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(54) **Title**: CLEANING COMPOSITION

(57) **Abstract**: An alkaline cleaning composition for use in a wash liquor comprising nanoparticles or a nanoparticles precursor and a nanoparticle compatible protease.

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CLEANING COMPOSITION

TECHNICAL FIELD

The present invention is in the field of cleaning, in particular it relates to cleaning compositions comprising nanoparticles or a nanoparticle precursor and a nanoparticle-compatible protease. The invention also relates to a method of cleaning using the compositions.

BACKGROUND OF THE INVENTION

In the field of automatic dishwashing the formulator is constantly looking for improved and simplified cleaning compositions and methods. There is a need for finding compositions having a more environmentally friendly profile, i.e. using more environmentally friendly ingredients, reducing the number of ingredients, reducing the amount needed for achieving good cleaning and being more effective than current compositions.

Cleaning compositions comprising nanoparticles are known in the art. Nanoparticles can present serious incompatibility issues with other cleaning ingredients when placed in a wash liquor (aqueous medium). Nanoparticles have a substantial fraction of their atoms or molecules at the surface and can negatively interact with charged molecules.

It has been found that not all enzymes are effective in compositions comprising nanoparticles. While amylases commonly used in the cleaning field prove effective, the most commonly used proteases seem to be completely ineffective and hence compositions comprising nanoparticles fail to provide good proteinaceous cleaning. It is desirable to have a product that provides both strong overall cleaning and soil release benefits, as well as effective removal of proteolytic stains such as egg and meat.

Thus an objective of the present invention is to provide a cleaning composition that overcomes some or all of the above problems.

SUMMARY OF THE INVENTION

According to the first aspect of the present invention, there is provided an alkaline cleaning composition, i.e. a composition having a pH greater than 7, preferably from about 8 to about 12 and more preferably from about 9 to about 11 as measured at 1% by weight in aqueous solution at 20°C.

The composition of the invention is for use in an aqueous medium, i.e. for dissolving/dispersing the composition in water, usually tap water, to form an alkaline wash liquor. The wash liquor can be applied onto the surface to be cleaned but preferably, the surface is cleaned by immersion into the wash liquor.

The cleaning composition of the invention is suitable for use on any type of surfaces, in particular hard surfaces. The composition is especially suitable for use in automatic dishwashing.

The composition of the invention provides excellent cleaning of hard surfaces. In particular, the composition of the invention provides outstanding cleaning when used in automatic dishwashing, including first time cleaning, second time cleaning and finishing, including shine, glass and metal care. The composition of the invention provides excellent removal of proteinaceous soils as well as excellent removal of tough food soils, including cooked-, baked-, and burnt-on soils.

By “nanoparticles” herein are meant particles, preferably inorganic particles, having a particle size of from about 1 nm to about 500 nm, preferably from about 5 nm to about 400 nm, more preferably from about 10 to about 100 nm, and especially from about 15 to about 60 nm. The particle size can be measured using a Malvern zetasizer instrument as detailed herein below. The particle size referred to herein is the z-average diameter, an intensity mean size. Preferably, the nanoparticles for use in the composition of the invention are inorganic nanoparticles, more preferably clays (sometimes referred herein as “nanoclays”) and specially preferred synthetic nanoclays, such as those supplied by Rockwood Additives Limited under the Laponite trademark.

The cleaning composition of the invention comprises nanoparticles or a nanoparticles precursor, the nanoparticles precursor is a secondary particle which releases nanoparticles when introduced into a wash liquor. By “nanoparticles precursor” is herein meant a secondary particle (the terms “secondary particle” include aggregates) being able to generate nanoparticles when 0.2 g of the precursor is added to 1 l of water having a pH of 10.5 (KOH being the alkalising agent) at 20℃ and stirred at 500 rpm for 30, preferably for 15 and more preferably for 5 minutes.

The composition of the invention comprises a nanoparticle-compatible protease. The nanoparticle-compatible protease should have an isoelectric point that is substantially lower than the pH of the cleaning composition, differing by more than 1 pH unit, preferably more than 1.5 pH units, or even more than 2 pH units.

The pH of the wash liquor is measured at 20°C.

In a preferred embodiment the protease has an isoelectric point of from about 6 to about 9. Proteases with this isoelectric point present a good activity in the wash liquor provided by the composition of the invention.

According to another embodiment of the invention, the composition of the invention comprises less than 10% by weight of the composition of phosphate builder, preferably less than 5% and more preferably less than 2%. This composition is excellent from an environmental viewpoint.

In a preferred embodiment the composition comprises a polycarboxylate builder, preferably a low molecular weight (from 2,000 to 30,000, preferably from 3,000 to 20,000) homopolymer of acrylic acid.

According to another embodiment of the invention, the composition of the invention comprises an aminocarboxylate builder selected from MGDA (methyl-glycine-diacetic acid), and salts and derivatives thereof; GLDA (glutamic-N,N- diacetic acid) and salts and derivatives thereof and a mixture thereof. Compositions comprising a mixture of a polycarboxylate builder and an aminocarboxylate builder are preferred for use herein. These compositions provide outstanding cleaning and finishing.

According to a second aspect of the present invention, there is provided a method of cleaning a soiled load (i.e., soiled housewares such as pots, pans, dished, cups, saucers, bottles, glassware, crockery, kitchen utensils, etc) in an automatic dishwasher, the method comprises the step of contacting the load with the compositions of the invention. The method of the invention is especially effective for tough food cleaning, including cooked-, baked- and burnt on soils and for the removal of proteinaceous soils. The method also provides second time benefits and excellent finishing and care, including glass care and metal care.

The method of the invention allows for the use of a wide range of nanoparticle concentrations. The concentration of nanoparticle in the wash liquor is preferably from about 50 ppm to about

2,500 ppm, more preferably from about 100 to about 2,000 and especially from about 200 to about 1,000 ppm.

In a preferred embodiment builder is delivered into the wash liquor before the delivery of nanoparticles. This method provides excellent cleaning.

According to a third aspect of the invention, there is provided a layered particle comprising a core and surrounding layers, wherein the core comprises nanoparticles or a nanoparticle precursor.

It is also preferred that the composition comprises from about 2 to about 60%, more preferably from 5 to 50% by weight thereof of nanoparticles (or nanoparticles precursor). Preferably the composition comprises an alkalinity source in a level of from about 1 to about 40%, more preferably from about 5 to about 35% by weigh of the composition. Preferably, the composition comprises a source of univalent ions, in particular sodium or potassium hydroxide. Also preferred are compositions free of compounds which form insoluble calcium or magnesium salt, such as carbonates and silicates. Preferably the composition comprises a builder, more preferably a non-phophate builder, in a level of from about 10 to about 60%, preferably from about 20 to 50% by weigh of the composition.

DETAILED DESCRIPTION OF THE INVENTION

The present invention envisages a composition comprising nanoparticles (or a nanoparticle precursor) and a nanoparticle-compatible protease, the invention also envisages a method of automatic dishwashing using the composition of the invention. The method and composition provide excellent removal of tough food soils from cookware and tableware, in particular starchy and proteinaceous soils. Excellent results have been achieved when the dishwashing liquor comprises nanoparticles and enzymes as main soil removal active, either in absence of or in combination with other cleaning actives (such as builders, surfactants, etc). This obviates or reduces the use of traditional dishwashing detergents. The compositions are preferably free of phosphate builders.

Nanoparticles

The nanoparticles of the composition of the invention are preferably inorganic nanoparticles. Preferred inorganic nanoparticles can be selected from the group comprising metal oxides, hydroxides, clays, oxy/hydroxides, silicates, phosphates and carbonates. Nanoparticles selected from the group consisting of metal oxides and clays are preferred for use herein. Examples include silicon dioxide, aluminium oxide, zirconium oxide, titanium dioxide, cerium oxide, zinc oxide, magnesium oxide, clays, tin oxide, iron oxides (Fe_2O_3, Fe_3O_4) and mixtures thereof.

In one aspect, the nanoparticles for use in the present invention are layered clay minerals (referred herein sometimes as clays). Suitable layered clay minerals include those in the geological classes of smectites, kaolins, illites, chlorites, attapulgites and mixed layer clays. Smectites, for example, include montmorillonite, bentonite, pyrophyllite, hectorite, saponite, sauconite, nontronite, talc, beidellite, volchonskoite and vermiculite. Kaolins include kaolinite, dickite, nacrite, antigorite, anauxite, halloysite, indellite and chrysotile. Illites include bravaisite, muscovite, paragonite, phlogopite and biotite. Chlorites include corrensite, penninite, donbassite, sudoite, pennine and clinochlore. Atta- pulgites include sepiolite and polygorskyte. Mixed layer clays include allevardite and vermiculitebiotite.

The layered clay minerals may be either naturally occurring or synthetic. Natural or synthetic hectorites, montmorillonites and bentonites are suitable for use herein, especially preferred for use herein are hectorites clays commercially available. Typical sources of commercial hectorites are the LAPONITES from Rockwood Additives Limited; Veegum Pro and Veegum F from R. T. Vanderbilt, U.S.A.; and the Barasyms, Macaloids and Propaloids from Baroid Division, National Read Comp., U.S.A.

Natural clay minerals which may be used typically exist as layered silicate minerals and less frequently as amorphous minerals. A layered silicate mineral has SiO tetrahedral sheets arranged into a two-dimensional network structure. A 2:1 type layered silicate mineral has a laminated structure of several to several tens of silicate sheets having a three layered structure in which a magnesium octahedral sheet or an aluminum octahedral sheet is sandwiched between two sheets of silica tetrahedral sheets.

Synthetic hectorite is commercially marketed under the trade name LAPONITE™ by Rockwood Additives Limited. There are many grades or variants and isomorphous substitutions of LAPONITE™ marketed. Examples of commercial hectorites are Lucentite SWN™, LAPONITE S™, LAPONITE XLS™, LAPONITE RD™, LAPONITE B™ and LAPONITE RDS™.

Generally LAPONITE™ has the formula: $[Mg_wLi_xSi_8O_{20}OH_{4-y}F_y]^{z-}$ wherein w=3 to 6, x=0 to 3, y=0 to 4, z=12-2w-x, and the overall negative lattice charge may be balanced by counter-ions; and wherein the counter-ions are selected from the group consisting of Na+, K+, NH4 +, Cs+, Li+, Mg++, Ca++, Ba++, N(CH3)4 + and mixtures thereof.

Preferred for use herein is the synthetic hectorite commercially available under the name Laponit®RD. Synthetic hectorites, have been found better for cleaning than other nanoparticles.

Clay nanoparticles (also referred herein as nanoclyas) are charged crystals having a layered structure. The top and bottom of the crystals are usually negatively charged and the sides are positively charged, at alkaline pH. Due to the charged nature of nanoclays, they tend to aggregate in solution to form large structures that do not effectively contribute to the cleaning. Moreover, these structures may deposit on the washed load leaving an undesirable film on them. In particular the nanoclays tend to aggregate in the presence of calcium and magnesium found in the wash water. A key requirement of the composition and method of the invention is the nanoclay to be dispersed in the wash liquor. By "dispersed" is meant that the nanoclay is in the form of independent crystals, in particular in the form of individual crystals having a particle size of from about 10 nm to about 300 nm, preferably from about 20 nm to about 100 nm and especially form about 30 to about 90 nm. The particle size of the crystals can be measured using a Malvern zetasizer instrument. The nanoclay particle size referred to herein is the z-average diameter, an intensity mean size.

Nanoparticle-compatible protease

Examples of nano-compatible proteases include:

(a) Metalloproteases derived from Bacillus amyloliquefaciens described in WO 07/044993A2, which is incorporated herein by reference.

(b) Proteases derived from Bacillus Licheniformis, particularly subtilisin Carlsberg.

(c) The proteases derived from Bacillus GX6638, particularly proteases HS and AS, described by Durham *et al.* in Journal of Bacteriology, June 1987, p.2762 – 2768, which is incorporated herein by reference.

Preferred nano-compatible proteases for use herein include polypeptides demonstrating at least 90%, preferably at least 95%, more preferably at least 98%, even more preferably at least 99%

and especially 100% identity with the wild-type enzyme of either SEQ ID NO:1, SEQ ID NO:2 or the wild-type proteases AS and HS described above.
One example of such a nano-compatible protease is sold under the tradename Alacalase® by Novozymes A/S.

The proteases of the present invention exhibit low isoelectric points ("pI") relative to the wash liquor pH. As used herein, the term "low pI" refers to electrochemical properties of an enzyme such that the enzyme has a net charge of zero within the pH range of 4-8. The pI of an enzyme can be determined by methods known to those skilled in the art. In general, the use of the technique of isoelectric focusing, as described in Example 3 of US 5,718,895 (incorporated herein by reference), may be used to determine the pI of a protease.

Examples of native enzymes which may be modified for use in the present invention, include but are not limited to: pancreatin, trypsin, chymotrypsin, subtilisin, collagenase, elastase, keratinase, carboxypeptidase, papain, bromelain, aminopeptidase, Aspergillo peptidase, pronase E (from S. griseus) and dispase (from Bacillus polymyxa) and mixtures thereof. If papain, or any sulfhydryl protease is used, a reducing agent, such as N-acetylcysteine, may be required.

Microbially derived enzymes, such as those derived from Bacillus, Streptomyces, and Aspergillus microorganisms, represent a preferred type of enzyme to be modified for use in the present invention. Of this sub-group of enzymes, the most preferred are the Bacillus derived alkaline proteases genetically called "subtilisin" enzymes.

Examples of subtilisin enzymes include subtilisin BPN' and subtilisin Carlsberg. Subtilisin is commercially available from various commercial sources including Novo Industries (Bagsvaerd, Denmark), Fluka Biochemika (Buchs, Switzerland) and Boehringer Mannhelm (Indianapolis, Ind.).

The enzymes of the present invention may be selected from those that have had part of their amino acid sequence altered in favour of a lower pI. In general, amino acid residues exhibiting high (net positive charge at physiological pH) pKa's (pH at which half of the total quantity of the particular residue is charged) may be replaced with neutral or low pKa amino acids. For example, lysine or arginine (high pKa) residues may be replaced by alanine, leucine (non-ionic), aspartate, glutamate (low pKa) or other low pKa residues. This can be achieved by traditional genetic recombinant techniques like those described in WO 95/07991, the contents of which pertain to genetic recombinant techniques are incorporated herein by reference. As used herein, "genetic recombinant techniques" refer to any method of producing mutant enzymes of the present invention through the manipulation of DNA. Generally, a plasmid of a host bacterium is transfected with DNA coding for the modified amino acid sequence desired. The plasmid is reinserted in the host, and the host is grown under set conditions. Broth from the fermenting process, containing the bacterial exudate, is then separated from the bacterial colonies and is extracted for the target enzyme. Separation techniques including gel and affinity chromatography are generally employed to purify the mutant type enzymes exhibiting low pIs. Enzymes with lysine residues replaced with lower pI amino acids are preferred modified enzymes of this class of modified enzymes of the present invention.

The enzymes of the present invention may be selected from those that have been chemically modified, covalently, with organic monomer or polymer molecules. As used herein, "organic monomer covalent linkage" refers to the linking of small organic monomers covalently to an enzyme; and "organic polymer covalent linkage" refers to linking large organic polymers covalently to an enzyme. Examples of organic monomers include succinate, and methyl, ethyl or proplyl acylates. Examples of organic polymers include various polyethylene glycols (PEG), such as PEG 500, 1000 and 2000. Such modifications have been discused in U.S. Pat. No. 5, 122,614, the entire contents of which are incorporated herein by reference. The use of this technique or similar techniques known to those skilled in the art may be employed to modify various proteases so that they exhibit low pIs. Commonly assigned U.S. patent application Ser. No. 08/491, 754, filed Jun. 19, 1995 discloses novel PEG-subtilisins; the contents pertaining to these novel enzyme-polymer complexes is incorporated herein by reference. Examples of methods for monomeric modifications of enzymes are discussed in Johansen, Chemical Derivatives of Subtilisins with Modified Proteolytic Activities II. Succinyl-and Glutarylsubtilisin Type Carlsberg, Compt. Rend. Trav. Lab. Carlsberg, volume 37, pages 145-177 (1970), the entire contents of which, are incorporated herein by reference. Preferred enzymes of this class are succinylated-subtilisins and more generally, acylated-subtilisins.

As it is known to those skilled in the art, the degree of substitution can be controlled by adjusting the ratio of modifying reagent to enzyme concentration.

Examples of proteases with low Ip include Phycocyanin, β-Lactoglobulin B, Bovine carbonic anhydrase, Human carbonic anhydrase, Equine myoglobin, Human myoglobin, Human myoglobin C, Lentil lectin, Cytochrome C, Subtilisin A (Carlsberg), Succinylated subtilisin A, Acetylated subtilisin A, PEG-5000-subtilisin BPN', Me-PEG-5000-subtilisin A, Trypsin (Bovine), Acetylated Trypsin and Methylated Trypsin

The present inventors have found that nanoparticles should be dispersed in the cleaning medium to provide optimum cleaning and care benefits. The aqueous medium is usually tap water. Tap water usually contains hardness ions, the amount and type of ions varies from one geographic area to another. Nanoparticles dispersions can be easily destabilized by hardness ions and they can give rise to flocculation and precipitation of the flocculate, this not only impairs the cleaning capacity of the nanoparticles but might also contribute to soiling of the surfaces to be cleaned.

It is believed that the nanoparticles of the cleaning composition of the invention can be kept dispersed in aqueous medium by using a polymeric nanoparticle stabilizer. It is believed that the nanoparticles are dispersed by means of the formation of a core-shell structure with the nanoparticle stabilizer. The nanoparticles can be kept dispersed in aqueous medium independently of the amount of hardness ions present in the water. A “polymeric nanoparticle stabilizer” is capable of maintaining the nanoparticle stabilized as single particles, i.e. avoiding the formation of aggregates, under cleaning conditions.

By “polymeric nanoparticle stabilizer” is herein meant a polymer capable of maintaining nanoparticles dispersed in an aqueous solution in the presence of calcium, i.e. preventing aggregation. A detailed method to evaluate whether a polymer falls into the definition of nanoparticle stabilizer is provided herein below. The particle size of nanoparticles in an aqueous solution at a certain pH (pH 10.5) is measured (this particle size is referred herein as original particle size) and compared with the particle size of the nanoparticles in the presence of calcium and the polymeric nanoparticle stabilizer (this particle size is referred herein as modified particle size) at the same pH. If the modified particle size is less than 5, preferably less than 4, more preferably less than 3 and especially less than 2 times that of the original particle size, then the polymer is considered a nanoparticle stabilizer according to this invention.

The nanoparticles and the polymeric nanoparticle stabilizer, preferably form a "core-shell" structure in an aqueous medium, under alkaline conditions.

By "core-shell structure" is meant herein a central nuclei part (core) protected by a shield part (shell). The core can have any shape or geometry. The shell does not need to be a continuous layer, it suffices that the shell is capable of protecting the core from forming aggregates in the presence of hardness ions. Without wishing to be bound by theory, it is believed that the nanoparticle stabilizer adsorbs on the surface of the nanoparticle thereby making it stable with respect to water hardness ions. Again, without wishing to be bound by theory, it is believed that the nanoparticle and the nanoparticle stabilizer "coulombically interact" to form the core-shell structure. "Columbically interact" is used herein to include ionic interaction, hydrogen bonding and dipole-dipole interaction and it is to be distinguished from interactions which produce a covalent bond. It has been found that a dispersion having an excellent stability can be achieved by using nanoparticle stabilizers capable of forming hydrogen bonds with the nanoparticles.

The core shell structure of the composition of the invention has a zeta potential (as measured in 1% wt aqueous solution at 20°C) of from about -10 to about -50 mV, more preferably from about -15 to about -45 mV and even more preferably from about -20 to about -35 and a particle size of from about 1 to about 500 nm, more preferably from about 5 to about 400 and more preferably from about 10 to about 200 nm and especially from about 20 to about 100 nm. Aqueous compositions comprising core-shell structures having the claimed combination of size and zeta potential have been found to be outstanding in terms of first time cleaning, shine, second time cleaning and care (including metal and glass care), particularly on hard surfaces. Most of the hard surfaces, in particular the hard surfaces of dishware and tableware, are negatively charged. It could be expected that negatively charged nanoparticles would be repelled from the negatively charged surfaces. Surprisingly, this does not seem to be the case with the compositions of the invention.

The composition of the invention can be in any physical form, solid, liquid, gel, etc. Preferred for use herein is a compositions in solid form, for example powder, either loose powder or compressed powder. Preferably the composition of the invention is free of anionic surfactants.

In a preferred embodiment, the nanoparticle stabilizer comprises a moiety comprising at least one heteroatom selected from the group consisting of nitrogen, oxygen, sulphur or mixtures thereof. In a more preferred embodiment the moiety comprises a nitrogen-containing cyclic unit, more preferably a nitrogen heterocycle (i.e. a cyclic unit comprising nitrogen as part of it).

Nitrogen heterocycles are preferred for use herein. Preferred heterocycles are selected from azlactone, azlactam, more preferred heterocycles include pyrrolidone, imidazole, pyridine, pyridine-N-oxide, oxazolidone and mixtures thereof. Especially preferred polymers are polyvinyl imidazole, polyvinyl pyrrolidone, polyvinyl pyridine-N-oxide and mixtures thereof. Especially preferred are those polymers and copolymers wherein no optional anionic moiety (at pH of 10.5) is present.

In more detail, moieties containing a nitrogen heterocycle for use herein include but are not limited to: vinylpyridines such as 2-vinylpyridine or 4-vinylpyridine; lower alkyl (C_1-C_8) substituted N-vinylpyridines such as 2-methyl-5-vinylpyridine, 2-ethyl-5-vinylpyridine, 3-methyl-5-vinylpyridine, 2,3-dimethyl-5-vinylpyridine, and 2-methyl-3-ethyl-5-vinylpyridine; methyl-substituted quinolines and isoquinolines; N-vinylcaprolactam; N-vinylbutyrolactam; N-vinylpyrrolidone; vinyl imidazole; N-vinylcarbazole; N-vinylsuccinimide; maleimide; N-vinyl-oxazolidone; N-vinylphthalimide; N-vinylpyrrolidones such as N-vinylthiopyrrolidone, 3 methyl-1-vinylpyrrolidone, 4-methyl-1-vinylpyrrolidone, 5-methyl-1-vinylpyrrolidone, 3-ethyl-1-vinylpyrrolidone, 3-butyl-1-vinylpyrrolidone, 3, 3-dimethyl-1-vinylpyrrolidone, 4,5-dimethyl-1-vinylpyrrolidone, 5,5-dimethyl-1-vinylpyrrolidone, 3,3,5-trimethyl-1-vinylpyrrolidone, 4-ethyl-1-vinylpyrrolidone, 5-methyl- 5-ethyl-1-vinylpyrrolidone and 3,4,5-trimethyl-1-vinylpyrrolidone; vinylpyrroles; vinylanilines; and vinylpiperidines.

In a preferred embodiment, the nanoparticle stabilizer is a comb polymer comprising a backbone and pendant groups wherein the backbone comprises a moiety comprising nitrogen and the pendant groups are non-ionic.

Preferably the backbone comprises groups selected from one or more of alkylene amines, alkyl pyrrolidones and alkyl imidazoles or mixtures thereof.

Preferred pendant groups for use herein include moieties comprising alkoxylates, alkyl acetates and alkylene glycols. In particular, ethylene oxide, ethylene glycol, ethylene glycol dimethyl ether, ethylene glycol monomethyl ether, propylene oxide, propylene glycol, methyl methacrylate, vinyl alcohol, vinyl acetate, oxyethylene, vinyl methyl ether, and dimethylsiloxane, or mixtures thereof.

Especially preferred for use herein include comb polymers, the backbone comprises groups selected from one or more of alkylene amines, alkyl pyrrolidones and alkyl imidazoles or mixtures thereof and the pendant groups are selected from one or more of the group comprising alkyl acetates and alkylene glycols. Examples would include comb polymers wherein the backbone comprises vinylimidazole and/or vinylpyrrolidone units and the pendant groups are polyalkylene glycols, preferably polyethylene glycols. Preferably, the comb polymer comprises a plurality of different moieties, this increases the tolerance of the stabilizer to the medium.

Without wishing to be bound by theory it is believed that said pendant groups can provide enhanced charge and/or steric stabilization to the nanoparticles within the wash liquor thereby enabling strong performance across a wide range of water hardness.

Nanoparticle stabilizer determination

An aqueous solution containing 267 ppm of nanoparticles (Laponite™ RD) having a pH of 10.5 is prepared and the particle size measured (original particle size). An aqueous solution comprising 267 ppm of nanoparticles and 400 ppm, preferably 200 ppm of polymeric nanoparticle stabilizer having a pH of 10.5 is prepared, 200 ppm, preferably 400 ppm of calcium is added to the solution and the particle size is measured (modified particle size).

A 267 ppm nanoparticle solution is prepared by adding 0.267g of nanoparticles into 1 litre of deionised water with high agitation (600-1000rpm) to avoid the formation of lumps, the pH is adjusted to 10.5 by using 1M NaOH solution. The solution is stirred for at least 30 mins and then put it into ultrasonic water bath for 30 mins to ensure that the nanoparticles have fully dispersed in deionised water.

The particle size of the nanoparticles solution (original particle size) is measured by using a Malvern zetasizer. Settings of measurement: temperature 25°C, 3 replications, equilibrating time 2mins.

A 0.1% by weight polymer solution is prepared by dissolving a 1 g of polymer in 10 g of deionised water.

A solution comprising nanoparticles, polymer and calcium (modify particle size) is prepared by adding 1.5 ml of the polymer solution to 398.5 ml of the nanoparticle solution and then adding 0.053 g (preferably 0.106, more preferably 0.159 and especially 0.212) of $CaCl_2 2H_2O$. The particle size of this solution (modify particle size) is measured using a Malvern Zetasizer (using the above settings).

The modified particle size is compared with the original. If the original particle size is less than 5, preferably less than 4, more preferably less than 3 and especially less than 2 times that of the original particle size, then the polymer is considered a nanoparticle stabilizer within the meaning of the invention.

Polymeric nanoparticle stabilizer

Suitable nanoparticle stabilizer polymers should have a molecular weight of from 500 to 1,000,000, more preferably from 1,000 to 200,000, especially 5,000 to 100,000.

A composition that has been found to give excellent results comprises from about 2 to 60%, preferably from 5 to 50% by weight of the composition of nanoclay, from about 1 to about 40%, preferably from about 5 to about 35% by weight of the composition of an alkalinity source, from about 10 to about 60%, preferably from about 2 to about 50% by weight of the composition of a nanoparticle stabilizer (preferably a polymer comprising a nitrogen heterocycle), from about 5 to about 40%, preferably from about 10 to about 30% by weight of the composition of bleach and from about 0.5 to about 10%, preferably from about 0.01 to about 2% by weight of the composition of active enzyme.

Preferably, the nanoparticles and the nanoparticle stabilizer are in a weight ratio of from about 1:10 to 1:10, more preferably from about 1:0.5 to 1:5 and specially from about 1:1 to about 1:1.5. The level of polymeric nanoparticle stabilizer required to stabilize the nanoparticle in the presence of a certain amount of calcium seems to be lower than the level of polymeric builder required to bind that calcium.

Preferably the wash liquor has a pH of from about 9 to about 12, more preferably from about 10 to about 11.5 and an ionic strength of from about 0.001 to about 0.02, more preferably from about 0.002 to about 0.015, especially from about 0.005 to about 0.01 moles/l. The method provides excellent cleaning, in particular on starch and protein containing soils. Heavily soiled items such as those containing burn-on, baked-on or cook-on starchy food such as pasta, rice, potatoes, wholemeal, sauces thickened by means of starchy thickeners, etc. are easily cleaned using the method of the invention.

Ionic strength

Preferably the wash liquor in which the composition of the invention is used, has an ionic strength of from about 0.001 to about 0.02, more preferably from about 0.002 to about 0.015, especially form about 0.005 to about 0.01 moles/l.

Ionic strength is calculated from the molarity (m) of each ionic species present in solution and the charge (z) carried by each ionic species. Ionic strength (I) is one half the summation of $m.z^2$ for all ionic species present i.e.

$I = ½\Sigma\, m.z^2$

For a salt whose ions are both univalent, ionic strength is the same as the molar concentration. This is not so where more than two ions or multiple charges are involved. For instance a 1 molar solution of sodium carbonate contains 2 moles/litre of sodium ions and 1 mole/litre of carbonate ions carrying a double charge. Ionic strength is given by:

$I = ½[2(1^2) + 1 \text{ x } (2^2)] = 3$ moles/litre

Alkalinity source

Examples of alkalinity source include, but are not limited to, an alkali hydroxide, alkali hydride, alkali oxide, alkali sesquicarbonate, alkali carbonate, alkali borate, alkali salt of mineral acid, alkali amine, alkaloid and mixtures thereof. Sodium carbonate, sodium and potassium hydroxide are preferred alkalinity sources for use herein, in particular potassium hydroxide. The alkalinity source is present in an amount sufficient to give the wash liquor a pH of from about 9 to about 12, more preferably from about 10 to about 11.5. preferably, the composition herein comprises from about 1% to about 40%, more preferably from about 2% to 20% by weight of the composition of alkaline source.

The wash liquor comprises an alkalinity source in an amount sufficient to give the wash liquor the desired pH. Preferably the wash liquor contains from about 20 to about 1,200 ppm, more preferably from about 100 to about 1,000 of an alkalinity source. It is especially preferred that the alkalinity source comprises a source of univalent ions. Univalent ions contribute to high alkalinity and at the same time hardly raise the ionic strength of the wash solution. Preferred alkalinity sources for use herein are metal hydroxides, in particular sodium or potassium hydroxide and especially potassium hydroxide.

Builder

Suitable builder to be used herein may be any builder known to those skilled in the art such as the ones selected from the group comprising phosphonates, amino carboxylates or other carboxylates, or polyfunctionally-substituted aromatic builders or mixtures thereof.

A preferred builder for use herein is a low molecular weight polyacrylate homopolymer, having a molecular weight of from about 1,000 to about 30,000, preferably from about 2,000 to about 20,000 and more preferably from about 3,000 to about 12,000. Another preferred dispersant for use herein is an aminocarboxylate, in particular MGDA (methyl glycine di-acetic acid) and GLDA (glutamic acid-N,N-diacetate).

In other preferred embodiments the builder is a mixture of a low molecular weight polyacrlyate homopolymer and another builder, in particular an amino polycarboxylate builder. It has been found that the combination of low molecular weight polyacrylates with amino polycarboxylates is very good in terms of soil removal. MGDA and GLDA have been found most suitable amino polycarboxylates for use herein.

Phosphonate suitable for use herein may include etidronic acid (1-hydroxyethylidene-bisphosphonic acid or HEDP) as well as amino phosphonate compounds, including amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonates to be used herein are diethylene triamine penta methylene phosphonates. Such phosphonates are commercially available from Monsanto under the trade name DEQUEST®

Polyfunctionally-substituted aromatics may also be useful in the compositions herein. See U.S. Pat. No. 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

Suitable amino carboxylates for use herein include nitrilotriacetates (NTA), ethylene diamine tetra acetate (EDTA), diethylene triamine pentacetate (DTPA), N-hydroxyethylethylenediamine triacetate , nitrilotri-acetate, ethylenediamine tetraproprionate, triethylenetetraaminehexa-acetate (HEDTA), triethylenetetraminehexaacetic acid (TTHA), propylene diamine tetracetic acid (PDTA) and , both in their acid form, or in their alkali metal salt forms. Particularly suitable to be used herein are diethylene triamine penta acetic acid (DTPA) and propylene diamine tetracetic acid (PDTA). A wide range of aminocarboxylates is commercially available from BASF under the trade name Trilon®. A preferred biodegradable amino carboxylate for use herein is ethylene diamine N,N'-disuccinic acid (EDDS), or alkali metal or alkaline earth salts thereof or mixtures thereof. Ethylenediamine N,N'-disuccinic acids, especially the (S,S) isomer have been extensively described in U.S. Pat. No. 4,704,233, Nov. 3, 1987 to Hartman and Perkins. Ethylenediamine N,N'-disuccinic acid is, for instance, commercially available under the tradename ssEDDS® from Palmer Research Laboratories.

Aminodicarboxylic acid-N,N-dialkanoic acid or its salt are also suitable amino carboxylates for use herein. The compounds can be represented by the following formula:

$MOOC\text{-}CHZ^1\text{-}NZ^2Z^3$

wherein each of Z^1, Z^2 and Z^3 independently represents a COOM-containing group; wherein each of M independently represents either of a hydrogen atom, sodium, potassium or amine ion.

In the above formula, Z^1, Z^2 and Z^3 may either be same with or different from each other, and examples of those groups are found among carboxymethyl group, 1-carboxyethyl group, 2-carboxyethyl group, 3-carboxypropan-2-yl group, their salts, etc. As concrete examples, there are glutamic acid-N,N-diacetic acid, glutamic acid-N,N-dipropionic acid, and their salts. Above all, glutamic acid-N,N-diacetate is especially preferred, in particular L-glutamic acid-N,N-diacetate.

Other suitable builders include ethanoldiglycine and methyl glycine di-acetic acid (MGDA).

Further carboxylates useful herein include low molecular weight hydrocarboxylic acids, such as citric acid, tartaric acid malic acid, lactic acid, gluconic acid, malonic acid, salicylic acid, aspartic acid, glutamic acid, dipicolinic acid and derivatives thereof, or mixtures thereof.

Suitable carboxylated polymers include polymeric polycarboxylated polymers, including homopolymers and copolymers. Preferred for use herein are low molecular weight (from about 2,000 to about 30,000, preferably from about 3,000 to about 20,000) homopolymers of acrylic acid. They are commercially available from BASF under the Sokalan PA range. An especially preferred material is Sokalan PA 30. Sodium polyacrylate having a nominal molecular weight of about 4,500, is obtainable from Rohm & Haas under the tradename ACUSOL®445N. Other polymeric polycarboxylated polymers suitable for use herein include copolymers of acrylic acid and maleic acid, such as those available from BASF under the name of Sokalan CP and AQUALIC®ML9 copolymers (supplied by Nippon Shokubai Co. LTD).

Other suitable polymers for use herein are polymers containing both carboxylate and sulphonate monomers, such as ALCOSPERSE® polymers (supplied by Alco)and Acusol 588 (supplied by Rohm&Hass) .

With reference to the polymers described herein, the term weight- average molecular weight (also referred to as molecular weight) is the weight-average molecular weight as determined using gel permeation chromatography according to the protocol found in Colloids and Surfaces A. Physico Chemical & Engineering Aspects, Vol. 162, 2000, pg. 107-121. The units are Daltons.

If present, the composition of the invention comprises from about 5 to about 40%, more preferably from about 10 to about 30% by weight of the composition of a builder. Preferably the composition is free of phosphate builder.

Other cleaning actives

Any traditional cleaning ingredients can be used in the method, composition and product of the invention.

Bleach

Inorganic and organic bleaches are suitable cleaning actives for use herein. Inorganic bleaches include perhydrate salts such as perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. Alternatively, the salt can be coated.

Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates for use herein. The percarbonate is most preferably incorporated into the products in a coated form which provides in-product stability. A suitable coating material providing in product stability comprises mixed salt of a water-soluble alkali metal sulphate and carbonate. Such coatings together with coating processes have previously been described in GB- 1,466,799. The weight ratio of the mixed salt coating material to percarbonate lies in the range from 1: 200 to 1: 4, more preferably from 1: 99 to 1 9, and most preferably from 1: 49 to 1: 19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula Na2S04.n.Na2CO3 wherein n is from 0. 1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Another suitable coating material providing in product stability, comprises sodium silicate of Si02: Na20 ratio from 1.8: 1 to 3.0: 1, preferably L8:1 to 2.4:1, and/or sodium metasilicate, preferably applied at a level of from 2% to 10%, (normally from 3% to 5%) Of Si02 by weight of the inorganic perhydrate salt. Magnesium silicate can also be included in the coating. Coatings that contain silicate and borate salts or boric acids or other inorganics are also suitable.

Other coatings which contain waxes, oils, fatty soaps can also be used advantageously within the present invention.

Potassium peroxymonopersulfate is another inorganic perhydrate salt of utility herein.

Typical organic bleaches are organic peroxyacids including diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid, and diperoxyhexadecanedioc acid. Dibenzoyl peroxide is a preferred organic peroxyacid herein. Mono- and diperazelaic acid, mono- and diperbrassylic acid, and Nphthaloylaminoperoxicaproic acid are also suitable herein.

The diacyl peroxide, especially dibenzoyl peroxide, should preferably be present in the form of particles having a weight average diameter of from about 0.1 to about 100 microns, preferably from about 0.5 to about 30 microns, more preferably from about 1 to about 10 microns. Preferably, at least about 25%, more preferably at least about 50%, even more preferably at least about 75%, most preferably at least about 90%, of the particles are smaller than 10 microns, preferably smaller than 6 microns. Diacyl peroxides within the above particle size range have also been found to provide better stain removal especially from plastic dishware, while minimizing undesirable deposition and filming during use in automatic dishwashing machines, than larger diacyl peroxide particles. The preferred diacyl peroxide particle size thus allows the formulator to obtain good stain removal with a low level of diacyl peroxide, which reduces deposition and filming. Conversely, as diacyl peroxide particle size increases, more diacyl peroxide is needed for good stain removal, which increases deposition on surfaces encountered during the dishwashing process.

Further typical organic bleaches include the peroxy acids, particular examples being the alkylperoxy acids and the arylperoxy acids. Preferred representatives are (a) peroxybenzoic acid and its ring-substituted derivatives, such as alkylperoxybenzoic acids, but also peroxy-α-naphthoic acid and magnesium monoperphthalate, (b) the aliphatic or substituted aliphatic peroxy acids, such as peroxylauric acid, peroxystearic acid, ε-phthalimidoperoxycaproic acid[phthaloiminoperoxyhexanoic acid (PAP)], o-carboxybenzamidoperoxycaproic acid, N-nonenylamidoperadipic acid and N-nonenylamidopersuccinates, and (c) aliphatic and araliphatic peroxydicarboxylic acids, such as 1,12-diperoxycarboxylic acid, 1,9-diperoxyazelaic acid, diperoxysebacic acid, diperoxybrassylic acid, the diperoxyphthalic acids, 2-decyldiperoxybutane-1,4-dioic acid, N,N-terephthaloyldi(6-aminopercaproic acid).

If present, the composition of the invention comprises from about 5 to about 40%, more preferably from about 10 to about 30% by weight of the composition of a bleach. Preferably the composition comprises percarbonate bleach.

Bleach activators

Bleach activators are typically organic peracid precursors that enhance the bleaching action in the course of cleaning at temperatures of 60° C and below. Bleach activators suitable for use herein include compounds which, under perhydrolysis conditions, give aliphatic peroxoycarboxylic acids having preferably from 1 to 10 carbon atoms, in particular from 2 to 4 carbon atoms, and/or optionally substituted perbenzoic acid. Suitable substances bear O-acyl and/or N-acyl groups of the number of carbon atoms specified and/or optionally substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, in particular tetraacetylethylenediamine (TAED), acylated triazine derivatives, in particular 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, in particular tetraacetylglycoluril (TAGU), N-acylimides, in particular N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, in particular n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS), carboxylic anhydrides, in particular phthalic anhydride, acylated polyhydric alcohols, in particular triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran and also triethylacetyl citrate (TEAC). Bleach activators if included in the compositions of the invention are in a level of from about 0.1 to about 10%, preferably from about 0.5 to about 2% by weight of the composition.

Bleach catalyst

Bleach catalysts preferred for use herein include the manganese triazacyclononane and related complexes (US-A-4246612, US-A-5227084); Co, Cu, Mn and Fe bispyridylamine and related complexes (US-A-5114611); and pentamine acetate cobalt(III) and related complexes(US-A-4810410). A complete description of bleach catalysts suitable for use herein can be found in WO 99/06521, pages 34, line 26 to page 40, line 16. Bleach catalyst if included in the compositions of the invention are in a level of from about 0.1 to about 10%, preferably from about 0.5 to about 2% by weight of the composition.

Surfactant

Preferably the compositions (methods and products) for use herein are free of surfactants. A preferred surfactant for use herein is low foaming by itself or in combination with other components (i.e. suds suppressers). Preferred for use herein are low and high cloud point nonionic surfactants and mixtures thereof including nonionic alkoxylated surfactants (especially ethoxylates derived from C_6-C_{18} primary alcohols), ethoxylated-propoxylated alcohols (e.g., Olin Corporation's Poly-Tergen®SLF18), epoxy-capped poly(oxyalkylated) alcohols (e.g., Olin Corporation's Poly-Tergen®SLF18B - see WO-A-94/22800), ether-capped poly(oxyalkylated) alcohol surfactants, and block polyoxyethylene-polyoxypropylene polymeric compounds such as PLURONIC®, REVERSED PLURONIC®, and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan; amphoteric surfactants such as the C_{12}-C_{20} alkyl amine oxides (preferred amine oxides for use herein include lauryldimethyl amine oxide and hexadecyl dimethyl amine oxide), and alkyl amphocarboxylic surfactants such as Miranol™ C2M; and zwitterionic surfactants such as the betaines and sultaines; and mixtures thereof. Surfactants suitable herein are disclosed, for example, in US-A-3,929,678 , US-A- 4,259,217, EP-A-0414 549, WO-A-93/08876 and WO-A-93/08874. Surfactants are typically present at a level of from about 0.2% to about 30% by weight, more preferably from about 0.5% to about 10% by weight, most preferably from about 1% to about 5% by weight of a detergent composition. Preferred surfactant for use herein, if any, are low foaming and include low cloud point nonionic surfactants and mixtures of higher foaming surfactants with low cloud point nonionic surfactants which act as suds suppresser therefor.

Enzyme

Other enzymes suitable for use herein include alpha-amylases, those of bacterial or fungal origin. Chemically or genetically modified mutants (variants) are included. A preferred alkaline alpha-amylase is derived from a strain of Bacillus, such as Bacillus licheniformis, Bacillus amyloliquefaciens, Bacillus stearothermophilus, Bacillus subtilis, or other Bacillus sp., such as Bacillus sp. NCIB 12289, NCIB 12512, NCIB 12513, DSM 9375 (USP 7,153,818) DSM 12368, DSMZ no. 12649, KSM AP1378 (WO 97/00324), KSM K36 or KSM K38 (EP 1 ,022,334). Preferred amylases include:

(a) the variants described in WO 94/02597, WO 94/18314, WO96/23874 and WO 97/43424, especially the variants with substitutions in one or more of the following positions versus the enzyme listed as SEQ ID No. 2 in WO 96/23874: 15, 23, 105, 106, 124, 128, 133, 154, 156, 181 , 188, 190, 197, 202, 208, 209, 243, 264, 304, 305, 391, 408, and 444.

(b) the variants described in USP 5,856,164 and WO99/23211, WO 96/23873, WO00/60060 and WO 06/002643, especially the variants with one or more substitutions in the following positions versus the AA560 enzyme listed as SEQ ID No. 12 in WO 06/002643: 26, 30, 33, 82, 37, 106, 118, 128, 133, 149, 150, 160, 178, 182, 186, 193, 203, 214, 231, 256, 257, 258, 269, 270, 272, 283, 295, 296, 298, 299, 303, 304, 305, 311, 314, 315, 318, 319, 339, 345, 361, 378, 383, 419, 421, 437, 441, 444, 445, 446, 447, 450, 461, 471, 482, 484 that also preferably contain the deletions of D183* and G184*.

(c) variants exhibiting at least 90% identity with SEQ ID No. 4 in WO06/002643, the wild-type enzyme from Bacillus SP722, especially variants with deletions in the 183 and 184 positions and variants described in WO 00/60060, which is incorporated herein by reference.

Suitable commercially available alpha-amylases are DURAMYL®, LIQUEZYME® TERMAMYL®, TERMAMYL ULTRA®, NATALASE®, SUPRAMYL®, STAINZYME®, STAINZYME PLUS®, FUNGAMYL® and BAN® (Novozymes A/S), BIOAMYLASE - D(G), BIOAMYLASE® L (Biocon India Ltd.), KEMZYM® AT 9000 (Biozym Ges. m.b.H, Austria), RAPIDASE®, PURASTAR®, OPTISIZE HT PLUS® and PURASTAR OXAM® (Genencor International Inc.) and KAM® (KAO, Japan). In one aspect, preferred amylases are NATALASE®, STAINZYME® and STAINZYME PLUS® and mixtures thereof.

Enzymes are preferably added herein as prills, granulates, or cogranulates at levels typically in the range from about 0.0001% to about 5%, more preferably from about 0.001% to about 2% pure enzyme by weight of the cleaning composition.

Preferably the compositions of the invention comprise from 0.0001% to about 5%, more preferably from about 0.001% to about 2% pure protease by weight of the cleaning composition.

Low cloud point non-ionic surfactants and suds suppressers

The suds suppressers suitable for use herein include nonionic surfactants having a low cloud point. "Cloud point", as used herein, is a well known property of nonionic surfactants which is the result of the surfactant becoming less soluble with increasing temperature, the temperature at which the appearance of a second phase is observable is referred to as the "cloud point" (See Kirk Othmer, pp. 360-362). As used herein, a "low cloud point" nonionic surfactant is defined as a nonionic surfactant system ingredient having a cloud point of less than 30° C., preferably less than about 20° C., and even more preferably less than about 10° C., and most preferably less than about 7.5° C. Typical low cloud point nonionic surfactants include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohol, and polyoxypropylene/polyoxyethylene/polyoxypropylene (PO/EO/PO) reverse block polymers. Also, such low cloud point nonionic surfactants include, for example, ethoxylated-propoxylated alcohol (e.g., BASF Poly-Tergen® SLF18) and epoxy-capped poly(oxyalkylated) alcohols (e.g., BASF Poly-Tergen® SLF18B series of nonionics, as described, for example, in US-A-5,576,281).

Preferred low cloud point surfactants are the ether-capped poly(oxyalkylated) suds suppresser having the formula:

$$R^1O-(CH_2-\underset{\displaystyle R^2}{CH}-O)_x-(CH_2-CH_2-O)_y-(CH_2-\underset{\displaystyle R^3}{CH}-O)_z-H$$

wherein R^1 is a linear, alkyl hydrocarbon having an average of from about 7 to about 12 carbon atoms, R^2 is a linear, alkyl hydrocarbon of about 1 to about 4 carbon atoms, R^3 is a linear, alkyl hydrocarbon of about 1 to about 4 carbon atoms, x is an integer of about 1 to about 6, y is an integer of about 4 to about 15, and z is an integer of about 4 to about 25.

Other low cloud point nonionic surfactants are the ether-capped poly(oxyalkylated) having the formula:

$$R_IO(R_{II}O)_nCH(CH_3)OR_{III}$$

wherein, R_I is selected from the group consisting of linear or branched, saturated or unsaturated, substituted or unsubstituted, aliphatic or aromatic hydrocarbon radicals having from about 7 to about 12 carbon atoms; R_{II} may be the same or different, and is independently selected from the group consisting of branched or linear C_2 to C_7 alkylene in any given molecule; n is a number from 1 to about 30; and R_{III} is selected from the group consisting of:

(i) a 4 to 8 membered substituted, or unsubstituted heterocyclic ring containing from 1 to 3 hetero atoms; and

(ii) linear or branched, saturated or unsaturated, substituted or unsubstituted, cyclic or acyclic, aliphatic or aromatic hydrocarbon radicals having from about 1 to about 30 carbon atoms;

(b) provided that when R^2 is (ii) then either: (A) at least one of R^1 is other than C_2 to C_3 alkylene; or (B) R^2 has from 6 to 30 carbon atoms, and with the further proviso that when R^2 has from 8 to 18 carbon atoms, R is other than C_1 to C_5 alkyl.

The nanoparticles can negatively interact with some cleaning actives either in the wash liquor. In preferred embodiments of the method of the invention, there is a delayed release of the nanoparticles with respect to other ingredients. This ameliorates negative interactions and improves cleaning performance. By "delayed release" is meant that at least 50%, preferably at least 60% and more preferably at least 80% of one of the components is delivered into the wash solution at least one minute, preferably at least two minutes and more preferably at least 3 minutes, than at less than 50%, preferably less than 40% of the other component. The nanoparticle can be delivered first and the enzyme second or vice-versa. Good cleaning results are obtained when the enzyme, in particular protease, is delivered first and the nanoclay second. Delayed release can be achieved by for example using a multi-compartment pouch wherein different compartments have different dissolution rates, by having multi-phase tablets where different phases dissolve at different rates, having coated bodies, layered particles, etc.

Water-soluble pouch

In a preferred embodiment of the present invention the detergent composition is in the form of a water-soluble pouch, more preferably a multi-phase unit dose pouch, preferably an injection-moulded, vacuum- or thermoformed multi-compartment, wherein at least one of the phases comprises the nanoparticles. Preferred manufacturing methods for unit dose executions are described in WO 02/42408 and EP 1,447,343 B1. Any water-soluble film-forming polymer which is compatible with the compositions of the invention and which allows the delivery of the composition into the main-wash cycle of a dishwasher can be used as enveloping material.

Most preferred pouch materials are PVA films known under the trade reference Monosol M8630, as sold by Chris-Craft Industrial Products of Gary, Indiana, US, and PVA films of corresponding solubility and deformability characteristics. Other films suitable for use herein include films known under the trade reference PT film or the K-series of films supplied by Aicello, or VF-HP film supplied by Kuraray.

Delayed release

Delayed release can be achieved by means of coating, either by coating active materials or particle containing active material. The coating can be temperature, pH or ionic strength sensitive. For example particles with a core comprising either nanoparticles (or a nanoparticle precursor) or enzyme and a waxy coating encapsulating the core are adequate to provide delayed release. For waxy coating see WO 95/29982. pH controlled release means are described in WO 04/111178, in particular amino-acetylated polysaccharide having selective degree of acetylation.

Other means of obtaining delayed release are pouches with different compartments, where the compartments are made of film having different solubilities (as taught in WO 02/08380).

Delayed release can also be obtained by layering of actives in solid particles are described in WO2007/146491.

In the case of free builder formulations it has been found that an improved cleaning can be obtained by delivering enzymes and an alkalinity source to the wash liquor, followed by bleach and then the nanoparticles and the nanoparticle stabilizer. In the case of build compositions it has been found that an improved cleaning is obtained if the builder and alkalinity source are delivered first, followed by enzymes then nanoparticle stabilizer and finally nanoparticles.

In the case in which the cleaning composition comprise layered particles comprising different actives in different layers, it has been found that excellent cleaning is provided by a cleaning composition

Examples.

Abbreviations used in Examples

In the examples, the abbreviated component identifications have the following meanings:

MGDA	Disolvine GL (tetrasodim N,N-bis(carboxylato methyl-L- glutamate) from Azko Nobel
GLDA	Glutamic-N,N- diacetic acid
STPP	Sodium tripolyphosphate anhydrous
KOH	Potassium Hydroxide
Sodium Carbonate	Anhydrous sodium carbonate
Laponite	Laponite® RD synthetic hectorite available from Rockwood Additives Limited.
Polymer	Polyvinylpirrolidone vinylimidazole/polyethylene glycol copolymer
PA30	Polyacrylic acid available from BASF
Percarbonate	Sodium percarbonate of the nominal formula $2Na_2CO_3.3H_2O_2$
TAED	Tetraacetylethylenediamine
Bleach catalyst	Cobalt bleach catalyst
Protease	Protease enzyme having a pI of 7
Amylase	Stainzyme Plus available from Novozymes

In the following examples all levels are quoted as parts by weight of the composition.

100% activity	Example 1	Example 2	Example 3	Example 4	Example 5
MGDA	0	13%	0	0	9.5%
GLDA	0	0	15.8%	0	0
STPP	0	0	0	25.9%	0
NaOH	6.0%	5.2%	5%	0	0
Sodium Carbonate	0	0	0	18.9%	26.7%
Laponite	23.9%	20.8%	20.1%	14.0%	15.3%
Polymer	31.7%	27.6%	26.7%	18.6%	20.2%
PA30	0	0	0	0	3.81%
Percarbonate	26.3%	22.9%	22.2%	15.4%	16.8%
TAED	7.2%	6.2%	6.0%	4.21%	4.58%
Catalyst	0.02%	0.017%	0.017%	0.012%	0.013%
Protease	2.4%	2.08%	2.01%	1.40%	1.53%
Amylase	2.0%	1.77%	1.71%	1.19%	1.30%
Perfume	0.48%	0.42%	0.40%	0.28%	0.31%

Example 1 and 5 illustrate the use of compositions comprising a synthetic clay, Laponite®, for the removal of different types of soil in a dishwasher. The dishwasher load comprises different soils and different substrates: Macaroni & Cheese on stainless steel baked for 7 minutes at 200°C, scrambled eggs on ceramic bowls microwaved for 2 minutes, cooked rice on ceramic dishes, scrambled eggs on stainless steel slides and cooked pasta on glass slides. The dishware is allowed to dry for 12 hours and then is ready to use. The dishware is loaded in a dishwasher (i.e GE Model GSD4000, Normal Wash at 50 °C).

The cleaning was good in all cases and especially in the case of starch based soils.

CLAIMS

What is claimed is:

1. A cleaning composition for use in a wash liquor comprising:

a) nanoparticles or a nanoparticles precursor; and

b) a nanoparticle-compatible protease

the cleaning composition having an alkaline pH wherein the protease has an isoelectric point which is at least one unit below the pH of the wash liquor.

2. A cleaning composition according to claim 1 wherein the protease has an isoelectric point of from about 6 to about 9.

3. A cleaning composition according to any preceding claim wherein the nanoparticle is a synthetic clay.

4. A cleaning composition according to any preceding claim comprising less than 10% by weight of the composition of phosphate builder.

5. A cleaning composition according to any preceding claim comprising a polycarboxylated builder.

6. A cleaning composition according to any preceding claim wherein the composition further comprises an aminocarboxylate builder.

7. A method of cleaning glassware/tableware in an automatic dishwashing machine comprising the step of contacting the glassware/tableware with a wash liquor comprising a composition according to any preceding claim.

8. A method of cleaning according to claim 7 wherein the wash liquor comprises from about 50 to about 1,000 ppm of nanoparticle.

9. A method of cleaning glassware/tableware in an automatic dishwashing machine comprising the step of contacting the glassware/tableware with a wash liquor comprising a composition according to any of claims 5 or 6 wherein the builder is delivered into the wash liquor before the nanoparticles.

10. A particle comprising a nanoparticle precursor containing core surrounded by a polymeric surrounding layer.