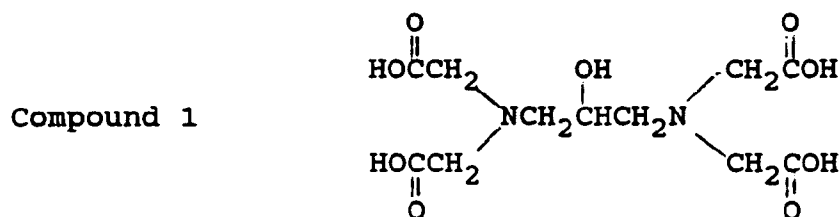


(3) $-\text{CH}_2\text{CH}_2-$; (4) $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$; and

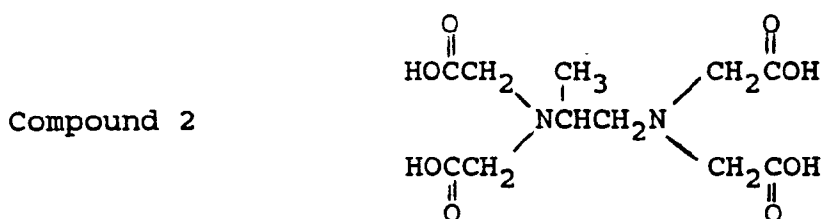


and water soluble salts thereof; and where R1, R2, R3 and R4 are selected from the group consisting of - (CH₂)_nOH, -CH₂COOH, and -H wherein n is 1, 2 or 3; provided that when M is (1), (2), (3) or (4) then at least three of R1, R2, R3 and R4 are -CH₂COOH; and further provided that when M is (5) at least R1 and R2 or R3 and R4 are each -CH₂COOH, individually.

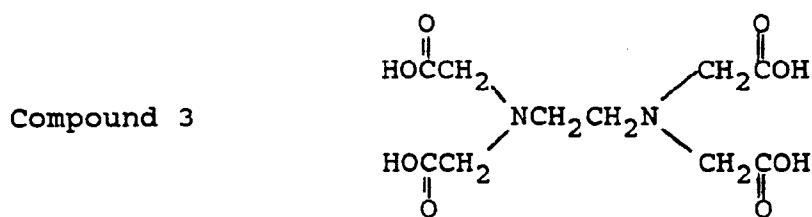
The following are representative compounds of this invention:



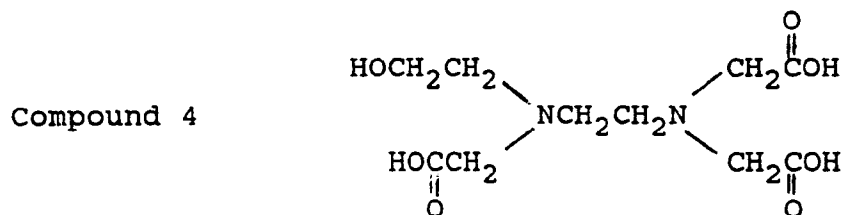
1,3-Diamino 2-hydroxypropane N,N,N',N'-tetraacetic acid



1,2-Diaminopropane N,N,N',N'-tetraacetic acid

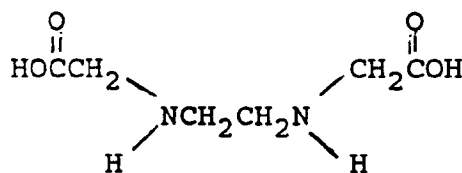


Ethylenediamine tetraacetic acid (EDTA)



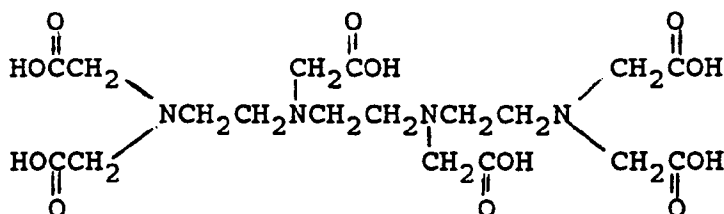
N(2-hydroxyethyl)ethylenediamine N,N,N'-triacetic acid

Compound 5



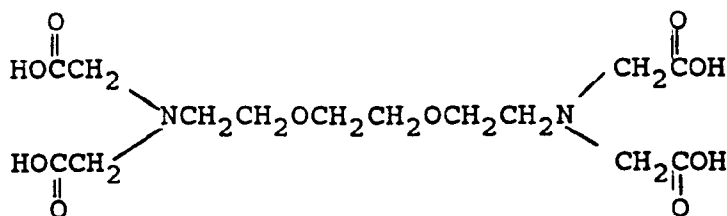
Ethylenediamine N,N'-diacetic acid

Compound 6



Triethylenetetramine hexaacetic acid

Compound 7



Ethylene bis(oxyethylene nitrilo) tetraacetic acid

In a second embodiment, the cleaning composition comprises a detergent composition including:

- (a) an alkali-metal carbonate builder;
- (b) an encrustation prevention system comprising substoichiometric levels of polyamino polycarboxylic acid or water-soluble salts thereof; and
- (c) a surfactant.

Components (a) and (b) are as described previously with respect to the first embodiment. Component (c) is further described below.

Surfactant

A myriad of surfactants are known to be suitable for laundry applications, including anionic, cationic, non-ionic and amphoteric surfactants. Preferred surfactants are anionic, nonionic and mixtures thereof, and if added are present in a cleaning-effective amount. Preferred anionics are selected from surfactants such as alkali metal alkyl sulfates, primary and secondary alkane sulfonates, linear alkyl benzene sulfonates, alkyl ether sulfates, and mixtures thereof. These anionic surfactants will preferably have alkyl chain groups averaging about 8 to 18 carbon atoms. The preferred anionic surfactant is a LAS having an alkyl group averaging 8 to 18 carbons. Commercial sources of such surfactants are the Stephan Chemical Company (Northfield, IL) and the Vista Chemical Company (Houston, TX). An additionally preferred anionic surfactant, principally for its cleaning effectiveness, is a secondary alkane sulfonate. An example of a particularly preferred secondary alkane sulfonate is HOSTAPUR SAS, a trade marked product manufactured by Farbwerke Hoechst A. G. (Frankfurt, West Germany).

It is most preferred to include with the anionic surfactant at least one nonionic, especially C₁₋₄ alkoxyated aliphatic alcohols and C₁₋₄ alkoxyated alkyl phenols. Particularly preferred are ethoxylated/propoxylated C₈₋₁₄ alcohols. There should be at least about three alkoxy groups per alcohol, preferably at least about nine. Examples of preferred ethoxylated/propoxylated aliphatic alcohols are BASF Corporation's (Parsippany, NJ) trademarked INDUSTROL, and PLURAFAC. Certain C₁₋₄ alkylene oxide copolymers such as ethylene oxide/propylene oxide copolymers are also preferred as surfactants. These are exemplified by BASF's

trademarked PLURONIC series. Other suitable nonionic surfactants are polyethoxylated alcohols manufactured and marketed by the Shell Chemical Company (Houston, TX) under the trademark NEODOL. Examples of preferred NEODOLS are NEODOL 25-7 which is a mixture of 12 to 15 carbon chain length alcohols with about 7 ethylene oxide groups per molecule, NEODOL 23-65, a C₁₂₋₁₃ mixture with about 6.5 moles of ethylene oxide, and NEODOL 25-9, a C₁₂₋₁₅ mixture with about 9 moles of ethylene oxide. Also useful are a trimethyl nonyl polyethylene glycol ether, manufactured and marketed by Union Carbide Corporation under the trademark TERGITOL TMN-6, and an octyl phenoxy polyethoxy ethanol sold by Rohm and Haas (Philadelphia, PA) under the trademark TRITON X-114. Total surfactant content is preferably from 1% to about 20%, more preferably from about 2% to 15%.

In a third embodiment, the present invention comprises a dry, granular laundry detergent composition comprising:

- (a) an alkali-metal carbonate builder;
- (b) a polyamino polycarboxylic acid or a water-insoluble salt thereof as encrustation inhibitor system;
- (c) a surfactant;
- (d) a bleach;
- (e) an alkali-metal silicate;
- (f) a filler; and
- (g) laundry adjuncts.

Elements (a), (b) and (c) are as described in the first and second embodiments. Elements (d) through (g) are further described hereinbelow.

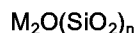
Bleach

Preferred peroxygen bleaches are available in solid form and include sodium percarbonate, sodium perborate, sodium phosphate peroxyhydrate, potassium permonosulfates and metal peroxides. Bleach activators, also known as peracid precursors, can be included with the peroxygen compounds. Examples of activators include tetraacetyl ethylenediamine (TAED), nonanoyloxy benzene-sulfonate (NOBS), and nonanoylglycolate phenol sulfonate (NOGPS). NOBS and TAED are disclosed, for example, in U.S. 4,417,934, Chung et al., and NOGPS is disclosed, for example, in U.S. 4,778,618, Fong et al., the disclosures of which are incorporated herein by reference. Peracid bleaches (including monoperacids and diperacids) may be advantageous in terms of bleaching performance. Suitable peracid bleaching species include C₈₋₁₂ alkyl peracids, especially perazelaic and diperazelaic acids, diperoxydodecanedioic acid (DPDDA), and alkyl monoperoxysuccinic acid. Peracid bleaching species, and a method for their production, are described in U.S. 4,337,213 to Marynowski et al., the disclosure of which is incorporated herein by reference. The bleach is present in an amount sufficient to provide effective bleaching, e.g., from about 0% to 10% by weight active, more preferably from about 0.05% to 5% by weight active depending on the bleaching species chosen.

Also, chlorine bleach could be used either added preformed suspended on a substrate, mitigated or generated *in situ*.

Alkali-metal Silicate

An alkali-metal silicate can be included to provide alkalinity and corrosion resistance. Preferred is one having the formula:



where M represents an alkali-metal and n is between about 1 and 4. Preferred alkali-metal silicates are sodium, potassium and lithium silicates, with sodium silicate being the most preferred, and with a preferred n value of 2.0-2.4. A most preferred maximum value for n is about 3.2 in order to minimize insoluble silicates during storage. It is further preferred that at least about 10% of the total silicates have an n value of greater than about 1.6 to impart suitable anti-corrosive properties. Examples of other suitable silicates include sodium or potassium orthosilicates and metasilicates. As used hereinafter, the term "silicate" will be taken to mean any of these alkali-metal silicates, individually or combined.

Mixtures of any of the foregoing alkali-metal silicates are also suitable. The alkali-metal silicate is present in an amount of from about 0% to 10%, preferably about 2% to 5%. A minimum of about 1% silicate is preferred to provide adequate corrosion resistance. A commercially available sodium silicates is sold by the Philadelphia Quartz Corporation (Valley Forge, PA) under the trademarks RU (as a 47% solution) and D (as a 44.1% solution). In addition to their anti-corrosive effects, the silicates provide alkalinity and serve as processing and granulating aids to increase particle size of the agglomerates. Sodium silicates also aid in cleaning, especially

on oil and grease stains.

Filler

5 The filler is preferably a salt such as sodium chloride, nitrate or sulfate, and is used to adjust the composition density to achieve desired physical characteristics, e. g., grain size and flowability. Depending on the filler and the process used, the filler can also provide surface area for loading of actives. The filler material additionally assists in solubility under cold water washing conditions. Sodium chloride is preferred due to its low cost and availability. However, other materials, such as puffed borax, bentonite clays and inorganic salts such as sodium
10 or potassium sulfate, chloride, bromide, nitrate, and borate, and organic materials like sugars may also be suitable. Some water may be deliberately added as a filler. Generally, about 0-30% filler will be present, preferably about 5-25 %.

Co-Builder

15 Optionally, any non-phosphate builder material known in the art to be compatible with the high carbonate formulation herein may be included as a co-builder selected from the group consisting of silicates, citrates, alkali metal carbonates, polymeric polycarboxylic acids such as polyacrylates and maleic anhydride based co-polymers, zeolites, salts of ethylene diamine, tetraacetic acid and sodium nitrilotriacetate. Silicates at levels above
20 about 10%, and citrates may be added as co-builders. If added, the co-builder should comprise no more than about 30% of the total weight of the composition, and preferably no more than about 20%. Zeolites are preferred as optional co-builders since they perform well when used in a non-encrustation promoting amount. A non-encrustation promoting amount is that amount which will not contribute to or encourage the encrustation formation when present in a detergent formulation and in the presence of water hardness ions.

25 Zeolite A is available, for example, from the PQ Corp., Valley Forge, PA, under the trademark VALFOR 100. Zeolite A typically includes about 21% moisture.

Adjuncts

30 While the alkali-metal carbonate is generally sufficient to keep the wash pH range within the desired limits, it may be desirable to adjust the pH of the wash water by including an electrolyte/buffer. Generally, these are alkali metal inorganic acid salts, hydroxides or oxides. It may also be suitable to use such materials as aluminates and organic materials, such as gluconates, citrates, succinates, maleates, and their alkali metal salts. The wash pH range should be maintained between about 8.0 to 13.0, more preferably about 9.0 to 12.0. If an
35 electrolyte/buffer is needed, sodium hydroxide is preferred, as it does not interact adversely with any other ingredients and is very cost effective. The amount of electrolyte/buffer added solely for purposes of buffering can vary from about 0% to 10%.

In the standard composition, minor additions can be included in the present invention. These include dyes, such as Monastral blue and anthraquinone dyes (such as those described in Zielske, U.S. 4,661,293 and U.S. 4,746,461). Pigments, which are also suitable colorants, can be selected, without limitation, from titanium
40 dioxide, ultramarine blue (see also, Chang et al., U.S. 4,708,816), and colored aluminosilicates. Fluorescent whitening agents are other desirable adjuncts. These include the stilbene, styrene, and naphthalene derivatives, which upon being impinged by ultraviolet light, emit or fluorescent light in a visible wavelength. These fluorescent whitener agents or brighteners are useful for improving the appearance of fabrics which have become dingy through repeated soiling and washings. Preferred fluorescent whitener agents are TINOPAL
45 5BM-GX and TINOPAL AMS, both from Ciba Geigy A. G., (Tom River, NJ) and PHORWITE RKH, from Mobay Chemicals (Union, NJ).

Enzymes, particularly hydrolases such as lipases, proteases and amylases, are useful additives in the compositions herein. Suitable commercial sources include ESPERASE and SAVINASE, both trademarked products of Novo Industries (Danbury, CT). Generally, very low levels of enzymes are needed, i.e. from about 0.1%
50 to 1.0% by weight. Fragrances are also desirable adjuncts in these compositions. The total composition minors will range from 0% to about 5%. Anti-redeposition agents, such as carboxymethyl-cellulose, are potentially desirable. Foam boosters, such as appropriate anionic surfactants, may be appropriate for inclusion herein. Also, in the case of excess foaming resulting from the use of certain surfactants, anti-foaming agents, such as alkylated polysiloxanes, e.g., dimethylpolysiloxane, would be desirable. Water may be present as free water or as
55 water of hydration of the inorganic salts such as sodium carbonate. The detergent composition is prepared by a process which yields a dry, free-flowing granular mixture, for example agglomeration or spray drying. However, the compositions herein are not limited to such forms, and may also be formulated in other dry forms,

such as tablets or beads, or may be formulated as pastes, gels or liquids. An example formulation is shown below as Example A.

EXAMPLE A

<u>Ingredient</u>	<u>Wt.% Active</u>
Alkali metal carbonate	30-80
Surfactant	1-20
Bleaching agent	0-10
Alkali metal silicate (SiO ₂ /M ₂ O)	0-10
Filler	0-30
Polyamino polycarboxylic acid	0.1-15
Composition Minors (enzymes, FWA's, fragrances, etc.)	0-5
Co-builder	0-30
Water	0-15

EXPERIMENTAL

To assess effectiveness of the compositions herein in reducing encrustation deposition, compounds of this invention related to 1,3-diamino-2-hydroxypropane N,N,N',N'-tetraacetic acid were tested for their effectiveness at reducing encrustation in beaker studies. The compounds and results are given in the following table.

Procedure

The turbidity measurement comprises measuring percent transmittance using a dipping probe and colorimeter. The probe is placed in deionized water and the percent transmittance (%T.) is set to 100%. The detergent is predissolved in 50 ml of water, then added to 950 ml of water containing hardness ions as [Ca²⁺] / [Mg²⁺] = 3:1 molar ratio. The final solution hardness was 300 ppm. Percent transmittance is continuously plotted and measured vs time. Results are presented as time before the onset of calcium precipitation (t_m) as determined by an abrupt change in the slope of a graph of %T vs time. The longer the t_m, the better the ability of the compound to prevent precipitation of inorganic salts. Ideally, the t_m should be longer than the wash cycle, i.e., about 12-15 minutes in the case of washing conditions in the United States. In practice, a t_m of greater than about 10, preferably 12 minutes, provides commercially-acceptable results, as calcium precipitation will still be inhibited to a degree sufficient to avoid consumer preception thereof.

Simultaneously with the %T measurement, each container of detergent sample has immersed therein a 3.5 x 4 inch 100% cotton swatch, trimmed to 1.00 grams. Slits approximately 3 inches long were cut about 0.25 inch apart for better circulation in the test container. After washing for 10 minutes, the swatch is rinsed twice with 2 L deionized water, and placed in a flask containing 25 ml of water and 10 ml each of 1.2M HCl to dissolve the CaCO₃. Fifteen ml of a standard NH₄OH hardness buffer and a Calmagite indicator are then added and the solution is titrated with standardized EDTA. Results are reported as mg CaCO₃ per gram of fabric (swatch). Preferably, this value should be below about 4 mg/g, most preferably below about 2 mg/g.

TABLE I^a

	<u>Cmpd. No.</u>	<u>Concentration</u>	<u>(gms/l)^b</u>	<u>tm</u>	<u>mg as CaCO₃/</u> <u>gm fabric</u>
5	1	$4.44 \times 10^{-4}M$	0.143	20	1.55
	2	$5.0 \times 10^{-4}M$	0.153	5.8	6.70
	3	$1.3 \times 10^{-3}M$	0.380	4.5	5.75
10	4	$5.0 \times 10^{-4}M$	0.190	4.6	3.56
	5	$5.0 \times 10^{-4}M$	0.088	2.4	15.30
	6	$5.0 \times 10^{-4}M$	0.247	4.2	11.30
15	7	$5.0 \times 10^{-4}M$	0.190	9.7	4.85
	Base Only		-	4.5	12.90

a An agglomerated no-P detergent base was used which contains 1.16 gm/l of Na₂CO₃ (corresponding to 78.6 gm/use Na₂CO₃ in 68 l wash).

b gm/l are for the acid forms of the compounds.

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Multicycle Wash Study

To assess effectiveness of the compositions herein in reducing encrustation deposition, 100% terry cloth washcloths were washed for multiple cycles, under the given wash conditions. A base detergent composition consisting of 61% Na₂CO₃, 11.0% surfactant, 5.0% sodium silicate and 5.0% sodium perborate were used. The polyamino polycarboxylic acid compound was added to the base composition in the amounts indicated in each case as exemplified in Table II. About 3/4 cup (125 g/use) of detergent and about 68 L of wash water was used for each washload.

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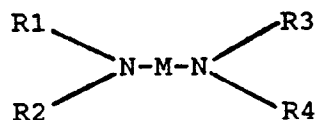
TABLE II
Multicycle Wash Studies

Treatment ^a	Wt. % Ash/5 Cycles/Cotton Washcloths ^b	
	35°C/100 ppm	50°C/200 ppm
Base + 7.5 g Acrysol LMW45N 4500 MW polyacrylic acid	0.4	4.7
Base + 4.44 x 10 ⁻⁴ M (9.72gm) 1,3-diamino-2-hydroxy- propane N,N,N',N'-tetraacetic acid	0.7	1.0
^a Multicycle wash studies were done with an agglomerated detergent base containing 61 gm/use Na₂CO₃. All studies were done with 3:1 Ca/Mg molar concentration water hardness. Concentrations are on an "actives" basis. ^b Ash is defined as the residue remaining after pyrolysis of 950°C in oxygen. Values are expressed at weight percent.		

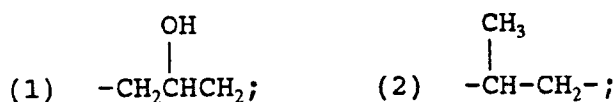
Table II shows that substoichiometric levels of the instant encrustation preventative system utilizing a polyamino polycarboxylic acid yielded less calcium residue (as ash) than the base detergent composition. With the observed results for the inhibition of calcium carbonate deposition, polyamino polycarboxylic acid could be a direct replacement for polyacrylate which is known for its anti-precipitation nature. Furthermore, since the polyamino polycarboxylic acids described within are non-polymeric, they should be more biodegradable than polyacrylic acid.

Claims

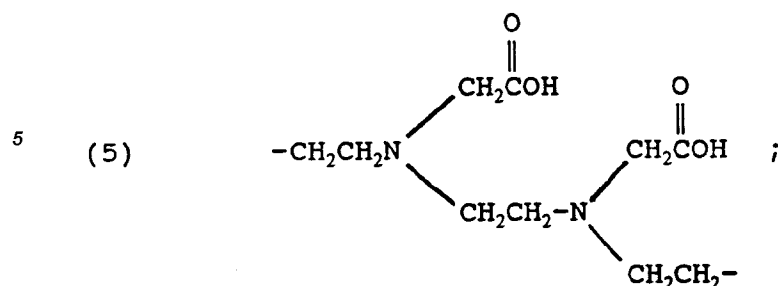
1. A non-phosphate fabric cleaning composition characterised in that it comprises:
 - (a) a building effective amount of an alkali metal carbonate detergent builder from about 20 to about 80 weight percent; and
 - (b) a fabric encrustation preventing amount of an encrustation preventing system, including a sub-stoichiometric amount of a polyamino polycarboxylic acid, a water-soluble salt or mixtures thereof, having the formula:



wherein M represents:



(3) -CH₂CH₂-; (4) -CH₂CH₂OCH₂CH₂OCH₂CH₂-; or



and water-soluble salts thereof; and R1, R2, R3 and R4 independently represent $-(\text{CH}_2)_n\text{OH}$, $-\text{CH}_2\text{COOH}$ or $-\text{H}$, wherein n represents 1, 2 or 3; provided that, when M represents (1), (2), (3) or (4), then at least three of R1, R2, R3 and R4 represent $-\text{CH}_2\text{COOH}$; and further provided that, when M represents (5), at least R1 and R2 or R3 and R4 each represent $-\text{CH}_2\text{COOH}$.

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2. A non-encrustation fabric cleaning composition characterised in that it consists essentially of:
 - (a) a building effective amount of an alkali metal carbonate from about 20 to about 80 weight percent;
 - (b) from about 1 to about 10 percent of a sodium silicate having a ratio of $\text{SiO}_2/\text{M}_2\text{O}$ of from about 1:1 to about 4:1, wherein M represents an alkali metal;
 - (c) a sub-stoichiometric amount of a polyamino polycarboxylic acid, a water-soluble salt or mixtures thereof as defined in claim 1;
 - (d) a deterative cleaning-effective amount of a surfactant selected from anionic, non-ionic, cationic, amphoteric surfactants and mixtures thereof; and
 - (e) a bleach effective amount of a bleaching species.

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 3. A composition as claimed in claim 1 or claim 2 wherein the amount of alkali metal carbonate builder is from about 30 to about 70 weight percent.
 4. A composition as claimed in any of claims 1 to 3 wherein the amount of polyamino polycarboxylic acid or a water-soluble salt thereof is from about 1 to about 20 weight percent.
 5. A composition as claimed in any of claims 1 to 4 wherein it includes a deterative cleaning-effective amount of a surfactant selected from anionic, non-ionic, cationic, amphoteric surfactants and mixtures thereof, preferably selected from alkyl sulfates, primary and secondary alkyl sulfonates, linear alkyl aryl sulfonates, alkyl ether sulfates, alkoxyated aliphatic alcohols, alkoxyated alkyl phenols, copolymers of C_1 - C_4 alkylene oxides and mixtures thereof.
 6. A composition as claimed in any of claims 1 to 5 wherein it includes a bleaching effective amount of a bleaching species.
 7. A composition as claimed in any of claims 1 to 6 wherein it includes a non-encrustation promoting amount of a co-builder selected from silicates, citrates, alkali metal carbonates, polymeric polycarboxylic acids, salts of ethylene diamine tetraacetic acid and sodium nitrilotriacetate, and preferably zeolites.
 8. A composition as claimed in any of claims 1 to 7 wherein it includes from about 1 to about 10 % of an alkali metal silicate.
 9. A composition as claimed in any of claims 1 to 8 wherein the alkali metal carbonate is sodium carbonate; and the polyamino polycarboxylic or water-soluble salt is selected from 1,3-diamino-2-hydroxypropane N,N,N',N'-tetraacetic acid, 1,2-diaminopropane N,N,N',N'-tetraacetic acid, ethylenediamine tetraacetic acid (EDTA), N(2-hydroxyethyl)-ethylenediamine N,N,N'-triacetic acid, ethylenediamine N,N'-diacetic acid, triethylenetetramine hexaacetic acid and ethylene bis(oxyethylene nitrilo) tetraacetic acid.
 10. A method for reducing water causing precipitation and deposition on fabric characterised in that it comprises contacting the fabric with a cleaning effective amount of an aqueous solution of a composition as claimed in any of claims 1 to 9.
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