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(54) Method of preventing fabric encrustation

Verfahren zur Verhinderung der Gewebeinkrustation

Procédé pour prévention de l'incrustation sur le tissu

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(56) References cited:
EP-A- 94 723 **DE-A- 2 240 309**
DE-A- 2 730 951 **FR-A- 2 121 568**
FR-A- 2 396 076

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Description

This invention relates to 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 certain organic dicarboxylic acids to prevent growth or deposition of insoluble compounds on fabric surfaces during washing operations. The invention is primarily concerned with inhibition 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 are affected. The fabric acquires a rough feel and colored garments have a faded appearance.

The insoluble compounds primarily are calcium and magnesium carbonate precipitates caused by 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 are that phosphonates can contribute to eutrophication and polyacrylates are not biodegradable.

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.

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 ions from interfering with the surfactant action. The builder also may provide alkalinity thus improve fatty acid saponification and 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 necessarily as the sole builder. Polycarboxylate builders are costly.

High levels of alkali-metal carbonates have been found to be an 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-precipitating sequestrants. Non-precipitating sequestering and complexing agents tend to be expensive due to the stoichiometric levels needed, adding significantly to the overall formula cost.

U.S. Pat. 3,896,056, Benjamin et al., relates to a built detergent compositions which contain as essential ingredients, an organic surface-active agent; a precipitating builder; and a precipitation modifier. This patent describes a functional test to assess the ability of compounds to prevent the formation of precipitation as an indication of its effectiveness as a crystal growth inhibitor. A detergent matrix consisting of an inorganic precipitating builder is used. A number of polycarboxylic acid compounds are disclosed as precipitation modifiers.

U.S. Pat. 4,097,016, Brahm, J., et al., relates to a solid composition for washing, cleaning and bleaching, including at least one basic compound, as a solid polylactone is a sequestering agent and can include activators for per-salts, such as anhydrides of organic acids, succinic acid, phthalic acid, and the like.

U.S. Pat. 4,814,102, Baur, R. et al., describes copolymers consisting of acrylic, maleic, fumaric, itaconic or hydroxy alkyl esters of these acids as builders, encrustation inhibitors, or dispersants in detergents.

Non-phosphate detergent formulations are disclosed in numerous patents. Larrabee et al., EP 130,640, discloses a laundry detergent comprising a surfactant, 5 to 80% of a non-phosphorus detergent builder which may be a carbonate, and about 0.3 to 5% of a polyacrylate polymer. EP 137,669, Kermod et al., describes a detergent composition including 5 to 60% of a surfactant, 7 to 80% of a polycarboxylate/zeolite builder, and a bleach system.

DeRider et al., EP 82 564, discloses machine dishwashing and rinsing compositions having nonionic detergent

surfactants, a water-soluble calcium sequestering agent, specific polymeric material and an alkaline detergent material to produce a composition which has improved non-filming, non-spotting or non-streaking properties. The calcium sequestering agents are taught to be an organic builder salt, such as water-soluble citrates, water-soluble salt of nitrilotriacetic acid (NTA), water-soluble salt of carboxymethoxy succinic acid, or other builders such as zeolites, or organic chelating agents.

EP 82 564 shows an example of the calcium sequestering agent; dipicolinic acid is disclosed as not causing filming on dishes. Similarly, in U.S. 3,850,852, Neillie et al., sodium carbonate is combined with polyacrylate, phosphonate, and a calcium sequestering agent.

EP 233 730, Sanderson et al. discloses the use of 2,6-pyridine dicarboxylic acid as a chelating stabilizer for potassium sulfoperoxybenzoate in detergent compositions. This is necessary in the situation where inorganic or organic peroxy acids are unstable in the presence of nonionic surfactants. It was not feasible to contemplate storing liquid compositions containing both components without the use of a chelating peroxidic stabilizer such as dipicolinic acid.

EP 266 904, Frankena, H., relates to machine dishwashing compositions comprising low or zero phosphates using dipicolinic acid derivatives as the builder. Also provided for are enzymes to increase performance.

There may also be mentioned: DE-A-2 240 309 (= GB 1 398 263), which is said to be based on the finding that a detergent composition with an alkali metal carbonate detergency builder is improved by incorporating therein a calcium sequestering agent and a calcium carbonate anti-deposition agent; EP-A-0 094 723, which relates to a method for washing textiles in hard water and to phosphate-free detergent compositions for use therein; and FR-A-2 396 076 (= GB 2 000 177), which concerns a detergent composition wherein the acidic constituent and the alkaline constituent are separately present.

The prior art describes polymers of aliphatic polycarboxylic acids as builders in detergent formulations. However, it has not been recognized that substoichiometric concentrations of the monomeric forms of some of these compounds alter the kinetics or crystalline morphology of calcium carbonate, and hence can be used to prevent industrial scaling, and reduced fabric encrustation in non-phosphorus detergent formulations. 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 present invention is primarily effective at preventing encrustation of fabrics in high-carbonate, non-phosphorus detergent. Therefore, the present invention provides an alternative to phosphonate and polyacrylates for prevention of encrustation.

The present application relates to the method for using certain organic dicarboxylic acids and water-soluble derivatives thereof as effective fabric encrustation preventatives in detergent applications and formulations. The prior art relates only to the use of certain organic dicarboxylic acids to reduce hardness of water, or as a stabilizer against degradation of peroxy bleaching compounds. Clearly, the addition of certain organic dicarboxylic acid and their water-soluble salts and anhydrides into detergent compositions in order to decrease and/or suppress the formation of encrustation residue on fabrics from hard water minerals due to the presence of the sodium carbonate builder in the detergent formulation is not 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.

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

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

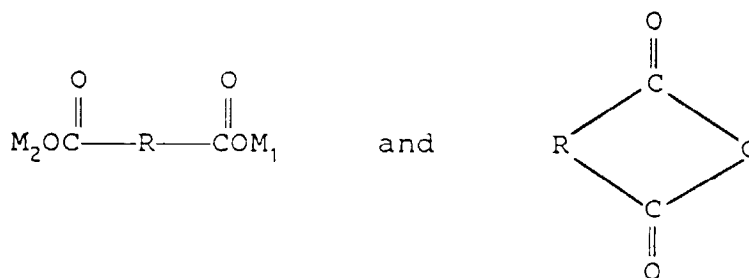
It is another object of the present invention to provide the use of a biodegradable, entirely non-phosphorus-containing compound which prevents carbonate salt precipitation and/or controls encrustation.

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

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

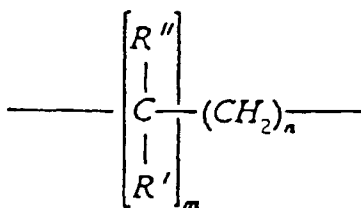
The present invention provides a method for water working a fabric so as to prevent encrustation characterised in that it comprises using a non-phosphate fabric cleaning composition providing a wash pH range of between 8.0 and 13.00 and comprising:

- (a) at least 20 weight percent of an alkali metal carbonate detergent builder;
- (b) a fabric encrustation preventing amount of not more than 20 weight percent of an encrustation preventing organic dicarboxylic acid, a water-soluble salt, an anhydride or mixtures thereof, having the formula:



wherein

R represents 2,3-pyridenyl, 2,4-pyridenyl, 2,6-pyridenyl, 1,2-phenylene, 1,3-phenylene or



wherein R' and R'' independently represent H, -OH or C₁-C₄ alkyl or R' and R'' taken together represent oxygen; n represents 0 or an integer of from 1 to 3; m represents 0, 1 or 2; and M₁ and M₂ independently represent hydrogen, sodium, potassium, lithium and ammonium;

and

(c) from 0.1 to 20 weight percent of a surfactant;

(b) being present in a sub-stoichiometric amount in relation to the hardness ions in the washing water.

It has now been found that by using the method in accordance with the present invention, fabric encrustation can be reduced or eliminated when using high carbonate, non-phosphate detergents with water containing calcium and/or magnesium ions. The method is characterized by utilizing certain water-soluble organic dicarboxylic acids, anhydrides, salts and derivatives thereof. More preferably, this invention relates to the use of certain organic dicarboxylic acids, water-soluble salts and anhydrides thereof, especially ketomalonic acid, hydroxymalonic acid and 2,6-pyridine dicarboxylic acid.

More particularly, this invention relates to the use of detergent compositions which contain ketomalonic acid and 2,6-pyridine dicarboxylic acid or a water-soluble salt thereof with monovalent cations in a concentration of from 1 to 20 percent by weight, preferably from 2 to 12 percent by weight.

Alkali metal salts, particularly sodium salts, potassium salts or ammonium salts, can be used as water-soluble salts of the organic dicarboxylic acids of the instant invention 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 or anhydride forms of the organic dicarboxylic acids are equivalent to the salt forms except where the acid has limited solubility. It is understood that the anhydride can hydrolyze to form the diacid in situ. 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 organic dicarboxylic acid 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.

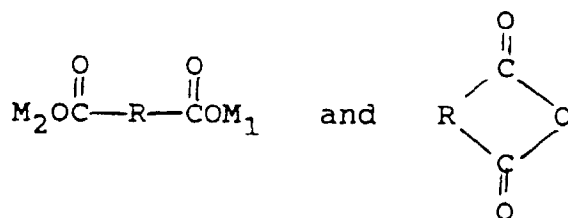
Alkali-metal carbonate. The alkali metal carbonate is the primary and may be the only builder material of the composition used according to the present invention. As used herein, the primary builder is defined as that builder which, in total amount, has the higher capacity for hardness ions (e.g., calcium (+2) and magnesium (+2)). The term "co-builder" will refer to any remaining builder which has the lesser capacity (typically less than 30%) 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 used 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 additionally hereinafter). Generally, in terms of weight percent, and assuming 68 liters of wash water and about 100 g of composition, at least about 30 percent, preferably 40 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 used. 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.

Organic Dicarboxylic Acid Encrustation Preventative System

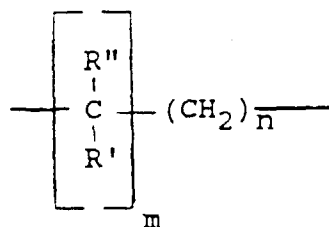
The preventative system comprises substoichiometric levels of an organic dicarboxylic acid, water-soluble salt or anhydrides thereof, which act to inhibit fabric encrustation. For purposes herein, substoichiometric levels of the certain organic dicarboxylic acid are defined to mean levels which are not able 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 "organic dicarboxylic acid" it is meant an organic compound having at least 2 carboxyl groups. The certain and particular organic dicarboxylic acid compounds used according to this invention relate to the following general formulae



wherein

R is selected from the group consisting of 2,3-pyridenyl, 2,4-pyridenyl, 2,6-pyridenyl, 1,2-phenylene, 1,3-phenylene and



wherein

R' and R'' are independently H, -OH or lower alkyl having 1-4 carbon atoms, inclusive or R' and R'' taken together are oxygen;

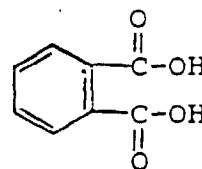
n is 0 or an integer from 1 to 3, inclusive;

m is 0, 1 or 2; and

M₁ and M₂ are independently selected from the group consisting of hydrogen, sodium, potassium, lithium and ammonium.

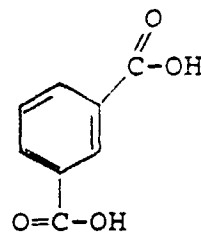
The following are representative compounds used according to this invention:

Compound 1



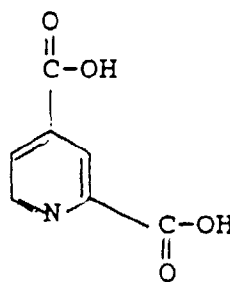
Phthalic acid

Compound 2



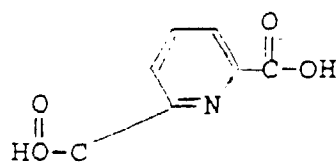
Isophthalic acid

Compound 3



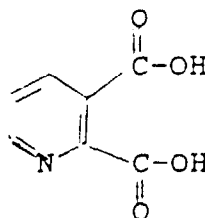
2,4-Pyridine dicarboxylic acid

Compound 4



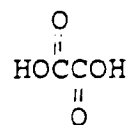
2,6-Pyridine dicarboxylic acid

Compound 5



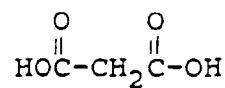
2,3-Pyridine dicarboxylic acid

Compound 6



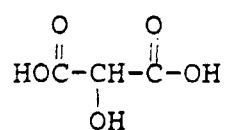
Oxalic acid

Compound 7



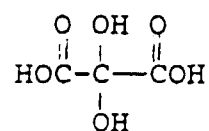
Malonic acid

Compound 8



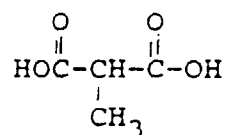
Hydroxy malonic acid

Compound 9



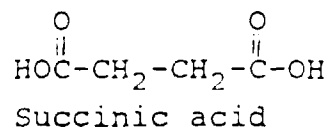
Ketomalonic acid

Compound 10



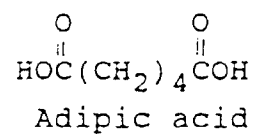
Methyl malonic acid

Compound 11



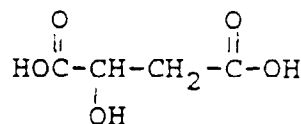
Succinic acid

Compound 12



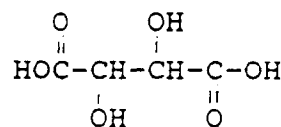
Adipic acid

Compound 13



Hydroxy succinic acid

Compound 14



Tartaric acid

Components (a) and (b) are as described previously. Component (c) is further described below.

Surfactant

A myriad of surfactants are known to be suitable for laundry applications, including anionic, cationic, nonionic 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 trademarked 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 PLU-RAFAC. 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 0.1% to about 20%, more preferably from about 2% to 15%.

Elements (a), (b) and (c) are as described hereinabove. Elements (d) through (g) are further described hereinbelow.

Bleach

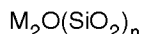
Preferred peroxygen bleaches are available in solid form and include sodium percarbonate, sodium perborate, sodium phosphate peroxyhydrate, potassium permonosulfates and metal peroxides. Bleach activators, also known as peracid precursors, can be included with the peroxygen compounds. Examples of activators 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 suitable are chlorine bleaches which could be preformed and 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 silicate 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 aids to increase particle size of the agglomerates. Sodium silicates also aid in cleaning, especially on oil and grease stains.

Filler

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 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

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, polymeric polycarboxylic acids such as polyacrylates and malonic anhydride based co-polymers, zeolites, salts of ethylene diaminetetraacetic acid and sodium nitrilotriacetate. Silicates at levels above 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.

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

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 must be maintained between 8.0 and 13.0, preferably 9.0 to 12.0. If an 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 0% to 10%.

In the standard composition used, 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 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 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 soilings and washings. Preferred fluorescent whitener agents are TINOPAL 5BM-GX and TINOPAL AMS, both from Ciba Geigy A.G., (Tom River, NJ) and PHORWHITE RKH, from Mobay Chemicals (Union, NJ).

Enzymes, particularly hydrolases such as lipases, proteases and amylases, are useful additives in the compositions used 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% 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 water of hydration of the inorganic salts such as sodium carbonate. The detergent composition used is prepared by a process which yields a dry, free-flowing granular mixture, for example agglomeration or spray drying. However, the compositions used 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	
Ingredient	Wt.% Active
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
organic dicarboxylic acid, salt or anhydride	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 used herein in reducing encrustation deposition, they were tested for their effectiveness at reducing encrustation in beaker studies. The compounds used 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 more effective the crystal growth inhibitor. Ideally, with the crystal growth inhibitor type compounds, 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 1.0 grams. Slits approximately 2.6 cm (approximately 3 inches) long were made about 0.6 cm (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 of 1.2M HCl to dissolve the CaCO_3 . Fifteen ml of a standard NH_4OH hardness buffer and a Calmagite indicator are then added and the solution is titrated with standardized EDTA. Results are reported as mg CaCO_3 per gram of fabric (swatch). Preferably, this value should be below about 4 mg/g, most preferably below about 2 mg/g.

The preferred level of calcium carbonate deposits per gram of fabric can be achieved without necessarily extending the t_m value. Although it is understood that this invention is not bound by theory, it is believed that precipitation modifiers will have little or no effect or may actually shorten the t_m value and still provide low levels of fabric encrustation. Crystal growth inhibitors, on the other hand, will extend the t_m value. The presence of either of these compound types in a high carbonate non-phosphate built detergent has been found to result in lower levels of encrustation on the fabric surface.

TABLE I

Cmpd. No.	Time Before Precipitation in Solution t_m (mins)	Titration of Calcium Deposits (mg as CaCO_3 /gm)
Beaker Studies ^a		
Base only	4.5	12.90
1	5.0	6.68
2	9.5	1.80
3	3.2	9.80
4	<1.0	1.10
5	2.5	10.20
6 ^b	7.5	6.38
7 ^b	10.5	4.30
8	15.8	0.90
9	<1.0	1.30
10	2.0	2.69
11 ^b	11.4	3.50
12 ^b	7.8	5.90
13	4.9	6.88
14	6.1	5.20

(a) An agglomerated no-P detergent base was used which contained 1.16 gm/l of Na_2CO_3 . All acids were evaluated at $1.0 \times 10^{-3}\text{M}$ unless otherwise specified.

(b) Compounds evaluated at $1.27 \times 10^{-3}\text{M}$.

Multicycle Wash Study

To assess effectiveness of the compositions used 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% Na_2CO_3 , 11.0% surfactant, 5.0% sodium silicate and 5.0% sodium perborate were used. The organic dicarboxylic 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 gm/use) of detergent and about 68 l of wash water was used for each washload.

Table II

Multicycle Wash Studies		
B. Multicycle Wash Studies		
Wt. & Ash/5 Cycles/Cotton Washcloths ^b		
Treatment ^a	35°C/100 ppm	50°C/200ppm
Base + 7.5 g Acrysol LMW 45N (4500 MW polyacrylic acid)	0.4	4.7

(a) Multicycle wash studies were done with an agglomerated detergent containing 61 gm/use Na_2CO_3 . 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 at 950°C in oxygen. Values are expressed as weight percent.

Table II (continued)

Multicycle Wash Studies		
B. Multicycle Wash Studies		
Wt. & Ash/5 Cycles/Cotton Washcloths ^b		
Treatment ^a	35°C/100 ppm	50°C/200ppm
Base + 5x10 ⁻⁴ M 2,6-pyridine dicarboxylic acid (5.68 gm)	1.5	1.2
Base + 2.5 x 10 ⁻⁴ M ketomalonic acid (2.31 gm)	0.7	0.9
Base + 5 x 10 ⁻⁴ M ketomalonic acid (4.62 gm)	0.2	0.5

(a) Multicycle wash studies were done with an agglomerated detergent 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 at 950°C in oxygen. Values are expressed as weight percent.

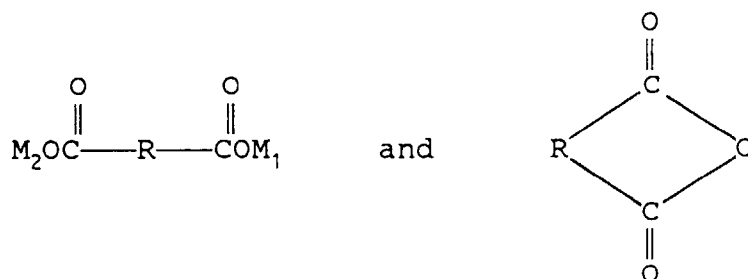
Table II shows that using substoichiometric levels of the present encrustation preventative system utilizing an organic dicarboxylic acid according to this invention yielded less calcium residue (as ash) than the base detergent composition at two different treatment levels. With the observed results for the inhibition of calcium carbonate deposition, an organic dicarboxylic acid used according to this invention could be a direct replacement for polyacrylate which is known for its anti-precipitation nature. Furthermore, the organic dicarboxylic acid and water-soluble salts and anhydrides thereof should be more biodegradable than polyacrylates.

Claims

1. A method for water washing a fabric so as to present encrustation characterised in that it comprises using a non-phosphate fabric cleaning composition providing a wash pH range of between 8.0 and 13.00 and comprising:

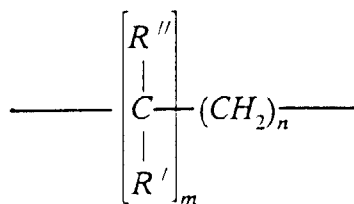
(a) at least 20 weight percent of an alkali metal carbonate detergent builder;

(b) a fabric encrustation preventing amount of not more than 20 weight percent of an encrustation preventing organic dicarboxylic acid, a water-soluble salt, an anhydride or mixtures thereof, having the formula:



wherein

R represents 2,3-pyridenyl, 2,4-pyridenyl, 2,6-pyridenyl, 1,2-phenylene, 1,3-phenylene or



wherein R' and R'' independently represent H, -OH or C₁-C₄ alkyl or R' and R'' taken together represent oxygen; n represents 0 or an integer of from 1 to 3; m represents 0, 1 or 2; and M₁ and M₂ independently represent hydrogen, sodium, potassium, lithium and ammonium;
and

- (c) from 0.1 to 20 weight percent of a surfactant;
(b) being present in a sub-stoichiometric amount in relation to the hardness ions in the washing water.

2. A method as claimed in claim 1 wherein the composition further comprises:

- (d) from 1 to 10 weight percent of a sodium silicate having a ratio of SiO₂/M₂O of from 1:1 to 4:1, wherein M represents an alkali metal;
(e) a bleach effective amount of a bleaching species; and the surfactant (c) in the composition is selected from anionic, non-ionic, cationic, amphoteric surfactants and mixtures thereof.

3. A method as claimed in claim 1 or claim 2 wherein the amount of alkali metal carbonate builder (a) in the composition is from 20 to 80 weight percent, preferably from 30 to 70 weight percent.

4. A method as claimed in any of claims 1 to 3 wherein the amount of organic dicarboxylic acid, water-soluble salt or anhydride thereof (b) in the composition is from 1 to 20 weight percent.

5. A method as claimed in any of claims 1 to 4 wherein the surfactant (c) in the composition is selected from alkyl sulfates, primary and secondary alkyl sulfonates, linear alkyl aryl sulfonates, alkyl ether sulfates, alkoxyated aliphatic alcohols, alkoxyated alkyl phenols, copolymers of C₁-C₄ alkylene oxides and mixtures thereof.

6. A method as claimed in any of claims 1 to 5 wherein the composition further comprises a non-encrustation promoting amount of co-builder selected from silicates, citrates, polymeric polycarboxylic acids, salts or ethylene diamine tetraacetic acid and sodium nitrilotriacetate, and, preferably, zeolites.

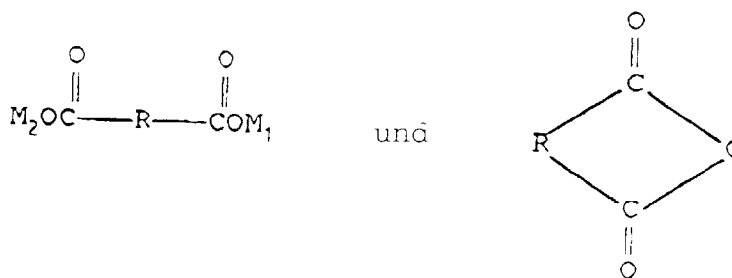
7. A method as claimed in any of claims 1 to 6 wherein in the composition the alkali metal carbonate is sodium carbonate; and the organic dicarboxylic acid or water-soluble salt is selected from phthalic acid, isophthalic acid, 2,4-pyridine dicarboxylic acid, 2,6-pyridine dicarboxylic acid, 2,3-pyridine dicarboxylic acid, malonic acid, hydroxy malonic acid, ketomalonic acid, methyl malonic acid, succinic acid, adipic acid, hydroxy succinic acid and tartaric acid, preferably 2,6-pyridine dicarboxylic acid, ketomalonic acid and hydroxymalonic acid.

Patentansprüche

1. Verfahren zum Waschen eines textilen Flächengebildes bzw. Gewebes mit Wasser, so daß eine Krustenbildung verhindert wird, dadurch gekennzeichnet, daß es die Verwendung einer phosphatfreien Gewebereinigungszusammensetzung umfaßt, die einen Wasch-pH-Bereich von zwischen 8,0 und 13,00 ergibt und folgendes enthält:

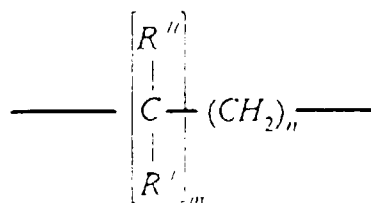
(a) mindestens 20 Gew.-% eines Alkalimetallcarbonat-Detergensbuilders,

(b) eine die Krustenbildung des Gewebes verhindernde Menge von nicht mehr als 20 Gew.-% einer eine Krustenbildung verhindernden organischen Dicarbonsäure, eines wasserlöslichen Salzes, eines Anhydrids oder Gemischen davon mit der Formel



worin

R für 2,3-Pyridenyl, 2,4-Pyridenyl, 2,6-Pyridenyl, 1,2-Phenylen, 1,3-Phenylen oder



steht, wobei R' und R'' unabhängig voneinander für H, -OH oder C₁-C₆-Alkyl stehen, oder R' und R'' miteinander Sauerstoff darstellen, n 0 oder eine ganze Zahl von 1 bis 3 ist, m 0, 1 oder 2 ist, und M₁ und M₂ unabhängig voneinander für Wasserstoff, Natrium, Kalium, Lithium und Ammonium stehen, und

(c) 0,1 bis 20 Gew.-% eines oberflächenaktiven Mittels, wobei (b) in einer substöchiometrischen Menge bezogen auf die Härteionen im Waschwasser vorliegt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Zusammensetzung weiterhin folgendes enthält:

(d) 1 bis 10 Gew.-% eines Natriumsilicats mit einem Verhältnis SiO₂/M₂O von 1:1 bis 4:1, wobei M für ein Alkalimetall steht,

(e) eine bleichwirksame Menge eines Bleichmittels,

und daß das oberflächenaktive Mittel (c) in der Zusammensetzung aus anionischen, nichtionischen, kationischen, amphoteren oberflächenaktiven Mitteln und Gemischen davon ausgewählt wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Menge des Alkalimetallcarbonatbuilders (a) in der Zusammensetzung 20 bis 80 Gew.-%, vorzugsweise 30 bis 70 Gew.-%, beträgt.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Menge der organischen Dicarbonsäure, des wasserlöslichen Salzes oder des Anhydrids davon (b) in der Zusammensetzung 1 bis 20 Gew.-% beträgt.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das oberflächenaktive Mittel (c) in der Zusammensetzung aus Alkylsulfaten, primären und sekundären Alkylsulfonaten, linearen Alkylarylsulfonaten, Alkylethersulfaten, alkoxylierten aliphatischen Alkoholen, alkoxylierten Alkylphenolen, Copolymeren von C₁-C₄-Alkylenoxiden und Gemischen davon ausgewählt wird.

6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß die Zusammensetzung weiterhin eine die nicht-Krustenbildung fördernde Menge eines Cobuilders, ausgewählt aus Silicaten, Citraten, polymeren Polycarbonsäuren, Salzen oder Ethylendiamintetraessigsäure und Natriumnitilotriacetat, und vorzugsweise Zeolithe enthält.

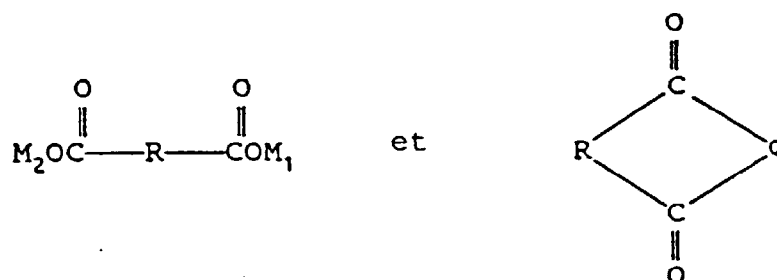
7. Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß das Alkalimetallcarbonat Natriumcar-

bonat ist, und daß die organische Dicarbonsäure oder das wasserlösliche Salz aus Phthalsäure, Isophthalsäure, 2,4-Pyridindicarbonsäure, 2,6-Pyridindicarbonsäure, 2,3-Pyridindicarbonsäure, Malonsäure, Hydroxymalonsäure, Ketomalonsäure, Methylmalonsäure, Bernsteinsäure, Adipinsäure, Hydroxybernsteinsäure und Weinsäure, vorzugsweise 2,6-Pyridindicarbonsäure, Ketomalonsäure und Hydroxymalonsäure, ausgewählt wird.

Revendications

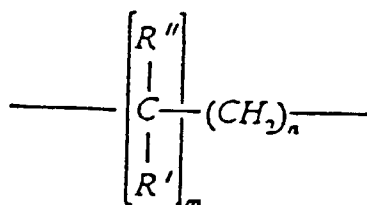
1. Procédé pour le nettoyage à l'eau d'un tissu de façon à empêcher l'incrustation, caractérisé en ce qu'il comprend l'utilisation d'une composition de nettoyage de tissu non phosphate conférant une plage de pH de lavage entre 8,0 et 13,00 et comprenant :

- (a) au moins 20 % en poids d'un adjuvant de détergent à base de carbonate de métaux alcalins ;
- (b) une quantité empêchant l'incrustation de tissu de pas plus de 80 % en poids d'un acide dicarboxylique organique empêchant l'incrustation, un sel hydrosoluble, un anhydride ou leurs mélanges, avec la formule :



dans laquelle

R représente 2,3-pyridényle, 2,4-pyridényle, 2,6-pyridényle, 1,2-phénylène, 1,3-phénylène ou



dans laquelle R' et R'' représentent indépendamment H, -OH ou alkyle en C₁-C₄ ou R' et R'' pris ensemble représentent l'oxygène ; n représente 0 ou un nombre entier allant de 1 à 3 ; m représente 0, 1 ou 2 ; et M₁ et M₂ représentent indépendamment l'hydrogène, le sodium, le potassium, le lithium et l'ammonium ; et

- (c) de 0,1 à 20 % en poids d'un agent tensioactif ; (b) étant présent dans une quantité sous-stoechiométrique par rapport aux ions dureté dans l'eau de lavage.

2. Procédé selon la revendication 1, dans lequel une composition contient de plus :

- (d) de 1 à 10 % en poids d'un silicate de sodium ayant un rapport de SiO₂/M₂O de 1:1 à 4:1, dans lequel M représente un métal alcalin ;
- (e) une quantité efficace d'agent de blanchiment d'un produit de type blanchiment et l'agent tensioactif (c) dans la composition est choisi à partir d'agents tensioactifs anioniques, non ioniques, cationiques, amphotères et leurs mélanges.

3. Procédé selon la revendication 1 ou 2, dans lequel la quantité d'adjuvant de carbonate de métaux alcalins (a) dans la composition est de 20 à 80 % en poids, de préférence de 30 à 70 % en poids.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel la quantité d'acide dicarboxylique organique, de sel hydrosoluble ou de son anhydre (b) dans la composition est de 1 à 20 % en poids.
5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel l'agent tensioactif (c) dans la composition est choisi à partir d'alkylsulfates, d'alkylsulfonates primaires et secondaires, d'alkylarylsulfonates linéaires, d'alkyléthersulfates, d'alcools aliphatiques alcoylés, d'alkylphénols alcoylés, de copolymères d'oxydes d'alkylène en C₁-C₄ et leurs mélanges.
6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel la composition comprend de plus une quantité favorisant la non incrustation de coadjuvant choisi parmi les silicates, les citrates, les acides polycarboxyliques polymères, les sels ou l'acide tétraacétique de diamine-éthylène et le nitrilotriacétate de sodium et de préférence des zéolites.
7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel dans la composition, le carbonate de métaux alcalins est du carbonate de sodium ; et l'acide dicarboxylique organique ou le sel hydrosoluble est choisi à partir d'acide phtalique, d'acide isophtalique, d'acide 2,4-pyridine dicarboxylique, d'acide 2,6-pyridine dicarboxylique, d'acide 2,3-pyridine dicarboxylique, d'acide malonique, d'acide hydroxymalonique, d'acide cétomalonique, d'acide méthylmalonique, d'acide succinique, d'acide adipique, d'acide hydroxysuccinique et d'acide tartarique, de préférence d'acide 6-pyridine dicarboxylique, d'acide cétomalonique et d'acide hydroxymalonique.