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(54) AUTOMATIC DISHWASHING DETERGENT COMPOSITION

SPÜLMITTELZUSAMMENSETZUNG FÜR GESCHIRRSPÜLAUTOMAT

COMPOSITION DE DÉTERGENT DE LAVE-VAISSELLE AUTOMATIQUE

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Description

Technical field of the invention

[0001] The present invention relates to an automatic dishwashing detergent composition containing builder, bleach component, a graft copolymer having a polysaccharide backbone and one or more side chains of one or more synthetic monomeric units, a polyoxyethylene-based nonionic surfactant and optionally one or more other ingredients.

[0002] The automatic dishwashing (ADW) detergent composition of the present invention combines a very good cleaning action with minimal spotting and film-forming.

Background of the invention

[0003] Automatic dishwashing (ADW) detergents constitute a distinct class of detergent compositions. Unlike most other detergents, ADW detergents have to be low-foaming. In addition, a spotless and film-free appearance of glasses and silverware is the expected final result of each automatic dishwashing run.

[0004] In general, ADW detergents are mixtures of ingredients whose purpose, in combination, is to break down and remove food soils; to inhibit foaming caused by certain food soils; and to remove stains which can be caused by beverages such as coffee and tea or by vegetable soils such as carotenoid soils.

[0005] Spotting and filming of glassware are the chief criteria by which the performance of a dishwashing formulation is judged. Spotting is an obvious reference to discrete residues on glassware which are formed when water droplets evaporate and leave behind dissolved solids. Filming refers to a more uniform deposition over a large, continuous portion of the glass surface. This film can sometimes be of organic origin (resulting from soil in the wash liquor or organic components in the detergent) but is also often inorganic in nature, due to the formation and deposition of some mineral precipitate.

[0006] ADW detergents may comprise a variety of detergent ingredients, including alkalinity sources, builders, bleaching systems, anti-scalants, corrosion inhibitors, surfactants, antifoams, sheeting polymers and/or enzymes. Builder materials are used to provide alkalinity and buffering capacity, maintain ionic strength, extract metals from soils and/or remove alkaline earth metal ions from washing solutions. Examples of builder materials include phosphates, alkali metal citrates, carbonates and bicarbonates; and the salts of nitrilotriacetic acid (NTA); methylglycine diacetic acid (MGDA); glutaric diacetic acid (GLDA), polycarboxylates such as polymaleates, polyacetates, polyhydroxyacrylates, polyacrylate/polymaleate and polyacrylate/polymethacrylate copolymers, as well as zeolites; layered silicas and mixtures thereof.

[0007] Phosphate-free or low-phosphate compositions rely on non-phosphate builders, such as salts of citrate, carbonate, silicate, disilicate, bicarbonate, aminocarboxylates and others to sequester calcium and magnesium from hard water, and upon drying, can leave an insoluble visible deposit. Polymers made from (meth)acrylic acid and maleic acid are known for use in inhibiting the scale or other insoluble deposits produced from non-phosphate builders.

[0008] Surfactants are amphiphilic compounds, i.e. compounds that contain hydrophobic as well as hydrophilic groups, a property which enables them to mix the hydrophobic soils from the dishes with the rinsing water. Nonionic surfactants are preferably used for dish washing applications as they are known to be low or moderate foamers, mild to human skin and have superior performance in removing oily soil. Nonionic surfactants are further well suited for mixing with other materials contained in the detergent formulation as they are known to be chemically inert and stable toward pH change. Nonionic surfactants typically have noncharged hydrophilic headgroups and are commonly based on polyoxyethylene or a glycoside.

[0009] US 2011/0028371 describes hybrid copolymer comprising:
a synthetic polymer derived from at least one anionic ethylenically unsaturated monomer and a naturally derived hydroxyl containing chain transfer agent as an end group, wherein the chain transfer agent is present from about 75% by weight to about 99% by weight, based on the total weight of the hybrid copolymer. Examples 24 and 28 describe automatic zero phosphate dishwash formulations containing the copolymer, builder and bleach.

[0010] WO 2013/092276 describes a detergent composition comprising 20-99.7 wt.% of a continuous phase containing glutamic-N,N-diacetate (GLDA), water and optionally other components; and 0.3-80 wt.% of a dispersed phase comprising at least 0.3% of bleach particles by weight of the composition. Dehypon™ Wet is mentioned as an example of a nonionic surfactant that can be applied in the detergent composition.

[0011] US 2016/0348036 describes a zero-phosphate machine dish wash composition in unit dose format comprising

a. non-phosphate builder;
b. alkali percarbonate;
c. one or more polycarboxylate polymers;
d. alkali carbonate, alkali silicates or mixtures thereof;
e. one or more nonionic surfactants; and

f. a manganese bleach catalyst.

[0012] The machine dishwash composition may include a nonionic surfactant of the formula R^3-$(PO)_x(EO)_y$-$CH_2CH(OH)$-R^4; wherein R^3 is C_6-C_{15}; R^5 is C_4-C_{10}, and x is an integer in the range of 0-10, and y is an integer in the range of 3-30. Suitable nonionics of this type include modified fatty alcohol polyglycolethers available as Dehypon® 3697 GRA or Dehypon® Wet from BASF.

[0013] US 2011/0118168 describes hard surface cleaning compositions comprising a hybrid copolymer and a surfactant. Nonionic surfactants with the structure R^1-O-$(CH_2CH_2O)_{n-}$ $(CH_2CHCH_3'O)_q$-$(CH_2CH(OH))$-R^4 are mentioned. In the examples, hybrid copolymers are described that are prepared from maltodextrin and acrylic acid/propylmethacrylamide

[0014] WO 2014/021902 describes an ADW detergent composition containing a hybrid copolymer that is based on maltodextrin and (among others) methacrylate. In the examples compositions are described containing approximately 6 wt.% of hybrid copolymer and 3.7 wt% of Dehypon LS-36 (an ethylene oxide/propylene oxide fatty alcohol).

[0015] WO 2013/022762 describes ADW detergent compositions containing a hybrid copolymer that is based on maltodextrin and acrylic acid in a 1: 1 w/w ratio. In the examples compositions are described containing 2-6 wt.% of this hybrid copolymer and 1.7 wt.% of Pluronic N-3 (an ethylene oxide/propylene oxide block copolymer).

[0016] WO 2011/014783 describes ADW detergents that contain a hybrid copolymer that is based on maltodextrin and acrylic acid/ 2-acrylamido-2-methylpropanesulphonic acid, builder and nonionic surfactant.

[0017] US 2009/0186795 describes a dry automatic dishwashing detergent comprising:

- 80-95% of a base that includes one or more of a sulfate, a carbonate, a citrate, and a silicate, wherein the carbonate is present in an amount less than about 25% of the composition;
- 0.1-10% of a nonionic surfactant;
- 0.55-4% of a spot reduction system that includes (i) a polyacrylate and (ii) a carboxymethyl inulin; and,
- 0.1-3% of an enzyme system.

[0018] WO 2011/014783 describes a scale inhibiting composition for aqueous systems, comprising an anionic hybrid copolymer composition wherein said copolymer comprises:

- at least one anionic ethylenically unsaturated monomer and a naturally derived hydroxyl containing chain transfer agent as an end group; and
- a hybrid synthetic copolymer comprising one or more synthetic polymers derived from the at least one anionic ethylenically unsaturated monomer with at least one initiator fragment as an end group, said hybrid synthetic copolymer having the structure: I -(- M_{hsc}-)- H

  wherein I is the initiator fragment, H is a proton abstracted from the naturally derived hydroxyl containing chain transfer agent and M_{hsc} is a synthetic portion of the hybrid synthetic copolymer derived from the at least one anionic ethylenically unsaturated monomer; and
  wherein the chain transfer agent is present in amounts greater than 75% by weight to about 99% by weight, based on the total weight of the hybrid copolymer, wherein the scale inhibiting composition has a greater than 80% carbonate inhibition at a 100 ppm dosage level of the anionic hybrid copolymer composition in an aqueous system.

[0019] WO 2015/169793 describes detergent compositions containing a combination of protease and hybrid polymer. Example 1 describes an automatic dishwashing detergent tablet that is composed of three different phases. The tablet contains builder, hybrid polymer, bleach and nonionic surfactant.

Summary of the invention

[0020] The inventors have developed an ADW detergent composition that combines a very good cleaning action with minimal spotting and film-forming.

[0021] The ADW detergent composition of the present invention consists of:

- 20-80 wt.% of builder;
- 5-25 wt.% of bleach component;
- 1-10 wt.% of a graft copolymer having a polysaccharide backbone and one or more side chains of one or more synthetic monomeric units;
- 1-15 wt.% of nonionic surfactant represented by the following formula:

$$R^1\text{-}O\text{-}(CH_2CH_2O)_n\text{-}(CHR^2CHR^{2'}O)_q\text{-}(CH_2CH(OH)R^3)_s\text{-}R^4$$

wherein

- R^1 is an linear or branched C_8-C_{22} alkyl radical or a linear or branched C_8-C_{22} alkylphenol radical;
- R^2 and $R^{2'}$ are independently selected from hydrogen and a C_1-$C_{.5.}$alkyl radical, and wherein either R^2 or $R^{2'}$ is hydrogen;
- R^3 is a covalent bond or a linear, aliphatic C_2-C_{26} alkyl radical;
- R^4 is selected from hydrogen, and an alkyl radical having 1-15 carbon atoms;
- $5 \leq n \leq 30$;
- $0 \leq q \leq 3$;
- s=1-5,

said nonionic surfactant being selected from homopolymers, statistical copolymers, block copolymers and combinations thereof; and

- 0-60 wt.% of one or more other ingredients.

[0022] The ADW detergent composition of the present invention produces very good cleaning results for earthenware, glassware, metal as well as plastic. In addition, the inventors have discovered that the combination of builder, graft copolymer and nonionic surfactant represented by the above described formula very effectively minimizes spotting and film-forming.

Detailed description of the invention

[0023] A first aspect of the present invention relates to an ADW detergent composition consisting of:

- 20-80 wt.% of builder;
- 5-25 wt.% of bleach component;
- 1-10 wt.% of a graft copolymer having a polysaccharide backbone and one or more side chains of one or more synthetic monomeric units;
- 1-15 wt.% of nonionic surfactant represented by the following formula:

$$R^1\text{-}O\text{-}(CH_2CH_2O)_n\text{-}(CHR^2CHR^{2'}O)_q\text{-}(CH_2CH(OH)R^3)_s\text{-}R^4$$

wherein

- R^1 is an linear or branched C_8-C_{22} alkyl radical or a linear or branched C_8-C_{22} alkylphenol radical;
- R^2 and $R^{2'}$ are independently selected from hydrogen and a C_1-$C_{.5.}$ alkyl radical, and wherein either R^2 or $R^{2'}$ is hydrogen;
- R^3 is a covalent bond or a linear, aliphatic C_2-C_{26} alkyl radical;
- R^4 is selected from hydrogen, and an alkyl radical having 1-15 carbon atoms;
- $5 \leq n \leq 30$;
- $0 \leq q \leq 3$;
- s=1-5,

said nonionic surfactant being selected from homopolymers, statistical copolymers, block copolymers and combinations thereof; and

- 0-60 wt.% of one or more other ingredients.

[0024] The term "builder" as used herein refers to a material that is capable of removing calcium ion from aqueous solution by ion exchange, complexation, sequestration and/or precipitation. Examples of builder materials include phosphates, alkali metal citrates, carbonates and bicarbonates; aminopolycarboxylates, polycarboxylates such as polymaleates, polyacetates, polyhydroxyacrylates, polyacrylate/polymaleate and polyacrylate/polymethacrylate copolymers, as well as zeolites; layered silicas and mixtures thereof.

[0025] The term "surfactant" as used herein refers to components within the classification described in "Surfactant Science Series", Vol.82, (1999) Handbook of detergents, part A: Properties, chapter 2 (Surfactants, classification), G. Broze (ed.).

[0026] The term "bleach component" as used herein refers to substances that are capable of removing coloured stains

by oxidizing or reducing the colour components of the stain. Examples of oxidizing bleach components include peroxides, such as hydrogen peroxide, sodium percarbonate and sodium perborate. Examples of reducing bleach components include sodium dithionite, sodium borohydride and sodium sulfite. Besides the bleach component, the detergent composition may suitably contain bleach activators and/or bleach catalysts.

[0027] The term "percarbonate" as used herein refers to an adduct of alkalimetal carbonate and hydrogen peroxide (a perhydrate), such as sodium percarbonate ($2Na_2CO_3 \cdot 3H_2O_2$).

[0028] The term "carbonate" as used herein refers to carbonic acid ($H_2CO^{2-}_3$) and salts thereof. The term "carbonate" as used herein does not encompass percarbonates.

[0029] The term "citrate" as used herein refers to citric acid and salts thereof. Likewise, the term "silicate" as used herein refers to silicic acid and salts thereof.

[0030] The term "polysaccharide" as used herein refers to a polymeric carbohydrate molecule composed of a chain of at least 5 monosaccharide units bound together by glycosidic linkages.

[0031] The terminology "one or more other ingredients" as used herein refers to ingredients other than builder; bleach component; graft copolymer having a polysaccharide backbone and one or more side chains of one or more synthetic monomeric units; and nonionic surfactant.

[0032] Whenever reference is made herein to the concentration of a salt or an acid, unless indicated otherwise, said concentration refers to the equivalent concentration of the salt or acid in anhydrous form.

Detergent composition

[0033] The ADW detergent composition of the present invention preferably is a particulate composition or a solid article. Accordingly, the detergent composition preferably is a powder or a tablet.

[0034] The combination of the builder, the bleach component, the graft copolymer and the nonionic surfactant typically represents at least 40%, more preferably at least 50% and most preferably at least 60% by weight of the detergent composition.

[0035] The detergent composition of the present invention preferably contains the graft copolymer and the builder in a weight ratio of at least 1:50, more preferably of 1:40 to 1:8 and most preferably of 1:30 to 1:10.

[0036] The graft copolymer and the nonionic surfactant are typically present in the detergent composition in a weight ratio of 1:4 to 3:1, more preferably of 1:3 to 5:2 and most preferably of 1:2.2 to 2:1.

[0037] According to a particularly preferred embodiment, the ADW detergent composition of the present invention consists of, calculated by weight of dry matter:

a. 30-70wt.% by weight of the builder;
b. 5-25 wt.% by weight of the bleach component;
c. 1-8 wt.% of the graft copolymer;
d. 1-10 wt.% of the nonionic surfactant;
e. 0.01-0.5 wt.% by weight of enzymes;
f. 0-60 wt.% of one or more additives selected from bleach catalysts, alkali carriers, corrosion inhibitors, dyes, fragrances and fillers.

Builder

[0038] The detergent composition typically contains at least 30 wt.% of builder, more preferably 35-70 wt.% of builder and most preferably 40-65 wt.% of builder.

[0039] According to a preferred embodiment, the builder contained in the detergent composition according to the invention comprises 20-80% of precipitating builder by weight of the builder, said precipitating builder being selected from carbonate, silicate and combinations thereof. More preferably, the detergent composition contains 25-75% of precipitating builder by weight of the builder, even more preferably 30-72% and most preferably 40-70% of precipitating builder by weight of the builder.

[0040] According to a particularly preferred embodiment, the detergent composition contains 20-80% carbonate by weight of the builder. More preferably, the detergent composition contains 25-75%, even more preferably 30-72% and most preferably 40-70% of carbonate by weight of the builder. As explained before, these concentrations refer to the equivalent concentration of the carbonate in anhydrous form.

[0041] Preferably, the carbonate is alkali metal carbonate, most preferably sodium carbonate.

[0042] The silicate content of the builder component of the detergent composition preferably is 0-20% by weight of the builder. More preferably, the detergent composition contains 1-10% silicate, most preferably 1.5-6% silicate by weight of the builder. As explained before, these concentrations refer to the equivalent concentration of the silicate in anhydrous form.

[0043] Preferably the silicate is an alkali metal silicate, most preferably sodium silicate. Examples of silicates that may be applied include disilicate, metasilicate and crystalline phyllosilicates and mixtures thereof. Most preferably, the silicate is selected from sodium disilicate, sodium metasilicate and combinations thereof.

[0044] Preferably, the builder contained in the detergent composition according to the invention, comprises 20-70% of citrate by weight of the builder. More preferably, the detergent composition contains 25-65% citrate by weight of the builder. Even more preferably, the detergent composition contains 30-60% of citrate by weight of the builder. As explained before, these concentrations refer to the equivalent concentration of the citrate in anhydrous form. Preferably, the citrate is alkali metal citrate, most preferably sodium citrate.

[0045] In accordance with a particularly preferred embodiment, citrate and carbonate together constitute at least 60 wt.%, more preferably at least 70 wt.% and most preferably at least 80 wt.% of the builder.

[0046] In a further preferred embodiment of the present invention the composition comprises citrate and carbonate, wherein the citrate and carbonate together constitute at least 30 wt.%, more preferably at least 35 wt.% of the detergent composition. Even more preferably the citrate and carbonate together constitute 35-75 wt.% of the detergent composition and most preferably 40-70 wt.% of the detergent composition.

[0047] Preferably, citrate and carbonate are present in the detergent composition in a molar ratio of citrate : carbonate of 0.15 to 0.9, more preferably of 0.2-0.8 and most preferably of 0.25 to 0.6.

[0048] According to another embodiment, the builder comprises less than 25% by weight of the builder of builder components other than citrate, carbonate and silicate, more preferably the builder comprises less than 15%, even more preferably less than 10% by weight of the builder of builder components other than citrate, carbonate and silicate.

[0049] The phosphate content of the ADW detergent composition preferably is less than 10%, more preferably less than 3% and most preferably less than 1% by weight of the builder.

[0050] The inventors have found that the inclusion of even small amounts of aminocarboxylate chelant can adversely affect the cleaning properties of the present detergent composition. Consequently in a preferred embodiment the detergent composition contains less than 3 wt.%, more preferably less than 2 wt.% and most preferably less than 1 wt.% of aminopolycarboxylate chelant. Examples of aminocarboxylate chelant include MGDA (methyl-glycine-diacetic acid), GLDA (glutamic,N,N-diacetic acid), iminodisuccinic acid (IDS), aspartic acid-N-monoacetic acid (ASMA), aspartic acid-N,N-diacetic acid (ASDA), aspartic acid-N- monopropionic acid (ASMP) , iminodisuccinic acid (IDA), N-(2-sulfomethyl) aspartic acid (SMAS), N-(2-sulfoethyl) aspartic acid (SEAS), N-(2-sulfomethyl) glutamic acid (SMGL), N-(2- sulfoethyl) glutamic acid (SEGL), iminodiacetic acid and salts and derivatives thereof.

Bleach

[0051] The detergent composition of the present invention preferably comprises 7-22 wt.%, more preferably 8-20 wt.% and most preferably 9-18 wt.% of bleach component

[0052] The bleach component employed in the present detergent composition preferably is an oxidizing bleach component. The oxidizing bleach component may suitably comprise a chlorine-, or bromine-releasing agent or a peroxygen compound. Preferably, the bleach component is selected from peroxides (including peroxide salts such as sodium percarbonate), organic peracids, salts of organic peracids and combinations thereof. More preferably, the bleach component is a peroxide. Examples of peroxides are acids and corresponding salts of monopersulphate, perborate monohydrate, perborate tetrahydrate, and percarbonate. Most preferably, the bleach component is a percarbonate, notably sodium percarbonate.

[0053] Organic peracids useful herein include alkyl peroxy acids and aryl peroxyacids such as peroxybenzoic acid and ring substituted peroxybenzoic acids (e.g. peroxy-alpha-naphthoic acid), aliphatic and substituted aliphatic monoperoxy acids (e.g. peroxylauric acid and peroxystearic acid), and phthaloyl amido peroxy caproic acid (PAP).

[0054] Typical diperoxy acids useful herein include alkyl diperoxy acids and aryldiperoxy acids, such as 1,12 di-peroxydodecanedioic acid (DPDA), 1,9 diperoxyazelaic acid, diperoxybrassylic acid, diperoxysebacic acid and diperoxy-isophthalic acid, and 2 decyldiperoxybutane 1,4 dioic acid.

[0055] The detergent composition may contain one or more bleach activators such as peroxyacid bleach precursors. Peroxyacid bleach precursors are well known in the art. As non-limiting examples can be named N,N,N',N'-tetraacetyl ethylene diamine (TAED), sodium nonanoyloxybenzene sulphonate (SNOBS), sodium benzoyloxybenzene sulphonate (SBOBS) and the cationic peroxyacid precursor (SPCC) as described in US-A-4,751,015.

[0056] If desirable, a bleach catalyst, such as a manganese complex, e.g. Mn-Me TACN, as described in EP-A-0458397, or the sulphonimines of US-A-5,041,232 and US-A-5,047,163, can be incorporated. This bleach catalyst may suitably be present in the composition in the form of an encapsulate, notably an encapsulate that is separate from the bleach particles (to avoid premature bleach activation). Cobalt or iron catalysts can also be used.

Graft copolymer

[0057] The graft copolymer employed in accordance with the present invention has a polysaccharide backbone and one or more side chains of one or more synthetic monomeric units. Preferably, the graft copolymer contains one or more side chains of two or more, even more preferably of three or more synthetic monomeric units.

[0058] The graft copolymer employed in the detergent composition typically has a molecular weight of at least 4,000 g/mol, more preferably of at least 8,000 g/mol and most preferably at least 15,000 g/mol.

[0059] The one or more synthetic monomeric units are preferably selected from olefinically unsaturated carboxylate monomers; sulfonate monomers; phosphonate monomers and combinations thereof. More preferably, the one or more synthetic monomeric units are selected from olefinically unsaturated carboxylate monomers; sulfonate monomers and combinations thereof. Most preferably, the synthetic monomeric units are olefinically unsaturated carboxylate monomers.

[0060] The olefinically unsaturated carboxyate monomers include, for example, aliphatic, branched or cyclic, mono- or dicarboxylic acids, the alkali or alkaline earth metal or ammonium salts thereof, and the anhydrides thereof. Examples of such olefinically unsaturated carboxylic acid monomers include acrylic acid, methacrylic acid, ethacrylic acid, α-chloro-acrylic acid, α-cyano acrylic acid, β-methyl-acrylic acid (crotonic acid), α-phenyl acrylic acid, β-acryloxy propionic acid, sorbic acid, α-chloro sorbic acid, angelic acid, cinnamic acid, p-chloro cinnamic acid, β-styryl acrylic acid (1-carboxy-4-phenyl butadiene-1 ,3), itaconic acid, maleic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, fumaric acid, tricarboxy ethylene, and 2-acryloxypropionic acid. Moieties such as maleic anhydride or acrylamide that can be derivatized to an acid containing group can also be used. Moreover, combinations of olefinically unsaturated carboxylic acid monomers may be used. In a preferred embodiment, the olefinically unsaturated carboxylic acid monomer is selected from acrylic acid, maleic acid, itaconic acid, or methacrylic acid and combinations thereof.

[0061] Examples of the sulfonate monomers include 2-acrylamido-2-methylpropane sulfonic acid (AMPS), as well as styrene sulfonic acid, (meth-)acrylic acidsulfoalkyl esters, itaconic acidsulfoalkyl esters, preferably in each case as C_1-C_6-alkyl esters, vinyl sulfonic acid and the alkali, alkaline earth and/or ammonium salts thereof. Preferred are monomers containing a (meth)acrylate, a (meth)acrylamide and/or a vinyl group, in particular 2-acrylamido-2-methylpropane sulfonic acid (AMPS), styrene sulfonic acid, acrylic acid-sulfopropyl ester, itaconic acid-sulfopropyl ester, vinyl sulfonic acid, as well as in each case the ammonium, sodium, potassium and/or calcium salts.

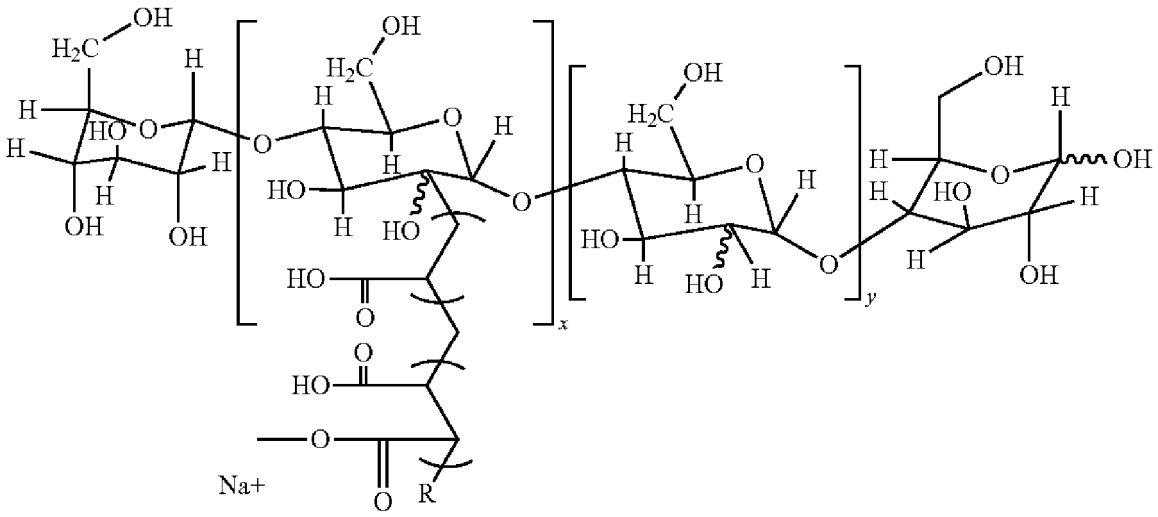
[0062] The polysaccharide that forms the backbone of the graft copolymer is preferably selected from starch, maltodextrin, cellulose, gums (e.g., gum arabic, guar and xanthan), alginates, pectin and gellan. More preferably, the polysaccharide is selected from starch and maltodextrin. The polysaccharides employed in the graft copolymer can be modified or derivatised by etherification (e.g., via treatment with propylene oxide, ethylene oxide, 2,3-epoxypropyl trimethyl ammonium chloride), esterification (e.g., via reaction with acetic anhydride, octenyl succinic anhydride ("OSA")), acid hydrolysis, dextrinization, oxidation (e.g. oxidized starch) or enzyme treatment, or various combinations of these treatments.

[0063] According to a particularly preferred embodiment, the polysaccharide of the copolymer is maltodextrin. Maltodextrins are polymers that can be produced by starch hydrolysis and that have D-glucose units linked primarily by α-1,4 bonds and a dextrose equivalent of less than about 20. Dextrose equivalent (DE) is a measure of the extent of starch hydrolysis. It is determined by measuring the amount of reducing sugars in a sample relative to dextrose (glucose). The DE of dextrose is 100, representing 100% hydrolysis.

[0064] The polysaccharide in the backbone of the graft copolymer preferably contains a chain of at least 8, more preferably of at least 10 monosaccharide units bound together by glycosidic linkages

[0065] The graft copolymer preferably has a high degree of polysaccharide. Typically, the polysaccharide represents at least 50 wt.%, more preferably at least 60 wt.%, even more preferably at least 70 wt.% and most preferably at least 80 wt.% of the graft copolymer.

[0066] The chemical structure of an exemplary embodiment of the hybrid polymer is shown below.



[0067] An example of a graft copolymer that may suitably be employed in accordance with the present invention is Alcoguard® H 5240, which is commercially available from AkzoNobel®.

Surfactants

[0068] The nonionic surfactant employed in the present detergent composition is a polyoxyalkylene condensate represented by the formula described hereinbefore: R^1-O-$(CH_2CH_2O)_n$-$(CHR^2CHR^{2'}O)_q$-$(CH_2CH(OH)R^3)_s$-R^4

[0069] According to a preferred embodiment R^2 or $R^{2'}$ in the above mentioned formula is selected from methyl or ethyl, most preferably R^2 or $R^{2'}$ is methyl.

[0070] In another preferred embodiment, the nonionic surfactant is represented by the above mentioned formula with q=0-2, more preferably q is 0 or 1. Most preferably, q equals 0.

[0071] In yet another preferred embodiment, the nonionic surfactant is represented by the aforementioned formula , and s=1-3, more preferably s=1-2 and most preferably s=1.

[0072] More particularly, the detergent composition according to the present invention contains a nonionic surfactant which is represented by the following formula:

$$R^1\text{-}O\text{-}(CH_2CH_2O)_n\text{-}(CHR^2CHR^{2'}O)_q\text{-}(CH_2CH(OH)R^3)_s\text{-}R^4$$

wherein:

- R^2 is hydrogen and $R^{2'}$ is methyl;
- R^3 is a covalent bond;
- q is0 or1; and
- sis1.

[0073] The nonionic surfactant employed in the present detergent composition preferably is a low foam nonionic surfactant. The term "low foam nonionic surfactant" as used herein refers to a nonionic surfactant that at a concentration of 1 wt.% in distilled water and at a temperature of 50 °C has an initial foam height of less than 50 mm, a foam height of less 5 mm after 1 minute, and a foam height of less than 1 mm after 5 minutes in the ASTM D1173-07 test.

[0074] The nonionic surfactant used typically has a cloud point of at least 25°C. More preferably the nonionic surfactant has a cloud point of 27-60°C, most preferably a cloud point of 28-50°C. The term "cloud point" as used herein refers to the temperature at which the nonionic surfactant starts to precipitate from an aqueous solution.

[0075] The inventors have found that, a detergent composition that is not only chemically but also physically very stable can be produced if the nonionic surfactant employed is solid at all temperatures which are relevant in the logistic chain. Thus, it is preferred that the nonionic surfactant is solid below 45°C.

[0076] According to a preferred embodiment,the detergent composition contains 1.5-10%, more preferably 2-8% of the nonionic surfactant by weight of the composition.

[0077] The detergent composition may contain other surfactant besides the nonionic surfactant. If an anionic surfactant is used, the total amount present preferably is less than 5 wt.%, more preferably less than 2 wt.%, even more preferably less than 1 wt.% and most preferably less than 0.5 wt.%..

Enzymes

[0078] The detergent composition preferably contains at least 0.03 wt.%, more preferably at least 0.05 wt.% and most preferably 0.07-3 wt.% of one or more enzymes.

[0079] Examples of enzymes suitable for use in the cleaning compositions of this invention include lipases, cellulases, peroxidases, proteases (proteolytic enzymes), amylases (amylolytic enzymes) and others which degrade, alter or facilitate the degradation or alteration of biochemical soils and stains encountered in cleansing situations so as to remove more easily the soil or stain from the object being washed to make the soil or stain more removable in a subsequent cleansing step. Both degradation and alteration can improve soil removal.

[0080] Preferably, the one or more active enzymes contained in the present composition are selected from protease, amylase, cellulase, peroxidase, mannanase, pectate, lyase and lipase. Most preferably, the active enzyme is selected from protease, amylase and combinations thereof.

[0081] According to a particularly preferred embodiment, the composition contains at least 10 mg/kg, more preferably at least 20 mg/kg and most preferably at least 50 mg/kg of active amylase.

[0082] According to another especially preferred embodiment, the composition contains at least 100 mg/kg, more preferably at least 200 mg/kg and most preferably at least 400 mg/kg of active protease.

[0083] Enzymes may be added in liquid or in encapsulated form. Examples of encapsulated enzymes are enzyme granule types D, E and HS by Genencor and granule types T, GT, TXT and Evity™ of Novozymes.

[0084] The proteolytic enzymes in this invention include metalloproteases and serine proteases, including neutral or alkaline microbial serine protease, such as subtilisins (EC 3.4.21.62). The proteolytic enzymes for use in the present invention can be those derived from bacteria of fungi. Chemically or genetically modified mutants (variants) are included. Preferred proteolytic enzymes are those derived from *Bacillus,* such as *B. lentus, B. gibsonii, B. subtilis, B. licheniformis, B. alkalophilus, B. amyloliquefaciens* and *Bacillus pumilus,* of which *B. lentus* and *B. gibsonii* are most preferred. Examples of such proteolytic enzymes are Excellase™, Properase™, Purafect™, Purafect™ Prime, Purafect™ Ox by Genencor; and those sold under the trade names Blaze™,Ovozyme™, Savinase™, Alcalase™, Everlase™, Esperase™, Relase™, Polarzyme™, Liquinase™ and Coronase™ by Novozymes.

[0085] The amylolytic enzymes for use in the present invention can be those derived from bacteria or fungi. Chemically or genetically modified mutants (variants) are included. Preferred amylolytic enzyme is an alpha-amylase derived from a strain of *Bacillus,* such as *B. subtilis, B. licheniformis, B. amyloliquefaciens* or *B. stearothermophilus.* Examples of such amylolytic enzymes are produced and distributed under the trade name of Stainzyme™, Stainzyme™ Plus, Termamyl™, Natalase™ and Duramyl™ by Novozymes; as well as Powerase™, Purastar™, Purastar™ Oxam by Genencor. Stainzyme™, Stainzyme™ Plus and Powerase™ are the preferred amylases.

[0086] Well known enzyme stabilizers such as polyalcohols/borax, calcium, formate or protease inhibitors like 4-formylphenyl boronic acid may also be present in the composition.

Filler

[0087] The detergent composition may suitably contain up to 70 wt.% of a filler. More preferably, the composition contains not more than 60 wt.% of filler, most preferably 10-50 wt.% of filler.

[0088] Preferably, the filler employed is a metal sulfate, e.g. sodium sulfate.

Other ingredients

[0089] Glass corrosion inhibitors can prevent the irreversible corrosion and iridescence of glass surfaces in automatic dishwash detergents. The claimed composition may suitably contain glass corrosion inhibitors. Suitable glass corrosion agents can be selected from the group the group consisting of salts of zinc, bismuth, aluminum, tin, magnesium, calcium, strontium, titanium, zirconium, manganese, lanthanum, mixtures thereof and precursors thereof. Most preferred are salts of bismuth, magnesium or zinc or combinations thereof.

[0090] Anti-tarnishing agents may prevent or reduce the tarnishing, corrosion or oxidation of metals such as silver, copper, aluminium and stainless steel. Anti-tarnishing agents such as benzotriazole, methyl benzotriazole or bis-benzotriazole and substituted or substituted derivatives thereof and those described in EP 723 577 (Unilever) may also be included in the composition. Other anti-tarnishing agents that may be included in the detergent composition are mentioned in WO 94/26860 and WO 94/26859. Suitable redox active agents are for example complexes chosen from the group of cerium, cobalt, hafnium, gallium, manganese, titanium, vanadium, zinc or zirconium, in which the metal are in the oxidation state of II, II, IV V or VI.

[0091] Optionally other components may be added to the formulation such as perfume, colorant or preservatives.

[0092] Accordingly, in a preferred embodiment of the detergent composition according to the present invention, the other ingredients are selected from enzymes, dispersing polymers, bleaches, bleach activators, bleach catalysts, alkali

carriers, corrosion inhibitors, dyes, fragrances and fillers.

[0093] Another aspect of the invention relates to the use of a detergent composition as defined herein before as a detergent in an automatic dishwashing apparatus.

[0094] The invention is further illustrated by the following non-limiting examples.

Examples

Example 1

[0095] Automatic dishwash compositions were prepared on the basis of the formulations shown in Table 1.

Table 1

	1	2	3	4
Na Citrate 2aq	40.0	40.0	30.0	35.0
Na Carbonate	27.0	17.0	27.0	22.0
Na percarbonate (coated)	13.0	13.0	13.0	13.0
Manganese catalyst	1.5	1.5	1.5	1.5
Enzymes	1.7	1.7	1.7	1.7
Alcoguard H5240 [1]	3.0	3.0	3.0	3.0
Dehypon WET [2]	3.3	3.3	3.3	3.3
Na Disilicate	3.0	3.0	3.0	3.0
Dequest 2016 [3]	1.0	1.0	1.0	1.0
Sodium sulfate	6.5	16.5	16.5	16.5

[1] Alcoguard H5240, a 45% solution of a graft copolymer consisting of a polysaccharide backbone and synthetic side chains ex Akzo Nobel

[2] Dehypon WET, a 90 % solution of low foaming fatty alcohol polyglycolether with typical molecular formula $C_{11}H_{23}$-O-$(CH_2CH_2O)_{20}$-$(CH_2CH(OH))$-C_8H_{17} ex BASF

[3] Dequest 2016, HEDP ex Monsanto

[0096] The aforementioned ADW detergent compositions were prepared as follows:
All solid ingredients (i.e. all ingredients in Table 1 except Alcoguard H5240 and Dehypon WET) were introduced into a powder mixer and mixed thoroughly. While mixing, Dehypon WET was carefully sprayed onto the powder in such a manner that it was evenly spread over the powder bed. The resulting powder was subsequently pressed into monolayer tablets. Combined weight of the tablet and Alcoguard H5240 was 18 grams.

[0097] In the dishwashing tests described below, the tablet and Alcoguard H5240 were introduced separately into the dishwasher. The tablet was inserted in the dispenser prior to starting the machine. Alcoguard H5240 was dosed by putting the correct amount in a cup and adding the cup manually when the dispenser opened.

[0098] The performance of the ADW detergent compositions was evaluated using the following test procedure:
A representative set of dishes consisting of earthenware, glassware, metal and plastics is washed 30 consecutive times in a Miele 1222GSL dishwasher using the 65 °C program. The detergent is dosed in the dispenser prior to every wash. A cup containing 50 grams of frozen Stiwa soil is dosed manually (e.g. opening the dishwasher and putting the cup upside down in the top rack) when the dispenser opens.

[0099] After every wash the dishwasher is opened and the dishes are allowed to dry completely and cool down to room temperature. After 30 washes the dishes are evaluated. The aesthetic scores were obtained by placing the dishware at 115 cm of a grey wall (RAL 7030) and 45 to 50 cm of the ceiling of the room. The dishware is illuminated with 4 light sources type Philips master TL-D 36 W / 865 2M, 120 cm long and is evaluated on overall appearance i.e. taking into account spots, film, etc. A scale going from 1 to 10 is used, 10 corresponding to a perfect dish.

[0100] The results of these tests are summarized in Table 2.

Table 2

	Aesthetic

(continued)

	1	2	3	4
Earthenware	6.00	6.00	6.00	6.00
Glass	6.50	4.50	6.50	6.00
Metal	5.50	5.50	4.50	4.50
Plastic	3.75	3.50	3.50	4.00
Combined	21.75	19.50	20.50	20.50

Example 2

[0101] Automatic dishwash compositions were prepared in the same way as described in Example 1 on the basis of the formulations shown in Table 3

Table 3

	1	2	3
Na Citrate anhydrous	17.6	8.8	0.0
Na Carbonate	27.0	27.0	27.0
Na percarbonate (coated)	13.0	13.0	13.0
Manganese catalyst	1.5	1.5	1.5
Enzymes	1.7	1.7	1.7
Alcoguard H5240	3.0	3.0	3.0
Dehypon WET	3.3	3.3	3.3
Na Disilicate	3.0	3.0	3.0
Dequest 2016	1.0	1.0	1.0
Sodium sulfate	28.9	37.7	46.5
Perfume & BTA solution[1]	0.3	0.3	0.3
[1.] Mixture of 80% Plurafac LF 301 (fatty alcohol alkoxylate ex BASF) and 20% Benzotriazole fine grade ex Helm AG			

[0102] The performance of the ADW detergent compositions was evaluated using the same test procedure as in Example 1.

[0103] The results of these tests are summarized in Table 4.

Table 4

	Aesthetic		
	1	2	A
Earthenware	4.50	4.00	2.50
Glass	5.67	3.44	2.33
Metal	4.25	2.75	1.75
Plastic	3.50	2.50	1.75
Combined	17.92	12.69	8.33

[0104] These results demonstrate that the performance of detergent composition A which did not contain citrate was inferior to that of the detergent compositions that did contain citrate.

Example 3

[0105] Automatic dishwash compositions were prepared in the same way as described in Example 1 on the basis of the formulations shown in Table 5. Compostions A and B are reference examples.

Table 5

	1	2	A	B
Na Citrate 2aq	25.0	25.0	25.0	25.0
Na Carbonate	27.0	27.0	27.0	27.0
Na percarbonate (coated)	13.0	13.0	13.0	13.0
Manganese catalyst	1.5	1.5	1.5	1.5
Enzymes	1.7	1.7	1.7	1.7
Alcoguard H5240	3.0	3.0		
Alcoguard 4160G [1]			7.0	
Sokalan CP50 [2]				7.0
Dehypon WET	3.3		3.3	3.3
Genapol EC50 [3]		3.0		
Na Disilicate	3.0	3.0	3.0	3.0
Dequest 2016	1.0	1.0	1.0	1.0
Sodium sulfate	21.3	21.6	17.3	17.3
BTA solution	0.2	0.2	0.2	0.2

[1] Alcoguard 4160G, copolymer of maleic acid/acrylic acid/methyl methacrylate/2-acrylamido-2-methyl propane sulfonic acid as the sodium salt ex Akzo Nobel
[2] Sokalan CP50, acrylic acid / amps copolymer ex BASF
[3] Genapol EC50, a low foaming fatty alcohol polyglycolether ex BASF

[0106] The performance of the ADW detergent compositions was evaluated using the same test procedure as in Example 1.

[0107] The results of these tests are summarized in Table 6.

Table 6

	Aest hetic			
	1	2	A	B
Earthenware	5.00	6.00	5.00	4.00
Glass	5.00	5.33	4.00	4.33
Metal	4.75	5.00	4.25	3.75
Plastic	4.00	4.50	3.75	3.50
Combined	18.75	20.83	17.00	15.58

[0108] These results demonstrate that the detergent compositions 1 and 2 that contained a hybrid copolymer having a polysaccharide backbone and one or more synthetic side chains outperformed the detergent compositions A and B that contained a synthetic polymer, even though the latter compositions contained substantially more polymer (7 wt.% versus 3 wt.%).

Example 4

[0109] Automatic dishwash compositions were prepared in the same way as described in Example 1 on the basis of

the formulations shown in Table 7.

Table 7

	1	2	3
Na Citrate 2aq	25.0	25.0	25.0
Light soda ash	27.0	27.0	27.0
MGDA granules [1]		2.0	
Dissolvine GL [2]			2.0
Na percarbonate (coated)	13.0	13.0	13.0
Manganese catalyst	1.5	1.5	1.5
Enzymes	1.7	1.7	1.7
Alcoguard H5240	3.0	3.0	3.0
Dehypon WET	3.3	3.3	3.3
Na Disilicate	3.0	3.0	3.0
Dequest 2016	1.0	1.0	1.0
Sodium sulfate	21.5	19.5	19.5
[1] MGDA granules prepared according to EP 2 257 522 [2] Dissolvine GL-PD-S, 80% powder of glutamic diacetic acid (GLDA) ex AKZO			

[0110] The performance of the ADW detergent compositions was evaluated using the same test procedure as in Example 1.

[0111] The results of these tests are summarized in Table 8.

Table 8

	Aesthetic		
	1	2	3
Earthenware	6.00	6.00	5.00
Glass	6.00	6.00	6.00
Metal	4.50	4.00	4.00
Plastic	4.00	3.75	4.25
Combined	20.50	19.75	19.25

Example 5

[0112] Automatic dishwash compositions were prepared in the same way as described in Example 1, but without tabletting, on the basis of the formulations shown in Table 9. Composition A is a reference example.

Table 9

	1	A
Na Citrate 2aq	30.9	30.9
Na Carbonate	27.6	27.6
Na percarbonate (coated)	13.0	13.0
Enzymes	1.7	1.7
Alcoguard H5240	5.0	5.0
Dehypon WET	3.3	

(continued)

	1	A
Lutensol AT 25 [1]		3.0
Acusol 460 [2]	0.3	0.3
PEG 4000	4.4	4.4
Zinc Sulphate monohydrate	0.1	0.1
Dequest 2016	1.0	1.0
Sodium sulfate	12.1	12.4
BTA solution	0.2	0.2
Dye	0.4	0.4
[1] Lutensol AT 25, fatty alcohol alkoxylate with molecular formula $C_{16-18}EO_{25}$ ex BASF [2] Acusol 460, copolymer of diisobutylene and maleic acid, 15 000 MW, ex the Dow chemical company.		

[0113] The performance of the ADW detergent compositions was evaluated using the same test procedure as in Example 1, except that another set of articles was cleaned in the dishwasher, the evaluation was limited to only spotting and the total number of washes was limited to 10.

[0114] The results of these tests are summarized in Table 10.

Table 10

	1	A
Plastic cup	4	2
Plastic dinner plate	6	4
Stainless steel dinner plate	7	2
Ceramic dinner plate	7	2
Glass	5	4

Claims

1. A detergent composition consisting of:

- 20-80 wt.% of builder;
- 5-25 wt.% of bleach component;
- 1-10 wt.% of a graft copolymer having a polysaccharide backbone and one or more side chains of one or more synthetic monomeric units;
- 1-15 wt.% of nonionic surfactant represented by the following formula:

$$R^1\text{-}O\text{-}(CH_2CH_2O)_n\text{-}(CHR^2CHR^{2'}O)_q\text{-}(CH_2CH(OH)R^3)_s\text{-}R^4$$

wherein

- R^1 is an linear or branched C_8-C_{22} alkyl radical or a linear or branched C_8-C_{22} alkylphenol radical;
- R^2 and $R^{2'}$ are independently selected from hydrogen and a C_1-$C_{.5.}$alkyl radical, and wherein either R^2 or $R^{2'}$ is hydrogen;
- R^3 is a covalent bond or a linear, aliphatic C_2-C_{26} alkyl radical;
- R^4 is selected from hydrogen, and an alkyl radical having 1-15 carbon atoms;
- $5 \leq n \leq 30$;
- $0 \leq q \leq 3$;
- s=1-5,

said nonionic surfactant being selected from homopolymers, statistical copolymers, block copolymers and combinations thereof; and
• 0-60 wt.% of one or more other ingredients.

2. Detergent composition according to claim 1, wherein the builder comprises 25-80% of precipitating builder by weight of the builder, said precipitating builder being selected from carbonate, silicate and combinations thereof.

3. Detergent composition according to claim 1 or 2, wherein the builder comprises 20-70% of citrate by weight of the builder.

4. Detergent composition according to any one of the preceding claims, wherein the polysaccharide in the graft copolymer is selected from starch, maltodextrin, cellulose, gums, alginates, pectin and gellan.

5. Detergent composition according to claim 4, wherein the polysaccharide is maltodextrin

6. Detergent composition according to any one of the preceding claims, wherein the one or more synthetic monomeric units in the graft copolymer are selected from acrylic acid, maleic acid, itaconic acid, or methacrylic acid and combinations thereof.

7. Detergent composition according to any one of the preceding claims, wherein the composition contains 5-25 wt.% of bleach component;

8. Detergent composition according to claim 7, wherein the bleach component is percarbonate.

9. Detergent composition according to any one of the preceding claims, wherein R^2 or $R^{2'}$ is methyl.

10. Detergent composition according to any one of the preceding claims, wherein q is 0 or 1.

11. Detergent composition according to any one of the preceding claims, wherein s=1.

12. Detergent composition according to any one of the preceding claims, wherein the nonionic surfactant is represented by the following formula:

$$R^1\text{-}O\text{-}(CH_2CH_2O)_n\text{-}(CHR^2CHR^{2'}O)_q\text{-}(CH_2CH(OH)R^3)_s\text{-}R^4$$

wherein:

• R^2 is hydrogen and $R^{2'}$ is methyl;
• R^3 is a covalent bond;
• q is 0 or 1; and
• s is 1.

13. Detergent composition according to any one of the preceding claims, wherein the composition contains 1.5-10% of the nonionic surfactant by weight of the composition.

14. Detergent composition according to any one of the preceding claims, wherein the composition is a powder or a tablet.

15. Use of a detergent composition according to any one of the preceding claims as a detergent in an automatic dishwashing apparatus.

Patentansprüche

1. Reinigungsmittelzusammensetzung, bestehend aus:

• 20-80 Gew.-% Builder;
• 5-25 Gew.-% Bleichmittelkomponente;
• 1-10 Gew.-% eines Pfropfcopolymers mit einem Polysaccharid-Grundgerüst und einer oder mehreren Seiten-

ketten aus einer oder mehreren synthetischen Monomereinheiten;
• 1-15 Gew.-% nichtionischem Tensid, dargestellt durch die folgende Formel:

$$R^1\text{-}O\text{-}(CH_2CH_2O)_n\text{-}(CHR^2CHR^{2'}O)_q\text{-}(CH_2CH(OH)R^3)_s\text{-}R^4,$$

worin

◦ R^1 ein linearer oder verzweigter C_8-C_{22}-Alkylrest oder ein linearer oder verzweigter C_8-C_{22}-Alkylphenolrest ist;
◦ R^2 und $R^{2'}$, unabhängig voneinander, aus Wasserstoff und einem C_1-C_5-Alkylrest ausgewählt sind und wobei entweder R^2 oder $R^{2'}$ Wasserstoff ist;
◦ R^3 eine kovalente Bindung oder ein linearer, aliphatischer C_2-C_{26}-Alkylrest ist;
◦ R^4 aus Wasserstoff und einem Alkylrest mit 1-15 Kohlenstoffatomen ausgewählt ist;
◦ $5 \leq n \leq 30$;
◦ $0 \leq q \leq 3$;
o s = 1-5,

wobei das nichtionische Tensid aus Homopolymeren, statistischen Copolymeren, Blockcopolymeren und Kombinationen davon ausgewählt ist; und
• 0-60 Gew.-% eines oder mehrerer anderer Inhaltsstoffe.

2. Reinigungsmittelzusammensetzung nach Anspruch 1, wobei der Builder 25-80% Fällungsbuilder, bezogen auf das Gewicht des Builders, umfasst, wobei der Fällungsbuilder aus Carbonat, Silikat und Kombinationen davon ausgewählt ist.

3. Reinigungsmittelzusammensetzung nach Anspruch 1 oder 2, wobei der Builder 20-70% Citrat, bezogen auf das Gewicht des Builders, umfasst.

4. Reinigungsmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei das Polysaccharid in dem Pfropfcopolymer aus Stärke, Maltodextrin, Cellulose, Gummi, Alginaten, Pektin und Gellan ausgewählt ist.

5. Reinigungsmittelzusammensetzung nach Anspruch 4, wobei das Polysaccharid Maltodextrin ist.

6. Reinigungsmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei die eine oder die mehreren synthetischen Monomereinheiten in dem Pfropfcopolymer aus Acrylsäure, Maleinsäure, Itaconsäure oder Methacrylsäure und Kombinationen davon ausgewählt sind.

7. Reinigungsmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei die Zusammensetzung 5-25 Gew.-% Bleichmittelkomponente enthält.

8. Reinigungsmittelzusammensetzung nach Anspruch 7, wobei die Bleichmittelkomponente Percarbonat ist.

9. Reinigungsmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei R^2 oder $R^{2'}$ Methyl ist.

10. Reinigungsmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei q 0 oder 1 ist.

11. Reinigungsmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei s = 1.

12. Reinigungsmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei das nichtionische Tensid durch die folgende Formel dargestellt ist:

$$R^1\text{-}O\text{-}(CH_2CH_2O)_n\text{-}(CHR^2CHR2'O)_q\text{-}(CH_2CH(OH)R^3)_s\text{-}R^4,$$

worin:

• R^2 Wasserstoff ist und $R^{2'}$ Methyl ist;
• R^3 eine kovalente Bindung ist;
• q 0 oder 1 ist; und

• s 1 ist.

13. Reinigungsmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei die Zusammensetzung 1,5-10% des nichtionischen Tensids, bezogen auf das Gewicht der Zusammensetzung, enthält.

14. Reinigungsmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche, wobei die Zusammensetzung ein Pulver oder eine Tablette ist.

15. Verwendung einer Reinigungsmittelzusammensetzung nach irgendeinem der vorhergehenden Ansprüche als Reinigungsmittel in einem automatischen Geschirrspülgerät.

Revendications

1. Composition de détergent consistant en :

• 20-80 % en masse d'adjuvant ;
• 5-25 % en masse de constituant de blanchiment ;
• 1-10 % en masse d'un copolymère greffé ayant un squelette de polysaccharide et une ou plusieurs chaînes latérales d'une ou plusieurs unités monomères synthétiques ;
• 1-15 % en masse de tensioactif non ionique représenté par la formule suivante :

$$R^1\text{-}O\text{-}(CH_2CH_2O)_n\text{-}(CHR^2CHR^{2'}O)_q\text{-}(CH_2CH(OH)R^3)_s\text{-}R^4$$

dans laquelle

◦ R^1 est un radical alkyle en C_8-C_{22} linéaire ou ramifié ou un radical alkylphénol en C_8-C_{22} linéaire ou ramifié ;
◦ R^2 et $R^{2'}$ sont indépendamment choisis parmi l'hydrogène et un radical alkyle en C_1-C_5, et dans laquelle soit R^2 soit $R^{2'}$ est l'hydrogène ;
◦ R^3 est une liaison covalente ou un radical alkyle en C_2-C_{26} aliphatique, linéaire ;
◦ R^4 est choisi parmi l'hydrogène, et un radical alkyle ayant 1-15 atomes de carbone ;
◦ $5 \leq n \leq 30$;
◦ $0 \leq q \leq 3$;
◦ s=1-5,

ledit tensioactif non ionique étant choisi parmi des homopolymères, copolymères statistiques, copolymères séquencés et des combinaisons de ceux-ci ; et
• 0-60 % en masse d'un ou plusieurs autres ingrédients.

2. Composition de détergent selon la revendication 1, dans laquelle l'adjuvant comprend 25-80 % d'adjuvant de précipitation en masse de l'adjuvant, ledit adjuvant de précipitation étant choisi parmi un carbonate, silicate et des combinaisons de ceux-ci.

3. Composition de détergent selon la revendication 1 ou 2, dans laquelle l'adjuvant comprend 20-70 % de citrate en masse de l'adjuvant.

4. Composition de détergent selon l'une quelconque des revendications précédentes, dans laquelle le polysaccharide dans le copolymère greffé est choisi parmi amidon, maltodextrine, cellulose, gommes, alginates, pectine et gellane.

5. Composition de détergent selon la revendication 4, dans laquelle le polysaccharide est la maltodextrine.

6. Composition de détergent selon l'une quelconque des revendications précédentes, dans laquelle les une ou plusieurs unités monomères synthétiques dans le copolymère greffé sont choisies parmi acide acrylique, acide maléique, acide itaconique, ou acide méthacrylique et des combinaisons de ceux-ci.

7. Composition de détergent selon l'une quelconque des revendications précédentes, dans laquelle la composition contient 5-25 % en masse de constituant de blanchiment.

8. Composition de détergent selon la revendication 7, dans laquelle le constituant de blanchiment est le percarbonate.

9. Composition de détergent selon l'une quelconque des revendications précédentes, dans laquelle R^2 ou $R^{2'}$ est le méthyle.

10. Composition de détergent selon l'une quelconque des revendications précédentes, dans laquelle q est 0 ou 1.

11. Composition de détergent selon l'une quelconque des revendications précédentes, dans laquelle s=1.

12. Composition de détergent selon l'une quelconque des revendications précédentes, dans laquelle le tensioactif non ionique est représenté par la formule suivante :

$$R^1\text{-}O\text{-}(CH_2CH_2O)_{n}\text{-}(CHR^2CHR^{2'}O)_q\text{-}(CH_2CH(OH)R^3)_s\text{-}R^4$$

dans laquelle :

- R^2 est hydrogène et $R^{2'}$ est méthyle ;
- R^3 est une liaison covalente ;
- q est 0 ou 1 ; et
- s est 1.

13. Composition de détergent selon l'une quelconque des revendications précédentes, dans laquelle la composition contient 1,5-10 % du tensioactif non ionique en masse de la composition.

14. Composition de détergent selon l'une quelconque des revendications précédentes, dans laquelle la composition est une poudre ou une tablette.

15. Utilisation d'une composition de détergent selon l'une quelconque des revendications précédentes comme un détergent dans un appareil de lave-vaisselle automatique.

REFERENCES CITED IN THE DESCRIPTION

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