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(54) **COATED CITRIC ACID PARTICLES IN CLEANING COMPOSITIONS**

(57) The present invention relates to detergent cleaning compositions comprising a bleaching system and particles having a core comprising or consisting of citric acid and a coating comprising or consisting of a

water soluble solid coating material, wherein said detergent cleaning composition preferably is a non-liquid detergent composition, more preferred a solid laundry composition or a dishwashing composition.

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Description

[0001] This invention refers to cleaning compositions comprising citric acid particles having a particle size below 800 μm and the use of such citric acid particles in cleaning compositions, particularly bleach comprising laundry detergent cleaning compositions to increase the wash and bleach performance of said composition.

[0002] Detergent cleaning compositions comprising builder systems commonly are effective either in a basic pH range of e.g. pH 9 to 11, or they are acidic, e.g. pH below 6. In particular for laundry and automatic dishwashing compositions the pH produced in water during treatment of the materials is highly alkaline. Often such types of detergent compositions comprise a bleach system to allow excellent cleaning performance even for colored staining.

[0003] Several approaches are known to increase the cleaning performance and the bleaching effect of such detergent compositions: bleach catalysts or bleach boosters are incorporated in the compositions, enzymes are used to cleave organic soiling, builders for absorption of delivered soil. However, it is a permanent endeavor of the detergent industry to increase the cleaning performance of detergent compositions to satisfy the desire of consumers.

[0004] US 5,702,635 describes particulate laundry bleaching compositions, wherein granules of bleaching agents comprise as a further ingredient citric acid esters as stabilizing agent for said bleaching agent.

[0005] WO 92/18594 A discloses granular detergent compositions comprising three different builder types in a particular ratio, wherein the builders are selected from aluminosilicate, sodium silicate and citric acid.

[0006] DE 100 20 767 A1 describes a heavy duty laundry detergent having a bleaching system, comprising sodium bicarbonate and citric acid, resulting in the formation of Na-citrate providing good complexing efficiency in aqueous solution.

[0007] It is an object of the present invention to provide a detergent cleaning composition, in particular a laundry cleaning composition, providing an excellent cleaning and bleaching performance whilst low color fading.

[0008] This object can be achieved by the present invention, i.e. by the invention as defined in the independent and dependent claims. The invention will be further described in detail in the following.

[0009] The detergent cleaning composition of the invention comprises a bleaching system and further particles comprising or consisting essentially of citric acid, wherein said particles have a particle size below 800 μm . In a preferred embodiment the particles have a core comprising or consisting essentially of citric acid and a coating comprising or consisting essentially of a water soluble solid coating material. Such particles may be represented e.g. by granules or powder particles. With the definition the particles or the core of said particles "comprising or consisting essentially of citric acid" is meant that said particles or said core comprise(s) at least 50 wt.%, more preferred at least 60 wt.%, even more preferred at least 70 wt.%, more preferred at least 80 wt.%, even more preferred at least 90 wt.% of citric acid. In a particularly preferred embodiment the particles or the core of the particles, respectively, comprise(s) at least 95 wt.%, more preferred at least 98 wt.% and most preferred at least 99 wt.% of citric acid. In the most preferred embodiment the particles or the core consist(s) essentially of citric acid, thus, comprise(s) more than 99 %, preferably at least 99,5 %, more preferably at least 99,7%, more preferred at least 99,8, even more preferred at least 99,9 % and most preferred 100% citric acid.

[0010] Preferably according to the invention the mean particle size of the citric acid comprising particles is in the range of 100 μm - 600 μm , wherein it is preferred that no particles are comprised having a particle size above 800 μm , preferably no particles have a size above 600 μm . On the other hand it is preferred that particles having a particle size below 100 μm are less than 10 %, more preferred particles being < 100 μm are at most up to 5%. The advantage of using particles with this particle size range is the provision of a large surface, thus allowing a fast dissolution of the particles, resulting in a fast delivering of the citric acid to the wash liquor. In particular if coated particles are used a fast dissolution of the coating of the particles results in a fast dissolution of the citric acid once freed from the coating. Further, due to the large surface the citric acid released after dissolution of the coating is readily fast available.

A particularly preferred commercially available product of citric acid particles useful according to the present invention for incorporation into the detergent composition is sold under the name CAA F6000 by Jungbunzlauer, Germany

[0011] If the particles are coated on their surface, the coating is covering the core essentially. With "essentially" in this connection is meant that the surface of the particle core is covered to at least 80%, preferably to at least 90%, more preferred to at least 95%, even more preferred to at least 98% and most preferred the surface of the particle core is fully covered by the coating. Fully covered means that on the surface of the particle no citric acid is present.

[0012] The material which can be used for the coating is any material which is suitable and commonly used for water dissolvable coatings. Examples of such material are:

A.) at least one water soluble or dissolvable polymer selected from:

A1) a protein (more than 100 amino acids up to "full length proteins" e.g. up to 2500 amino acids) or a peptide having at least 10, preferably at least 50, more preferred at least 80, most preferred at least 100 amino acids, alternatively a protein or peptide having a molecular weight of 20,000 to 350,000 g/mol, preferably from 100,000

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to 300,000 g/mol The most preferred protein is gelatine or a peptide thereof. Enzymes in their active form are not preferred.

A2) sugar polymers like cellulose, starch, starch derivatives, maltodextrin, pectines like glycogene.

5 The coating may consist essentially of one of these polymers or of a mixture of at least two of these.

B.) low molecular sugars comprising 1 to 10 sugar units or any amino acid, preferably natural amino acids or a mixture of sugars, a mixture of amino acids or a mixture of sugars and amino acids. The coating may consist essentially of these compounds.

C.) salts of low molecular weight acids, preferably acids comprising one, two or three acid groups.

10 D.) polymers, like

a) water-soluble nonionic polymers from the group of

a1) polyvinyl alcohol

15 a2) polyvinyl pyrrolidones,

a3) vinyl pyrrolidone/vinyl ester copolymers,

a4) cellulose ethers

a5) polyethylene glycol

20 b) water-soluble amphoteric polymers from the group of

b1) alkyl acrylamide/acrylic acid copolymers,

b2) alkyl acrylamide/methacrylic acid copolymers,

b3) alkyl acrylamide/methyl methacrylic acid copolymers,

25 b4) alkyl acrylamide/acrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b5) alkyl acrylamide/methacrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b6) alkyl acrylamide/methyl methacrylic acid/alkylaminoalkyl (meth)acrylic acid copolymers,

b7) alkyl acrylamide/alkyl methacrylate/alkylaminoethyl methacrylate/alkyl methacrylate copolymers,

b8) copolymers of

30

b8i) unsaturated carboxylic acids,

b8ii) cationically derivatized unsaturated carboxylic acids,

b8iii) optionally other ionic or nonionic monomers,

35 c) water-soluble zwitterionic polymers from the group of

c1) acrylamidoalkyl trialkylammonium chloride/acrylic acid copolymers and alkali metal and ammonium salts thereof,

40 c2) acrylamidoalkyl trialkylammonium chloride/methacrylic acid copolymers and alkali metal and ammonium salts thereof,

c3) methacryl ethyl betaine/methacrylate copolymers,

d) water-soluble anionic polymers from the group of

45 d1) poly(meth)acrylic acid (co)polymers,

d2), vinyl acetate/crotonic acid copolymers,

d3) vinyl pyrrolidone/vinyl acrylate copolymers,

d4) graft polymers of vinyl esters, esters of acrylic acid or methacrylic acid individually or in admixture copolymerized with crotonic acid, acrylic acid or methacrylic acid with polyalkylene oxides and/or poly-

50 alkylene glycols,

d5) grafted and crosslinked copolymers from the copolymerization of

d5i) at least one monomer of the nonionic type,

d5ii) at least one monomer of the ionic type,

55 d5iii) polyethylene glycol and

d5iv) a crosslinking agent,

d6) copolymers obtained by copolymerization of at least one monomer of each of the following three groups:

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d6i) esters of unsaturated alcohols and short-chain saturated carboxylic acids and/or esters of short-chain saturated alcohols and unsaturated carboxylic acids,
d6ii) unsaturated carboxylic acids,
d6iii) esters of long-chain carboxylic acids and unsaturated alcohols and/or esters of the carboxylic acids of group d6ii) with saturated or unsaturated, linear or branched C₈₋₁₈ alcohols,

d7) terpolymers of crotonic acid, vinyl acetate and an allyl or methallyl ester,
d8) tetrapolymers and pentapolymers of

d8i) crotonic acid or allyloxyacetic acid,
d8ii) vinyl acetate or vinyl propionate,
d8iii) branched allyl or methallyl esters,
d8iv) vinyl ethers, vinyl esters or straight-chain allyl or methallyl esters,

d9) crotonic acid copolymers with one or more monomers from the group consisting of ethylene, vinyl benzene, vinyl methyl ether, acrylamide and water-soluble salts thereof,
d10) terpolymers of vinyl acetate, crotonic acid and vinyl esters of a saturated aliphatic monocarboxylic acid branched in the α -position,
e) water-soluble cationic polymers from the group of

e1) quaternized cellulose derivatives,
e2) polysiloxanes containing quaternary groups,
e3) cationic guar derivatives,
e4) polymeric dimethyl diallylammonium salts and copolymers thereof with esters and amides of acrylic acid and methacrylic acid,
e5) copolymers of vinyl pyrrolidone with quaternized derivatives of dialkylaminoacrylate and methacrylate,
e6) vinyl pyrrolidone/methoimidazolium chlorid copolymers,
e7) quaternized polyvinyl alcohol,
e8) polymers known by the INCI names of polyquaternium 2, polyquaternium 17, polyquaternium 18 and polyquaternium 27.

[0013] All the compounds of D.) are described in detail in EP 1 173 539 B1.

[0014] A preferred coating comprises compounds mentioned above under A), B) or C), preferably maltodextrin or low molecular weight compounds B) or salts of low molecular weight acids C). A particular preferred coating is a coating with a salt of a low molecular weight acid. With low molecular weight compound or low molecular weight acid a compound or an acid (as free acid) is meant having a molecular weight of below 400g/mol, preferably below 350 g/mol, more preferred below 300 g/mol. Said low molecular weight acid comprises at least one carboxyl group, preferably at least two, more preferred three carboxyl groups. The salt of low molecular acid preferably is an alkali metal citrate, preferably Na-citrate. A coating with Tri-Na citrate is particularly preferred.

[0015] Another preferred water soluble low molecular weight compound is any type of a low molecular weight sugar or an amino acid or a salt thereof. Examples of "low molecular weight compounds" are C₃-C₆ sugars in aldose or ketose form like allose, altrose, glucose, mannose, gulose, idose, galactose, talose, psicose, fructose, sorbose, tagatose, xylulose, ribulose, ribose, arabinose, xylose, lyxose, threose, erythrose, erythrulose, dihydroxy acetone or glycerol aldehyde or disaccharides like for example saccharose, lactose, maltose or Isomalt or oligosaccharides comprising 3 to 10 sugar units or amino acids, preferably natural amino acids (commonly contained in natural proteins) without being restricted to the mentioned examples. One particularly preferred low molecular weight compound is the sugar Isomalt ST, comprising 6-O-a-D-glucopyranosyl-D-sorbite and 1-O- α -D-glucopyranosyl-D-mannite dihydrate units.

[0016] One particular advantage of these materials is on one side the water solubility / dispersibility on the other hand the non-toxicity of the compounds.

[0017] In a particularly preferred embodiment the coating consists essentially of the mentioned water dissolvable material(s), this means that the coating comprises less than 10 wt.%, preferably less than 5 wt.%, more preferred less than 2 wt.%, even more preferred less than 1 wt.% and most preferred less than 0.5 wt.% of other materials.

[0018] When referring to the water dissolvable material, a material herein is defined as being "water-soluble/dissolvable/dispersible" when more than 99% of a coating (layer) with a thickness of up to 0.5 mm of such material dissolves within 10 minutes, preferably within 5 min in a beaker containing 1 L of deionised water at 40° C which is stirred with a stirrer revolving at 200 r. p.m. It is pointed out that materials can be used as ingredients for the coating which itself may not be soluble, but e.g. dispersible, as long as the coating comprising said material is dissolved by water.

[0019] Particular preferred embodiments of the particle comprising a core of citric acid and a water dissolvable coating are the commercially available products "Citrocoat® N" or "citric acid DC" provided by Jungbunzlauer, Germany. Citrocoat® N represents particles having a core of citric acid coated with sodium citrate, prepared by applying NaOH-solution to the surface of granulated citric acid, whereas "citric acid DC" comprises a core of citric acid, coated with maltodextrin.

The most preferred embodiment is Citrocoat® N.

[0020] Providing the citric acid in form of particles having a particle size below 800 μm has the clear advantage that the citric acid is provided in the wash liquor very fast, thus, resulting in an acid pH of the wash liquor at the beginning of the wash cycle. It has been found by the present inventors that such a pH decrease below pH7 at the beginning of the wash cycle increases noticeably the bleaching performance of the detergent, in particular in laundry cleaning.

[0021] Providing the citric acid in form of coated particles has indeed two further advantages in comparison to the provision of uncoated citric acid:

1. Citric acid can be incorporated into the detergent cleaning composition in an amount of up to 15 wt.%, e.g. from 1 to 15 wt.% without resulting in an undesired caking of the detergent composition during storage,

2. Due to the incorporation of the coated citric acid in such an amount the pH of the wash liquor prepared by adding the inventive detergent cleaning composition to water shows a characteristic progression. Due to the coating of the citric acid the detergent composition when added to water provides an alkaline pH after first contact with water. As soon as the coating dissolved the wash liquor shows an abrupt pH decrease to a more acid pH. Thus, dependent from the thickness of the coating the citric acid is delivered into the wash liquor in a "delayed" manner, resulting in a pH progression of the wash liquor of being within the first seconds alkaline, followed by a rapid pH decrease by at least one, preferably at least 1,5 pH value(s), preferably a decrease resulting in an acid pH (below pH 7), followed by a re-increase up to a moderate alkaline pH (pH 7,5 to 10,5, preferably pH 8,5 to 10) during the further washing process. Such values are obtainable when the detergent cleaning composition is added to water in commonly used amounts, e.g. 20 - 30 g of the composition to about 5 l of water. Examples of such a characteristic pH progression is e.g. shown in Figure 1 (53,57 g of detergent composition added to an amount of 10 l of water) and Figure 2 (46,21 g of detergent composition added to an amount of 10 l of water).

[0022] The specific pH progression provided within the wash liquor by incorporating the citric acid in form of (optionally coated) particles thus allows the washing process to be carried out at a moderate alkaline pH, thus, a pH in the range of 8.5 to 10 after a "boosting" phase at an acid pH below pH 7. Said effect is more readily achievable if the detergent composition is "balanced" in view of the content of the citric acid in comparison to alkalic or alkali providing compounds, e.g. the amount of SODA (Na carbonate or hydrogen carbonate) is preferably at most 8 wt.%.

[0023] By this particular pH progression during the first minutes of the washing process and the provision of considerable amounts of citric acid in the washing liquor the washing performance of the detergent composition, in particular the bleaching performance, is considerably increased, without the fading of colours of the cleaned articles.

[0024] The detergent cleaning composition of the present invention comprises the (optionally coated) citric acid particles in an amount of from 1 to 15 wt.%, preferably in an amount of from 2 to 12 wt.%, more preferred in an amount of from 3 to 10 wt.%, and most preferred in an amount of from 4 to 8 wt.%.

[0025] If a coating is present, the thickness of the coating may vary dependent from the desired "delay" of release of the citric acid into the wash liquor, however according to the invention preferably is in the range of from 1 nm to 0.5 mm, preferably 10 nm to 200 μm , more preferred 50 nm to 100 μm , even more preferred 100 nm to 50 μm and most preferred 0.5 to 10 μm .

[0026] According to the invention it is preferred that the amount of carbonate or hydrogen carbonate in said cleaning composition is at most 8 wt% of the detergent cleaning composition. It is further preferred that the amount of carbonate or hydrogen carbonate is in the range of 1 wt.% to 6 wt.%, more preferred in the range of 1,5 wt.% to 5 wt.%, even more preferred from 2 wt.% to 4 wt.%.

[0027] Besides the coated citric acid particles and independent therefrom the detergent cleaning composition of the present invention further comprises preferably an additional amount of citrate. The citrate preferably is an alkali metal salt of citric acid, preferably sodium citrate, wherein tri-sodium citrate is particularly preferred. The amount of the citrate in the cleaning composition may range from 0.5 to 10 wt.%, preferably 1 to 8 wt.%, more preferred 2 to 6 wt.% whereas it is preferred that the ratio (wt/wt) of the citric acid comprising particles to separate citrate in the composition is in the range of 4:1 to 0,25 :1, preferably 3,5:1 to 0,3:1, more preferred 3:1 to 0,33:1, even more preferred 2,5:1 to 0,4:1 and most preferred about 2:1 to 1:1.

[0028] The detergent composition according to the present invention comprises a bleaching system, comprising at least one bleaching agent, preferably one delivering peroxide and further preferably a bleach activator. The bleaching agent preferably is at least one peroxy compound generally used in laundry or dishwashing cleaning detergents, such as hydrogen peroxide, alkali metal perborate that may be present as the tetra- or monohydrate, percarbonate, perpyrophosphate and persulfate, which are generally present as the alkali metal salts, particularly as the sodium salts, or

percarboxylic acids, for example diperoxy dodecane dioic acid or phthaloylaminoperoxycaproic acid,. Said bleaching agent(s) is/are present preferably in amounts in the range 2 wt.% to 70 wt.% of the composition, wherein percarbonate is particularly preferred. Such bleaching agents are present in laundry detergents in accordance with the invention, preferably in amounts from 5 wt.% up to 40 wt.%, more preferred from 8 wt.% up to 25 wt.% and particularly preferred from 10 wt.% to 20 wt.%, each based on the total composition, wherein percarbonate in particular is preferred. In automatic dishwashing compositions said bleaching agents can be present in amounts of 2 wt.% to 30 wt.% of the composition, preferably 3 wt.% to 20 wt.%, more preferred 4 wt.% to 15 wt.%, wherein percarbonate or perborate are preferred.

[0029] The cleaning composition according to the present invention can also include bleaches from the group of organic bleaches. Examples of organic bleaches include the diacyl peroxides, such as, for example, dibenzoyl peroxide. Further organic bleaches include the peroxy acids, particular examples being the alkylperoxy acids and the arylperoxy acids. Representative examples include (a) peroxybenzoic acid and its ring-substituted derivatives, such as alkylperoxybenzoic acids, but also peroxy- α -naphthoic acid and magnesium monopero-phthalate, (b) the aliphatic or substituted aliphatic peroxy acids, such as peroxy lauric acid, peroxy stearic acid, *e*-phthalimido-peroxycaproic acid [phthaliminoperoxyhexanoic acid (PAP)], *o*-carboxybenzamidoperoxycaproic acid, N-nonenylamidoperadipic acid and N-nonenylamido-persuccinates, and (c) aliphatic and araliphatic peroxydicarboxylic acids, such as 1, 12-diperoxy-carboxylic acid, 1,9-diperoxyazelaic acid, diperoxysebacic acid, diperoxybrassylic acid, the diperoxyphthalic acids, 2-decyldiperoxybutane-1,4-dioic acid, N,N-terephthaloyl-di(6- anilinopercaproic acid).

[0030] The bleaching system preferably comprises a bleach activator. Suitable components of the bleach activator include the customarily used N- or O-acyl compounds, for example polyacylated alkylenediamines, particularly tetraacetylenediamine (TAED); acylated glycolurils, in particular tetraacetyl glycoluril; N-acylated hydantoins; hydrazides; triazoles; urazoles; diketopiperazines; sulfuryl amides and cyanurates; as well as carboxylic acid anhydrides, particularly phthalic anhydride; carboxylic acid esters, particularly sodium isononanoyl phenol sulfonate; and acylated sugar derivatives, in particular pentaacetylglucose; as well as cationic nitrile derivatives such as trimethylammonium acetonitrile salts, N-acylirrides, in particular N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, in particular n-nonanoyl- or isonon-anoyloxybenzenesulfonate (n- or iso-NOBS) or n- methylmorpholinium acetonitrile methyl sulfate (MM A). In order to avoid interaction with the peroxy compounds during storage, the bleach activators can be coated or granulated in a known manner with coating materials, wherein tetraacetylenediamine granulated with carboxymethyl cellulose are preferred, e.g. such granules having a mean particle sizes of 0.01 mm to 0.8 mm, further e.g. granulated 1,5-diacetyl- 2,4-dioxohexahydro-1,3,5-triazine, and/or trialkylammonium acetonitrile in particle form may be suitably used. The laundry detergents preferably comprise these types of bleach activators in amounts of up to 15 wt.%, preferably in an amount in the range of from 1 wt.% to 15 wt.% , preferably 2 wt.% to 12 wt.%, more preferred 3 to 10 wt.% , particularly 5 wt.% to 10 wt.% each based on the total composition, dishwashing compositions comprise such bleach activators in an amount of 1 wt.% to 10 wt.%, preferably 2 wt.% to 7 wt.%.

[0031] The detergent composition of the present invention preferably does not comprise any bleach catalyst or bleach boosting component. Exemplary bleach-catalysts or boosting transition metal complexes, in particular with the central atoms Mn, Fe, Co, Cu, Mo, V, Ti and/or Ru, include those from the group of manganese and/or cobalt salts and/or complexes, such as the cobalt (ammine) complexes, the cobalt (acetate) complexes, the cobalt (carbonyl) complexes, the chlorides of cobalt or of manganese, and manganese sulphate as well as manganese complexes known in the art as being bleach catalysts.

[0032] The detergent composition of the present invention preferably comprises at least one anionic surfactant, in particular in case said composition is a laundry detergent composition. The anionic surfactant is preferably of the sulfate and/or sulfonate type, e.g. a fatty alkyl sulfate, fatty alkyl ether sulfate, sulfofatty acid ester and/or di-salts of sulfofatty acid, alkyl benzolsulfonate, alkylsulfonate, alkylethersulfonate or of the soap type. The anionic surfactant further can be selected from the alkyl or alkenyl sulfates and/or the alkyl or alkenyl ether sulfates, wherein it is preferred that the alkyl or alkenyl group has 8 to 22, particularly 12 to 18 carbon atoms. Among these are preferred those whose content of compounds having longer chain groups in the range 16 to 18 carbon atoms is more than 20 wt.%. As anionic surfactant of the soap type saturated fatty acid soaps are suitable, such as the salts of lauric acid, myristic acid, palmitic acid or stearic acid, as well as soaps derived from natural fatty acid mixtures such as coconut oil fatty acid, palm kernel oil fatty acid or tallow fatty acid. A particularly preferred anionic surfactant is alkyl benzolsulfonate. The anionic surfactants preferably are comprised in the detergent laundry cleaning composition in an amount in the range 2 wt.% to 25 wt.%, preferably from 5 to 20 wt.%, particularly in an amount of 8 to 15 wt.%. In automatic dishwashing compositions the anionic surfactant may comprised in amounts of 0,5 wt.% to 10 wt.%, preferably 0,8 wt.% to 5 wt.%, more preferred 1 wt.% to 2 wt.%.

[0033] Furthermore, the detergent cleaning composition may include at least one non-ionic surfactant in particular such non-ionic surfactants are comprised in automatic dishwashing compositions. Suitable non-ionic surfactants preferably are selected from fatty alkyl polyglycosides, fatty alkyl polyalkoxylates, especially ethoxylates and/or propoxylates, fatty acid polyhydroxyamides and/or ethoxylated and/or propoxylated products of fatty alkylamines, vicinal diols, fatty

acid alkyl esters and/or fatty acid amides as well as their mixtures. A preferred type of non-ionic surfactants is a fatty alcohol ethoxylate or a fatty alcohol ethoxylate comprising propoxylate groups. Examples of suitable surfactants are commercially available, e.g. the Lutensol AO or Lutensol M types of BASF (Germany), such as. Lutensol AO5, Lutensol M5, Lutensol AO7, Lutensol M7, or Dehydol LT7. For dishwashing said non-ionic surfactants preferably are incorporated in the detergent cleaning composition in an amount in the range 1 wt.% to 15 wt.%, preferably 2 to 10 wt.%, more preferred 5 to 8 wt.%, in laundry compositions an amount of 0,5 wt.% to 20 wt.%, preferably 2 to 15 wt.%, more preferred 4 to 10 wt.% may be added, if desired. All the amounts refer to the whole detergent composition.

[0034] The compositions can also, when desired, comprise betaines and/or cationic surfactants, which - when present - are preferably added in amounts of 0.5 wt.% to 7 wt.%. Among these, esterquats are particularly preferred. Such components may increase the soft appearance of the cleaned laundry.

[0035] According to the invention the detergent cleaning composition besides the citric acid comprising particles and separate from them comprises further water-soluble and/or water-insoluble builders, in combined amounts in the range of 2 wt.% to 60 wt.%, preferably 5 to 55 wt.%, more preferred from 10 to 50 wt.%, e.g. 15 to 40 wt.% or 20 to 30 wt.%.

[0036] The composition preferably comprises water-soluble and/or water-insoluble, organic and/or inorganic builder. The water-soluble organic builders particularly include those from the class of the polycarboxylic acids, e.g. - besides the coated citric acid - tartaric acid, succinic acid, malonic acid, adipic acid, maleic acid, fumaric acid, oxalic acid, gluconic acid and/or nitrilotriacetic acid, aspartic acid, ethylenediaminetetraacetic acid and sugar acids; as well as polymeric (poly)carboxylic acids, particularly the polycarboxylates that can be obtained by oxidation of polysaccharides, polymeric acrylic acid, methacrylic acid, maleic acid and mixed polymers thereof, which can also comprise minor amounts of copolymerized polymerizable substances that are free of carboxylic acid functionality. The relative molecular weight of the homopolymers of unsaturated carboxylic acids lies generally between 5000 g/mol and 200000 g/mol, that of the copolymers between 2000 g/mol and 200000 g/mol, preferably 50000 g/mol to 120000 g/mol, based on the free acid. A particularly preferred copolymer is an acrylic acid-maleic acid copolymer e.g. one having a relative molecular weight of 50000 g/mol to 100000 g/mol (molecular masses as described by the providing companies). A suitable copolymer of this type is available under the trade name Sokalan CP5® by BASF.

[0037] Further suitable compounds of this class are copolymers of acrylic acid or methacrylic acid with further monomers, e.g. with vinyl ethers, such as vinyl methyl ethers, vinyl esters, ethylene, propylene and styrene, in which the content of the acid is at least 50 wt.%. Terpolymers, which comprise two unsaturated acids and/or their salts as monomers as well as vinyl alcohol and/or an esterified vinyl alcohol or a carbohydrate as the third monomer, can also be used as water-soluble organic builders. The first acid monomer or its salt is derived from a monoethylenically unsaturated C₃-C₈ carboxylic acid and preferably from a C₃-C₄ monocarboxylic acid, particularly from (meth)acrylic acid. The second acid monomer or its salt can be a derivative of a C₄-C₈ dicarboxylic acid, maleic acid being particularly preferred. In this case the third monomer unit is formed from vinyl alcohol and/or preferably an esterified vinyl alcohol. In particular, vinyl alcohol derivatives are preferred which represent an ester of short chain carboxylic acids, for example C₁-C₄ carboxylic acids with vinyl alcohol. Preferred terpolymers comprise 60 wt.% to 95 wt.%, particularly 70 wt.% to 90 wt.% (meth)acrylic acid or (meth)acrylate, particularly preferably acrylic acid or acrylate, and maleic acid or maleate as well as 5 wt.% to 40 wt.%, preferably 10 wt.% to 30 wt.% vinyl alcohol and/or vinyl acetate. Terpolymers are quite particularly preferred, in which the weight ratio (meth)acrylic acid or (meth)acrylate to maleic acid or maleate is between 1: 1 and 4: 1, preferably between 2: 1 and 3: 1 and particularly 2: 1 and 2.5: 1. Here, both the quantities and the weight ratios are based on the acids. The second acid monomer or its salt can also be a derivative of an allyl sulfonic acid, which is substituted in the 2-position with an alkyl group, preferably a C₁-C₄ alkyl group, or an aromatic group that is preferably derived from benzene or benzene derivatives. Preferred terpolymers comprise 40 wt.% to 60 wt.%, particularly 45 wt.% to 55 wt.% (meth)acrylic acid or (meth)acrylate, particularly preferably acrylic acid or acrylate, 10 wt.% to 30 wt.%, preferably 15 wt.% to 25 wt.% methallyl sulfonic acid or methallyl sulfonate and as the third monomer 15 wt.% to 40 wt.%, preferably 20 wt.% to 40 wt.% of a carbohydrate. This carbohydrate can, for example, be a mono, di, oligo or polysaccharide, mono, di or oligosaccharides being preferred, saccharose being particularly preferred. Including the third monomer into the polymer presumably creates intended weak points in the polymer, which result in the good biological degradation of the polymer. In general, the terpolymers possess a relative molecular weight between 1000 g/mol and 200000 g/mol, preferably between 2000 g/mol and 50000 g/mol and particularly between 3000 g/mol and 10000 g/mol. In general, all the cited polycarboxylic acids are added in the form of their water-soluble salts, particularly their alkali metal salts.

[0038] Further examples of builder acids aminotrimethylenephosphonic acid, hydroxyethanediphosphonic acid.

[0039] The above mentioned organic builders are preferably comprised in combined amounts of from 0,5 wt.% up to 50 wt.%, preferably up to 40 wt.%, particularly up to 25 wt.% preferably from 0,5 wt.% to 10 wt.%, more preferred from 1 wt.% to 8 wt.% and particularly preferred from 2 wt.% to 6 wt.% of the detergent cleaning composition.

[0040] Besides the above mentioned organic builders or instead of them the detergent composition of the present invention can comprise inorganic builder compounds. In particular, the composition may comprise crystalline or amorphous inorganic builders in (combined) amounts of up to 60 wt.%, preferably from 2 wt.% to not more than 50 wt.%, more preferred in the range of 5 to 40 wt.%.

[0041] Among these, the detergent-quality crystalline sodium aluminosilicates, particularly zeolite types, e.g. NaA and optionally NaX, are preferred. Amounts close to the cited upper limit are preferably incorporated in the solid, particulate detergent cleaning composition. Suitable aluminosilicates exhibit in particular no particles with a particle size above 30 μm and preferably consist of at least 80 wt.% of particles smaller than 10 μm . Their calcium binding capacity, which can be determined according to the indications of German patent DE 24 12 837, is preferably in the range of 100 to 200 mg CaO per gram. Suitable substitutes or partial substitutes for the cited aluminosilicate are crystalline alkali metal silicates that can be incorporated as the sole inorganic binder or can be present in a mixture with amorphous silicates. The alkali metal silicates that can be used as builders in the inventive agents preferably have a molar ratio of alkali metal oxide to SiO_2 below 0.95, particularly 1: 1.1 to 1: 12 and can be amorphous or crystalline. Preferred alkali metal silicates are sodium silicates, particularly amorphous sodium silicates, having a molar ratio $\text{Na}_2\text{O} : \text{SiO}_2$ of 1: 2 to 1: 2.8. These types of amorphous alkali metal silicates are commercially available. Those with a molar ratio $\text{Na}_2\text{O} : \text{SiO}_2$ of 1: 1.9 to 1: 2.8 are preferably added as solids and not in the form of a solution in the context of manufacturing. Zeolite types may be present as inorganic binders in an amount of from 2 wt.% to not more than 50 wt.%, more preferred in the range of 5 to 40 wt.%, particularly preferred in an amount of from 10 to 35 wt.%.

[0042] Crystalline silicates that can be present alone or in a mixture with amorphous silicates are preferably crystalline, layered silicates corresponding to the general formula $\text{Na}_2\text{Si}_x\text{O}_{2x+1}y\text{H}_2\text{O}$, wherein x, the so-called modulus, is a number from 1.9 to 4 and y is a number from 0 to 20, preferred values for x being 2, 3 or 4. Preferred crystalline layered silicates are those in which x assumes the values 2 or 3 in the cited general formula. In particular, both beta - and d-sodium disilicates ($\text{Na}_2\text{Si}_2\text{O}_5y\text{H}_2\text{O}$) are preferred. Practically anhydrous crystalline alkali metal silicates of the abovementioned general formula, in which x is a number from 1.9 to 2.1 can also be prepared from amorphous alkali metal silicates.

[0043] Furthermore, in the composition according to the invention a crystalline sodium layered silicate, e.g. one with a modulus of 2 to 3 can be added, as can be prepared from sand and soda. Further, crystalline sodium silicates with a modulus in the range 1.9 to 3.5 can be added. The content of alkali metal silicates in the composition, if present, is preferably in the range 1 wt.% to 50 wt.% and particularly 5 wt.% to 35 wt.%, based on the composition. For the case that alkali metal aluminosilicate, particularly zeolite, is also present as an additional builder, then the content of alkali metal silicate is preferably in the range 0,1 wt.% to 15 wt.% and particularly 0,3 wt.% to 8 wt.%, based on the detergent cleaning composition. The weight ratio of aluminosilicate to silicate, each based on anhydrous active substances, is then preferably 4: 1 to 10: 1. In agents that comprise both amorphous and crystalline alkali metal silicates, the weight ratio of amorphous alkali metal silicate to crystalline alkali metal silicate is preferably 1: 2 to 2: 1 and particularly 1: 1 to 2: 1.

[0044] A further substance class of builder acids are the phosphonic acids or their salts. In particular, these are hydroxyalkane- or aminoalkanephosphonic acids. Among the hydroxyalkanephosphonic acids, 1 -hydroxy ethane- 1,1-diphosphonic acid (HEDP) is of particular importance. It may be neutralized to give a sodium salt; the disodium salt being neutral and the tetrasodium salt being alkaline (pH 9).

[0045] In addition to the cited builders, further water-soluble or water-insoluble inorganic compounds can be incorporated as ingredients into the detergent cleaning composition. In particular alkali metal carbonates, alkali metal hydrogen carbonates and alkali metal sulfates as well as their mixtures are suitable. This type of additional inorganic material can be present in amounts of up to 15 wt.%, however, according to a particularly preferred embodiment of the present invention said compounds are comprised in an amount of from 0,5 wt.% to at most 8 wt.%, preferably from 1 wt.% to 7 wt.%, more preferred from 2 wt.% to 6 wt.%, and most preferred in a range of from 3 wt.% to 5 wt.%. In a particularly preferred embodiment the composition of the present invention comprises not more than 5 wt.% of alkali metal carbonates, particularly of sodium carbonate (soda) or sodium bicarbonate.

[0046] In addition, the compositions can comprise further conventional ingredients of laundry detergent compositions and dishwashing compositions. These optional ingredients particularly include enzymes, enzyme stabilizers, chelating or complexing agents, in particular complexants for heavy metals, for example amino polycarboxylic acids, amino hydroxypolycarboxylic acids, polyphosphonic acids and/or amino polyphosphonic acids, foam inhibitors, for example organopolysiloxanes or paraffins, solvents, optical brighteners, for example stilbene sulfonic acid derivatives, buffering agents, soil suspending agents, soil release agents, suds control agents, -tarnishing or anti-corrosion agents, dyes, dye transfer inhibitors, pigments, perfumes or similar.

[0047] Enzymes that are optionally present are preferably selected from the group that includes protease, amylase, lipase, cellulase, hemicellulases, oxidase, peroxidase, mannanase or their mixtures. Protease isolated from microorganisms, such as bacteria and fungi, are considered first and foremost. They are obtained by means of fermentation processes from suitable microorganisms in a manner known per se. Proteases are commercially available, for example, under the trade names BLAP(R), Savinase(R), Esperase(R), Maxatase(R), Optimase(R), Alcalase(R), Durazym(R) or Maxapem(R). The suitable lipase can be obtained for example from Humicola lanuginosa, from Bacillus types, from Pseudomonas types, from Fusarium types, from Rhizopus types or from Aspergillus types. Suitable lipases are commercially available, for example, under the trade names Lipolase(R), Lipozym(R), Lipomax(R), Amano(R)-Lipase, Toyo-Jozo(R)-Lipase, Meito(R)-Lipase und Diosynth(R)-Lipase. Suitable amylases include, in particular, alpha-amylases, isoamylases, pullulanases and pectinases. Such amylases are commercially available, for example, under the trade names Max-

5 amyl(R), Termamyl(R), Duramyl(R) and Purafect(R) OxAm. Suitable cellulase can be an isolated enzyme from bacteria or fungi and exhibits a pH optimum preferably in the weakly acidic to weakly alkaline region of 6 to 9.5. These types of cellulases are commercially available under the trade names Celluzyme(R), Carezyme(R) and Ecostone(R). All the mentioned enzymes are only to be considered as examples, without restricting the usable or suitable enzymes. In some

10 [0048] The enzymes can be adsorbed on carrier substances or embedded in coating substances in order to protect them against premature decomposition. The proportion of the enzymes, enzyme mixtures or enzyme granulates can, for example, be about 0.1 to 5 percent by weight, for example from 0.5 percent to about 4.5 percent by weight, in each case based on the total weight of the

15 [0049] The conventional enzyme stabilizers that are optionally present, particularly in liquid compositions, include e.g. amino alcohols, for example mono-, di-, triethanolamine and mono-, di-, tripropanolamine and their mixtures, lower carboxylic acids, boric acid or alkali metal borates, boric acid carboxylic acid combinations, boric acid esters, boronic acid derivatives, calcium salts, for example the Ca formic acid combination, magnesium salts, and/or sulfur-containing reducing agents.

20 [0050] The suitable foam inhibitors include long chain soaps, especially behenic soap, fatty acid amides, paraffins, waxes, microcrystalline waxes, organopolysiloxanes and their mixtures, which can moreover comprise microfine, optionally silanized or otherwise hydrophobized silica. For use in particulate compositions, such foam inhibitors are preferably bound on granular, water-soluble carriers.

25 [0051] The well known polyester soil-release polymers that can be additionally incorporated or used include copolyesters of dicarboxylic acids, for example adipic acid, phthalic acid or terephthalic acid, diols, for example ethylene glycol or propylene glycol, and polydiols, for example polyethylene glycol or polypropylene glycol. The soil-release polymer is preferably water-soluble, wherein the term "water-soluble" should be understood to mean a solubility of at least 0.01 g, preferably at least 0.1 g of the polymer per litre water at room temperature and pH 8. Under these conditions however, particularly preferred polymers exhibit a solubility of at least 1 g per litre, more preferably at least 10 g per litre.

30 [0052] The detergent cleaning compositions according to the present invention may include derivatives of diaminostilbenedisulfonic acid or alkali metal salts thereof as optical brighteners. Suitable examples are salts of 4,4'-bis(2-anilino-4-Tnoipholino-1,3,5-triazinyl-6-amino)stilbene-2,2'-di sulfonic acid or similarly constructed compounds which bear a diethanolamino group, a methylamino group, an anilino group or a 2-methoxyethylamino group instead of the morpholino group. In addition, brighteners of the substituted diphenylstyryl type may also be present, for example the alkali metal salts of 4,4'-bis(2-sulfostyryl)diphenyl, 4,4'-bis(4-chloro-3-sulfostyryl)diphenyl, or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)diphenyl. Mixtures of the abovementioned brighteners can also be used.

35 [0053] Anti-caking agents which may be used in the detergent compositions according to the invention include several agents. For example, amorphous silicate material may be added to prevent and/or reduce agglomeration of the solid state detergent into cakes. In another example, sodium bicarbonate, talcum powder or tricalcium phosphate may be used as an anti-caking agent. Additionally, alumino silicates may have anti-caking activity. Accordingly, certain compounds- such as zeolites- may be able to provide more than one function, one of which may be preventing the agglomeration of the solid detergent into cakes.

40 [0054] The detergent compositions may also include further pH adjusting agents. Such pH adjusting agents may be either acids or bases, and may be used to either raise or lower the pH. Examples of suitable pH adjusting agents, some of which may also be able to serve additional functions in the detergent cleaning composition include alkali and alkaline earth metal salts of carbonate, bicarbonate, hydroxide, phosphate, silicate, and combinations thereof. Further examples of suitable pH adjusting agents may also include inorganic and/or organic acids, provided that these are compatible with the other ingredients. For example, a pH adjusting agent may include solid mono-, oligo- and polycarboxylic acids, such as citric acid (non-coated), tartaric acid, succinic acid, malonic acid, adipic acid, maleic acid, fumaric acid, oxalic acid, and polyacrylic acid. The anhydrides of organic acids may also be suitable, such as maleic anhydride and succinic anhydride.

50 [0055] The detergent compositions according to the present invention may include antiredeposition agents, which may also be able to act as soil release promoting agents. Examples of such agents include copolyesters containing dicarboxylic acid units, such as terephthalic acid or sulfoisophthalic acid, alkylene glycol units, such as ethylene glycol or propylene glycol, and polyalkylene glycol units, such as polyethylene glycol. Further examples of antiredeposition agents may include celluloses, such as carboxymethylcellulose, microfibrillar cellulose, nonionic celluloses, and the like.

55 [0056] The detergent cleaning composition according to the invention is a non-liquid detergent composition comprising a bleach system, preferably a solid laundry cleaning composition or a solid dishwashing composition, mostly preferred in form of particles, a granulate, a powder or a tablet. A laundry cleaning composition is particularly preferred.

[0057] In a preferred embodiment, a laundry detergent composition is in particulate form (e.g. powder, particles, granules) or in form of a pressed body, and comprises from 2 to 10 wt.% of the citric acid comprising particles, 2 to 6

wt.% citrate separate from the citric acid particles, preferably tri-sodium citrate, up to 25 wt.% , particularly 5 wt.% to 25 wt.% bleaching agent, especially alkali metal percarbonate, up to 15 wt.%, particularly 1 wt.% to 10 wt.% bleach activator, preferably TAED, 20 wt.% to 55 wt.% inorganic builder(s), up to 10 wt.% , particularly 2 wt.% to 8 wt.% water-soluble organic builder, 10 wt.% to 25 wt.% anionic surfactant, 1 wt.% to 10 wt.% non-ionic surfactant and up to 5 wt.%, particularly 2 wt.% to 5 wt.% alkali metal carbonate and/or alkali metal hydrogen carbonate. Further, said preferred composition may comprise a phosphonate.

[0058] In another preferred embodiment, an automatic dishwashing composition is in particulate form (e.g. powder, particles, granules) or in form of a pressed body, and comprises from 2 to 15 wt.% of the citric acid comprising particles, 2 to 6 wt.% citrate separate from the citric acid particles, preferably tri-sodium citrate, up to 15 wt.%, particularly 2.5 wt.% to 10 wt.% bleaching agent, especially alkali metal percarbonate, up to 15 wt.% , particularly 1 wt.% to 10 wt.% bleach activator, preferably TAED, 20 wt.% to 55 wt.% inorganic and/or organic builder(s), an anionic surfactant, 1 wt.% to 8 wt.% non-ionic surfactant and up to 5 wt.%, particularly 3 wt.% to 5 wt.% alkali metal carbonate and/or alkali metal hydrogen carbonate.

[0059] A solid detergent cleaning composition according to the present invention may be produced according to any of the known methods. Examples of suitable methods include extrusion, tableting, spray drying, granulation, particle coating techniques, pelletizing, pressing and combinations thereof.

[0060] By the use of the present cleaning compositions wash liquors can be prepared showing a particular pH progression during solution of the composition ingredients. A wash liquor prepared by adding a commonly used amount of the composition (e.g. 20 to 30 g per 5 l water) shows within the first two minutes after addition to water temporarily an acidic pH, followed by an increase to a moderate basic pH in the range of pH 8 to pH 9,8.

[0061] A further aspect of the invention is a method for cleaning laundry by using a detergent cleaning composition as described herein for laundry washing and/ or a method for cleaning dishes by using a detergent cleaning composition described herein for dishwashing.

Figures:

[0062]

Figure 1 shows the pH progression of three detergent formulations: Formulations A, B and C according to Example 3A.

Figure 2 shows the pH progression of three detergent formulations: Formulations A, B and C according to Example 3B.

Examples

Example 1 Cleaning performance of laundry cleaning compositions at different wash temperatures

[0063] A detergent cleaning formulation according to the invention was compared with two standard (marketed) laundry detergent compositions in view of their laundry wash performance on stained cotton samples. For this wash test 75 g of each of the detergent compositions were added to an amount of 16 l of water, respectively, resulting in the wash liquor. For wash tests 10 l of said wash liquor were used in the test washing machine.

Formulation A: A commercially available laundry detergent formulation comprising a bleach system with a bleach catalyst:

Formulation B: Standard laundry detergent powder, comprising a standard bleach system (TAED, Na-percarbonate) without any bleach catalyst:

Formulation C: Laundry detergent composition according to the invention comprising a standard bleach system (TAED, Na-percarbonate) without bleach catalyst, comprising based on the whole composition 5 wt.% of the citric acid comprising particles (Citrocoat N® from Jungbunzlauer), 2,5 wt.% citrate separate from the citric acid particles, 2,5 wt.% Na-carbonate and further standard ingredients like builder, anionic and non-ionic surfactants.

[0064] The cleaning performance was considered after the wash at three different wash temperatures. The results were rated according to a school note system (1= very good result, no stain remaining, 6= almost no stain removal, colored stain). Results are shown in table 1.

Table 1

Bleaching sensitive stains	Formulation A	Formulation B	Formulation C
20°C	3,8	3,5	3,2

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(continued)

Bleaching sensitive stains		Formulation A	Formulation B	Formulation C
Tea	40°C	1,9	2,4	1,5
	60°C	2,0	2,5	2,0
	20°C	3,7	3,6	2,9
Red wine	40°C	2,8	2,8	2,0
	60°C	2,5	2,5	2,0
	20°C	4,3	4,3	4,3
Blueberry juice	40°C	3,1	3,4	2,6
	60°C	2,5	2,8	2,0
	20°C	3,2	3,3	2,5
Cherry juice	40°C	2,6	2,6	2,3
	60°C	1,8	1,8	1,8

Example 2 : Cleaning performance of laundry cleaning compositions at a lower dosage

[0065] A detergent cleaning formulation according to the invention was compared with two standard (marketed) laundry detergent compositions in view of their laundry wash performance on stained cotton samples. For this wash test 75 g of Formulation A and 67,5 g of Formulation B and C, respectively, were added to an amount of 16 l of water, respectively, resulting in the wash liquor. For wash tests 10 l of said wash liquor were used in the test washing machine.

Formulation A: A commercially available laundry detergent formulation comprising a bleach system with a bleach catalyst:

Formulation B: Standard laundry detergent powder, comprising a standard bleach system (TAED, Na-percarbonate) without any bleach catalyst:

Formulation C: Laundry detergent powder according to the invention comprising a standard bleach system (TAED, Na-percarbonate) without bleach catalyst, comprising based on the whole composition 4 wt.% of the citric acid comprising particles (Citrocoat N ® from Jungbunzlauer), 4 wt.% citrate separate from the citric acid particles, 2 wt.% Na-carbonate and further standard ingredients like builder, anionic and non-ionic surfactants.

[0066] The cleaning performance was considered after the wash at 40 °C. The results were rated according to a school note system (1= very good result, no stain remaining, 6= almost no stain removal, colored stain). Results are shown in table 2.

Table 2

Bleaching sensitive stains		Formulation A	Formulation B	Formulation C
Tea	40°C	2,4	2,5	2,0
Red wine	40°C	3,2	4,1	2,9
Blueberry juice	40°C	3,3	4,1	2,7
Cherry juice	40°C	2,0	2,1	2,0

Example 3: pH measurement in the wash liquor

[0067] Wash liquors of Formulations A, B and C were prepared as follows:

A: 53,57 g of each of the detergent compositions were added to an amount of 10 l of water (corresponding to 75g each in a 16 l wash liquor), respectively.

B: 53,57 g of Formulation A and 48,21 g of Formulation B and C, respectively, were added to an amount of 10 l of water each (corresponding to 75 g or 67,5 g in 16 l wash liquor).

[0068] In each of the thus prepared wash liquors the pH values were observed for at least 40 min. The test started at room temperature (20°C) and after 5 minutes the wash liquor was heated to 40°C within 30 minutes. The pH progression of the first 2 minutes is shown in Figure 1. For Formulation C it can be clearly seen that after a very short alkaline pH in the wash liquor the dissolution of the coating of the citric acid comprising particles decreases the pH in the solution below 7, thus to an acidic pH, wherein during the first 1 to 2 minutes a moderate basic pH is reached again. By this "acidic boosting" effect the washing performance, in particular referring to colored staining, increases noticeably compared to a standard laundry detergent powder (Formulation B) and reaches the performance of a bleach catalyst comprising detergent composition (Formulation A), or even performs better (see tables 1 and 2).

Claims

1. A detergent cleaning composition comprising particles having a particle size of below 800 μm comprising or consisting of citric acid, wherein said detergent cleaning composition is a non-liquid detergent composition comprising a bleach system, preferably a solid laundry cleaning composition or a dishwashing composition.
2. Use of particles comprising or consisting of citric acid having a particle size of below 800 μm in a detergent cleaning composition including a bleaching system for increasing the bleach performance of said cleaning composition.
3. The detergent cleaning composition or use according to claims 1 or 2, wherein the mean particle size of the citric acid comprising particles is in the range of 100 μm to 600 μm , wherein it is preferred that no particles are comprised having a particle size above 800 μm , preferably no particles have a size above 600 μm and less than 10 %, more preferred at most up to 5% of the particles being < 100 μm .
4. The detergent cleaning composition or use according to any of claims 1 to 3, wherein said particles have a core comprising or consisting of citric acid and a coating comprising or consisting of a water soluble solid coating material.
5. The detergent cleaning composition or use according to any of claims 1 to 4, wherein the amount of carbonate or hydrogen carbonate in said composition is at most 8 wt% of the detergent cleaning composition, preferably the amount of carbonate or hydrogen carbonate is in the range of 1 wt.% to 6 wt.%, more preferred in the range of 1,5 wt.% to 5 wt.%, even more preferred from 2 wt.% to 4 wt.%.
6. The detergent cleaning composition or use according to any of claims 1 to 5, wherein the detergent composition besides the citric acid comprising particles further comprises separately a salt of citric acid, preferably an alkali metal salt of citric acid.
7. The detergent cleaning composition or use according to claim 6, wherein the ratio (wt/wt) of the citric acid comprising particles to separate citrate in the composition is in the range of 4:1 to 0,25 :1, preferably 3,5:1 to 0,3:1, more preferred 3:1 to 0,33:1, even more preferred 2,5:1 to 0,4:1 and most preferred about 2:1 to 1:1.
8. The detergent cleaning composition or use according to any of claims 1 to 7, wherein the cleaning composition comprises a bleaching system based on a bleaching agent and a bleach activator.
9. The detergent cleaning composition or use according to claim 8, wherein said bleaching system doesn't comprise any bleach catalyst.
10. The detergent cleaning composition or use according to any of claims 1 to 9, wherein said cleaning composition comprises at least one further ingredient selected from the group of further inorganic or organic builder compounds, surfactants, optical brighteners, enzymes, buffering agents, soil suspending agents, soil release agents, suds control agents, chelating agents, enzyme stabilizing agents, anti-tarnishing or anti-corrosion agents, dyes, dye transfer inhibitors, pigments, perfumes.
11. The detergent cleaning composition or use according to any of claims 1 to 10, wherein said composition is in the form of particles, a tablet, a granulate or a powder.
12. The detergent cleaning composition according to any of claims 1 to 11, wherein said composition is a laundry cleaning composition including at least an anionic surfactant, a bleaching system comprising a peroxygen developing bleaching agent and a bleach activator and further an inorganic builder providing in water an alkaline pH.

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13. The cleaning composition according to any of claims 1 to 11, wherein said composition is a phosphate containing or a non-phosphate containing automatic dishwashing cleaning composition comprising a nonionic detergent.

5 14. Use of the cleaning composition of any of claims 1 to 13 for providing a wash liquor having within the first two minutes after addition of the composition to water temporarily an acidic pH, followed by a moderate basic pH in the range of pH 8 to pH 9,8.

10 15. Method for cleaning laundry using a detergent cleaning composition according to any of claims 1 to 13.

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Figure 1

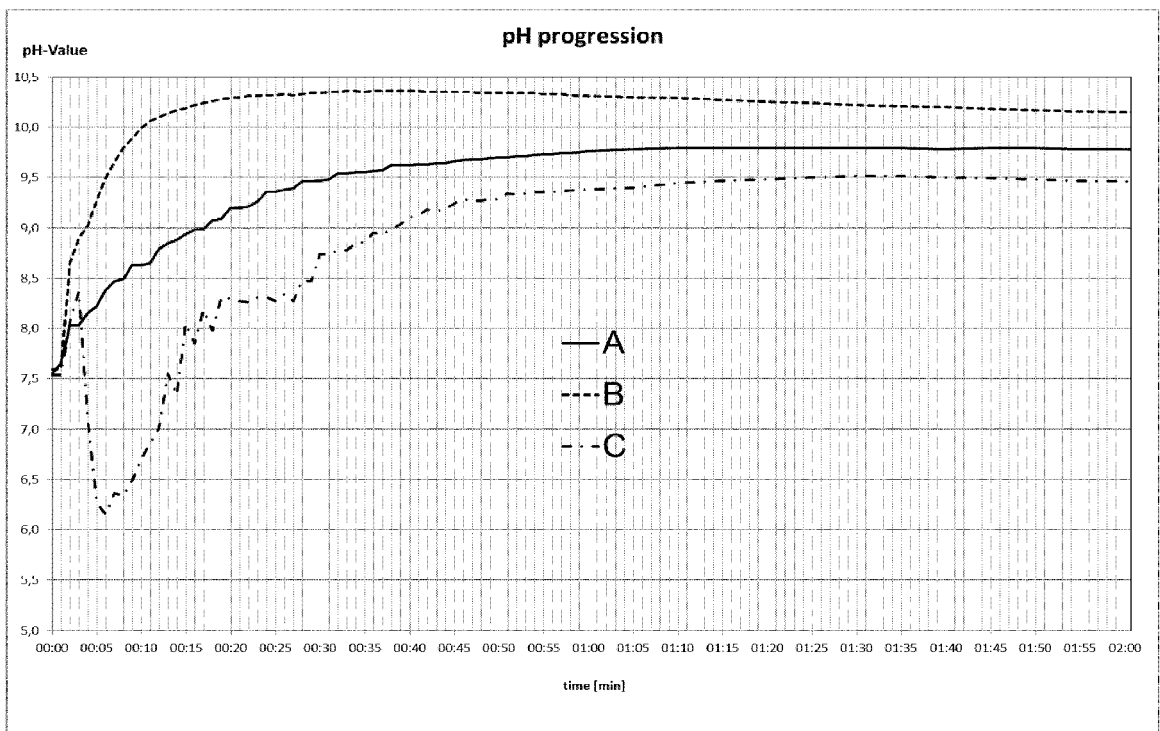
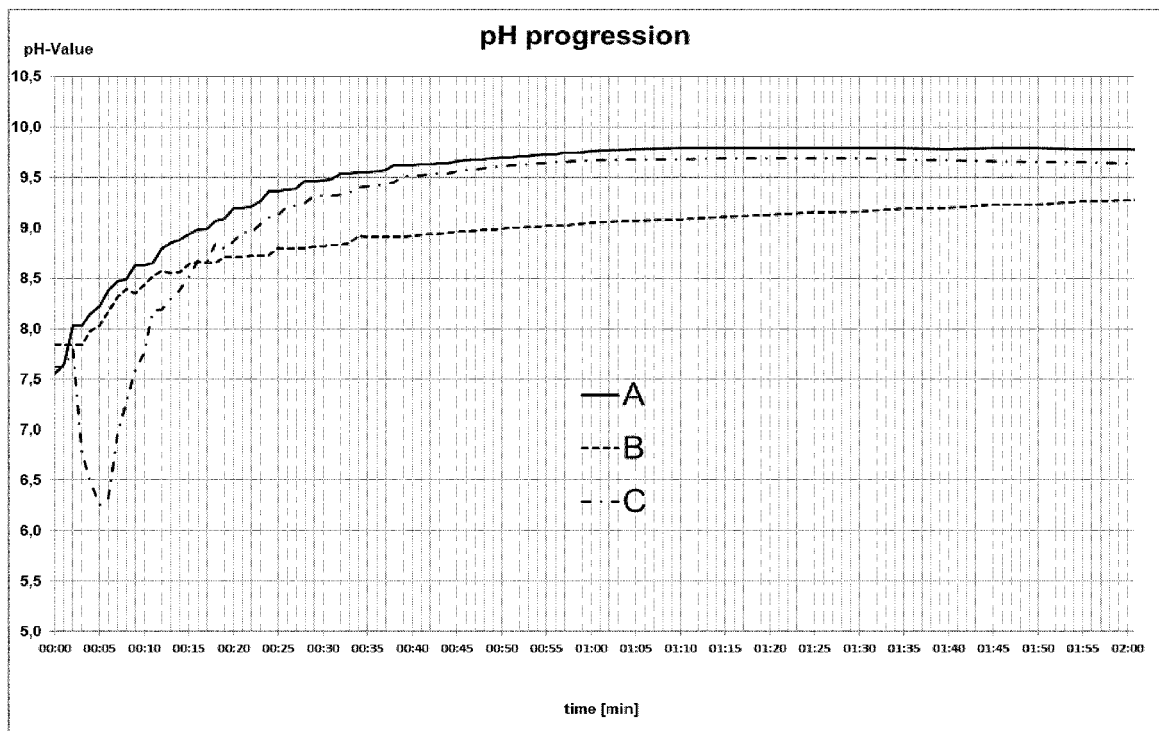


Figure 2





EUROPEAN SEARCH REPORT

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