(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 4 269 548 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
01.11.2023 Bulletin 2023/44

(21) Application number: **22170164.2**

(22) Date of filing: **27.04.2022**

(51) International Patent Classification (IPC):
C11D 3/22 *(2006.01)* ***C11D 3/37*** *(2006.01)*
C11D 3/20 *(2006.01)*

(52) Cooperative Patent Classification (CPC):
C11D 3/2089; C11D 3/225; C11D 3/3707; C11D 3/378

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(71) Applicant: **Dalli-Werke GmbH & Co. KG**
52224 Stolberg (DE)

(72) Inventors:
- **Mol, René**
  8181CR Heerde (NL)
- **Mahmud, Khalid**
  8181CR Heerde (NL)

(74) Representative: **f & e patent**
Braunsberger Feld 29
51429 Bergisch Gladbach (DE)

(54) **DETERGENT COMPOSITION WITH ANTISCALANTS**

(57) The invention relates to a phosphate free detergent composition comprising a combination of scale-inhibiting agents, a process for preventing scale formation in water-using and/or waterprocessing devices and the use of a combination of scale-inhibiting compounds for scaleinhibition when a low phosphonate content is present.

EP 4 269 548 A1

Description

[0001] The invention relates to a phosphate free detergent composition comprising a combination of scale-inhibiting agents, a process for preventing scale formation in water-using and/or water-processing devices and the use of a combination of scale-inhibiting compounds for scale-inhibition when a low phosphonate content is present.

[0002] Scale formation is a universal problem encountered in almost every machine or process wherein (tap) water is used. The main cause of scale formation, in particular when detergents are present, is precipitation of alkaline earth metal carbonates, phosphates or silicates, for example of calcium carbonate and calcium phosphate. The deposition of scale on surfaces may have several disadvantages, such as reducing equipment performance (e.g. heat exchangers), reducing equipment lifetime, clogging, dirty appearance, et cetera.

[0003] Scale formation is for example a well-known problem in dishwashers, wherein scale reduces the efficiency of cleaning and results in an undesirable appearance of the tableware, especially for glass objects. Therefore, dishwasher detergents or additives need to employ anti-scaling measures to ensure a longer service life and to achieve better cleaning performance. These antiscaling measures are often applied in the form of specific dishwasher detergent formulations or additives employing compounds which inhibit scale formation, for example by interfering with crystal growth.

[0004] Automatic dishwashing detergents have been in the market for nearly a century now. Environmental regulations in terms of cleaning ingredients and energy requirements have changed over time. Phosphate-free compositions presently are "state of the art", however, it is still difficult to obtain cleaning results comparable to those obtained with phosphate-comprising compositions. Users expect good cleaning and at the same time good finishing (lack of filming and spotting, and shine) of the washed items.

[0005] Several approaches to replace phosphates by more readily or inherently biodegradable polymeric sequestering agents are described in the art. WO 2021/213807 A1discloses ADDs comprising polyepoxysuccinic acid (PESA), an AA/AMPS copolymer and phosphonate, EP 3 092 294 B1 shows a combination of PESA with polyaspartic acid, EP 3 050 953 B1 a combination of carboxymethylinulin (CMI) with a sulphonated copolymer in ADD compositions. EP 3 850 072 A refers to silver protecting agent comprising PESA or polyaspartic acid or an itaconic acid/sulphonic acid copolymer in combination with bismuth citrate and MGDA. EP 3 674 386 A discloses the combination of itaconic acid/sulphonic acid copolymer with a special fatty alcohol ethoxylate for increasing filming performance, WO 2018/236810 A1 describes the use of itaconic acid/sulphonic acid copolymer with a complexing agent selected e.g. from MGDA or CMI in combination with any phosphonate.

[0006] Phosphonates are known as being highly effective to inhibit scale formation. However, most phosphonates show reduced performance at low temperatures and elevated pH. The current trend for machines, such as dishwashers or washing machines, to operate at reduced temperatures in order to improve energy-efficiency results in the need for adapted anti-scalant compositions. Furthermore, most of the commonly used phosphonates have a low biodegradability.

[0007] In detergents builders, optionally combined with co-builders or anti-redeposition agents, inhibit or reduce scale formation. Known builders include sodium tripolyphosphate, sodium carbonate, sodium bicarbonate, sodium percarbonate, sodium citrate, citric acid and its sodium and potassium salts and trisodium dicarboxymethyl alaninate. Known co-builders or anti-redeposition agents include polyacrylates, polycarbonates, polyacrylic acid, acrylic acid/maleic acid copolymer, styrene/maleic acid copolymer, polymers of acrylic and sulphonic acids, acrylic acid/ 2-acrylamido-2-methylpropane sulfonic acid copolymer, carboxymethyl cellulose, trisodium dicarboxymethyl alaninate and etidronic acid. All these ingredients can be applied as acid or as water soluble salts.

[0008] For environmental reasons, there is still a need for the use of biodegradable polymer(s) with a high technical performance in detergents, in particular in automatic dishwashing detergents (ADDs) and for such polymers to have a particularly high level of performance in citrate-based systems, especially in terms of anti-scaling performance (resulting in good cleaning and shining of table ware).

[0009] The above technical problems are addressed by the present invention, which provides a composition that demonstrates comparable or even superior performance in shine and cleaning performance tests compared to standard phosphate-free formulations comprising phosphonates.

[0010] It was an object of the present invention to provide an effective phosphate-free anti-scaling detergent composition with low phosphonate content, being efficient in a wide pH range and temperature range and further has a reduced environmental impact. The performance of the detergent composition should be comparable to the results of phosphate and / or phosphonate comprising compositions, or even better.

[0011] This object is met by a phosphate-free detergent comprising

(a) polyepoxysuccinic acid (PESA) or derivatives thereof,

(b) at least one additional polymeric compound, said polymeric compound is selected from

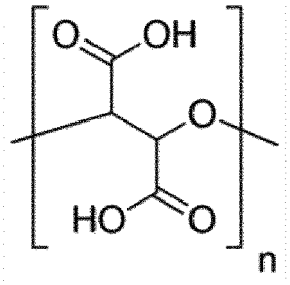
(b1) a copolymer having (i) itaconic acid monomers and (ii) at least one type of sulphonated monomer(s) and

(b2) carbohydrate polymer(s), wherein said composition comprises less than 3 wt.% of any phosphonate.

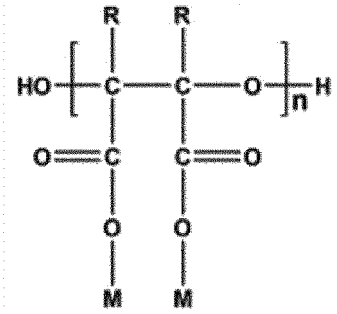
[0012] By "phosphate-free" is herein understood that the composition comprises less than 1 percent, preferably less than 0.5 percent by weight, even more preferred less than 0.1 percent by weight of the composition of phosphate. Most preferred the composition does not comprise any phosphate.

[0013] Polyepoxysuccinic acid is also known as epoxysuccinic acid homopolymer, polyoxirane-2,3-dicarboxylic acid, 2,3-oxiranedicarboxylic acid homopolymer, or poly(l-oxacyclopropane-2,3-dicarboxylic acid);

[0014] Polyepoxysuccinic acid has the general structure:



wherein its derivatives have the general structure:



where R can be hydrogen or an C1-8 alkyl, preferably C1-4 alkyl, M is a counter-ion, preferably Na^+, H^+, K^+, and/or $NH4^+$. All references to "PESA" here in the disclosure should be considered to refer to polyepoxysuccinic acid or said derivatives thereof, unless otherwise stated.

[0015] Preferably, the PESA, provided as sodium-salt, has an average molecular weight (M_w) of from 100 to 10,000 g/mol, preferably from 300 to 5000 g/mol, such as from 400 to 3000 g/mol, or from 500 to 2000 g/mol or from 800 to 1500 g/mol. Suitable PESA can have from 2 to 100 repeating monomer units, such as from 2 to 50, 2 to 45, 2 to 20 or 2 to 10.

[0016] The composition may comprise PESA in an amount of from 0.01 to 52 percent by weight, like 0.1 to 20 percent by weight, such as from 0.2 to 18 percent, from 0.3 to 15 percent, from 0.4 to 12 percent, from 0.5 to 10 percent, from 0.6 to 9 percent, from 0.7 to 8 percent, or from 0.8 to 7 percent by weight of the detergent composition.

[0017] Alternatively, the composition may comprise PESA in an amount of from 0.01 to 7.0 percent by weight, such as from 0.02 to 6.0 percent, from 0.04 to 5.0 percent, from 0.07 to 3.0 percent, or from 0.7 to 2.0 percent by weight of the detergent composition.

[0018] Alternatively, the composition may comprise PESA in an amount of from 1.0 to 35 percent by weight, such as from 2.0 to 30 percent, from 3.0 to 25 percent, from 4.0 to 20 percent, or from 5.0 to 15 percent by weight of the detergent composition.

[0019] Alternatively, the composition may comprise PESA in an amount of from 4.0 to 52 percent by weight, such as from 6.0 to 48 percent, from 8.0 to 44 percent, or from 10 to 40 percent by weight of the detergent composition. The additional polymeric compound (b) can be selected from a copolymer (b1) having (i) itaconic acid monomers and (ii) at least one type of sulphonic acid group comprising monomers.

[0020] The additional polymeric compound (b) is preferably at least inherently biodegradable, more preferably readily biodegradable according to the OECD (the Organisation for Economic Cooperation and Development) guidelines (status April 2022).

[0021] The additional polymeric compound (b) is at least 20% from a renewable source, preferably at least 30%, more preferably at least 40%, more preferably at least 50%, more preferably at least 60%, more preferably at least 70%, more

preferably at least 80%, even more preferably at least 90%, most preferably is 100% from a renewable source. The percentage is based on the amount of carbon atoms that are from renewable source compared to all carbon atoms in the polymeric compound. Preferred monomers containing sulphonic acid groups are 1-acrylamido-1-propanesulphonic acid, 2-acrylamido-2-propanesulphonic acid, 2-acrylamido-2-methyl-propanesulphonic acid, 2-methacrylamido-2-methyl-propanesulphonic acid, 3-methacrylamido-2-hydroxypropanesulphonic acid, allylsulphonic acid, methallylsulphonic acid, allyloxybenzenesulphonic acid, methallyloxybenzenesulphonic acid, 2-hydroxy-3-(2-propenyloxy)propanesulphonic acid, 2-methyl-2-propene-sulphonic acid, styrenesulphonic acid, vinylsulphonic acid, 3-sulphopropyl acrylate, 3-sulfopropyl methacrylate, sulphomethacrylamide, sulphomethylmethacrylamide and mixtures of the stated acids or the water-soluble salts thereof.

[0022] Preferably, the copolymer (b1) comprises at least a monomer selected from 2-acrylamido-2-methylpropanesulphonic acid, allylsulphonic acid, allyloxybenzenesulphonic acid, 2-hydroxy-3-(2-propenyloxy)propanesulfonic acid, 2-methyl-2-propene-sulphonic acid, styrenesulphonic acid, vinylsulphonic acid and alkali metal and ammonium salts thereof.

[0023] Preferred copolymers (b1) comprise styrene sulphonic acid, and/or 2-acrylamido-2-methylpropanesulphonic acid (AMPS), their salts or mixtures thereof. Preferably, the copolymer comprises from 5 percent to 40 percent by weight thereof of monomers units comprising sulphonic groups. Even more preferred the polymer comprises from 10 percent to 30 percent by weight of the polymer of monomers comprising styrene sulphonic acid, its salts or mixtures thereof. Preferred copolymers are described in WO2018/191326 A1 as "Copolymer A".

[0024] Preferred copolymers (b1) comprise styrene sulphonic acid, and/or 2-acrylamido-2-methylpropanesulphonic acid (AMPS), their salts or mixtures thereof. Preferably, the copolymer comprises from 5 percent to 40 percent, more preferably from 5 percent to 15 percent, or 10 percent to 30 percent, or 20 percent to 40 percent, by weight thereof of monomers units comprising sulphonic groups. Preferably the sulphonic acid group comprising monomer is 2-acrylamido-2-methyl-propanesulphonic acid (AMPS).

[0025] Preferably, the copolymer (b1) comprises from 10 percent to 95 percent, more preferably from 25 percent to 95 percent, or from 30 percent to 90 percent, or 35 percent to 85 percent, or 40 percent to 85 percent, by weight thereof of monomers units of itaconic acid.

[0026] Preferably the polymer has a weight average molecular weight of from about 500 g/mole to about 10,000 g/mole, preferably from about 800 g/mole to about 9,000 g/mole, preferably from about 1,200 g/mole to about 8,000 g/mole, preferably from about 1,500 g/mole to about 7,000 g/mole, preferably from about 2,000 g/mole to about 6,000 g/mole, preferably from about 3,000 g/mole to about 5,000 g/mole. Preferably the polymer has a number average molecular weight of from about 500 g/mole to about 10,000 g/mole, preferably from about 800 g/mole to about 5,000 g/mole (molar weight as provided by the distributor). Preferably the polymer has a polydispersity of about 2.0. A preferred method to determine the molecular weight distribution and the mass average molecular weight as used herein is by size exclusion chromatography (such as HPSEC) preferably coupled to an UV-Vis detector. In embodiments the UV-Vis detector operates at 260, 280 and 310 nm.

[0027] Preferably the molar ratio of the sulphonic to the itaconic monomers in the copolymer (b1) is in the range of from 1:7 to 1:3, preferably from 1:6 to 1:4, like e.g. 1:5.8 to 1:4.4 or 1:5.5 to 1:4.5 or 1:5.3 to 1:4.8.

[0028] One especially preferred copolymer for use herein as copolymer (b1) is Itaconix TSI 322 (like Itaconix TSI 322 G and Itaconix TSI 322 Q) or Itaconix CHT 122 (like Itaconix CHT 122 G and Itaconix CHT 122 Q) provided by Itaconix.

[0029] Other preferred copolymers comprise 2-acrylamido-2-methylpropane-sulphonic acid, its salts or mixtures thereof. Even more preferably the polymer comprises from 5 percent to 40 percent by weight, or 15 percent to 40 percent by weight, or 15 percent to 35 percent by weight, or 10 percent to 30 percent by weight, or 5 percent to 15 percent by weight, or 25 percent to 40 percent by weight of the polymer of monomers comprising 2-acrylamido-2-methylpropanesulphonic acid, its salts or mixtures thereof. Suitable polymers are described in WO2014/143773 A1 and WO2015/138872 A1 and supplied by Lubrizol.

[0030] The sulphonic acid groups and / or carboxylic acid groups (of the itaconic acid groups) may be present in the polymers entirely or in part in neutralized form, i.e. the acidic hydrogen atom of the sulphonic acid group and / or carboxylic acid groups may be replaced in some or all of the sulphonic acid groups and / or carboxylic acid groups with metal ions, preferably alkali metal ions and in particular with sodium ions. It is preferred according to the invention to use copolymers containing partially or completely neutralized sulphonic acid groups and / or carboxylic acid groups (of the itaconic acid groups). The molar mass of the copolymers (b1) preferably used according to the invention may be varied in order to tailor the properties of the polymers to the desired intended application.

[0031] Copolymer (b1) can further comprise additional monomers in addition to the itaconic acid monomer (i) and the sulphonated monomer (ii). Thus, copolymer (b1) can comprise three, four or more types of monomers. Optional further monomers may comprise acrylic acid, methacrylic acid, maleic acid, epoxysuccinic acid, ethyleneoxid, propene, 1-butene, styrene or olefin monomers, without being restricted to the mentioned.

[0032] The composition comprises the itaconic acid / sulphonic copolymer (b1) preferably in an amount of from 0.1 to 15 percent by weight of the detergent composition, like 0.5 to 15 percent by weight of the detergent composition, more

preferred in an amount of from 0.8 to 10 percent, or from 1 to 8 percent, even more preferred from 1.5 to 6 percent or from 2 to 4 percent by weight of the detergent composition.

[0033] Alternatively, the composition comprises the itaconic acid / sulphonic copolymer (b1) preferably in an amount of from 5 to 15 percent by weight of the detergent composition, more preferred in an amount of from 5 to 14 percent, or from 6 to 14 percent, or from 6 to 13 percent, even more preferred from 5 to 13 percent or from 5 to 12 percent by weight of the detergent composition.

[0034] Alternatively, the composition comprises the itaconic acid / sulphonic copolymer (b1) preferably in an amount of from 0.1 to 10 percent by weight of the detergent composition, more preferred in an amount of from 0.2 to 8 percent, or from 0.3 to 6 percent, even more preferred from 0.4 to 5 percent or from 0.5 to 4 percent by weight of the detergent composition.

[0035] The carbohydrate polymer (b2) preferably is selected from carboxymethylcellulose (CMC), carboxymethylinulin (CMI), carboxymethyl dextran (CM-Dextran), carboxymethyl sucrose (CMSU), carboxymethyl polysucrose (CM-polysucrose), carboxymethyl starch (CMS) and a polysaccharide hybrid polymer or polysaccharide copolymer provided by Nouryon Specialty Chemicals under the tradename Alcoguard H5941D (as available in April 2022).

[0036] As used herein, molecular weight (Mw) is the weight average molecular weight unless the context indicates otherwise. Molecular weights of carbohydrate polymers can be determined as described in US 2019/0390140 A.

[0037] As used herein, an "ultra-low molecular weight" for carbohydrate polymers means a molecular weight (Mw) no greater than from about 1,000 Dalton (Da) to 80,000 Dalton (Da).

[0038] "Conventional carbohydrate" refers to carbohydrate polymer having a molecular weight (Mw) that is greater than 80,000 Da.

[0039] A suitable carboxymethylcellulose component can be selected from sodium carboxymethyl cellulose or modified carboxymethyl cellulose such as, but not limited to, hydrophobic-modified CMC, cationic-modified CMC, or sulfate- or sulfonate-modified CMC. The interchangeability of the use of carboxymethyl cellulose and its modified forms in detergent applications is well known in the art as described in EP 2 302 025 B1 or U.S. Pat. No. 6,600,033. Reference herein to carboxymethyl cellulose (CMC) component is also meant to include modifications thereof, however sodium carboxymethylcellulose is preferred.

[0040] A preferred CMC has a degree of substitution between 0.4 and 0.8, more preferably between 0.45 and 0.75, more preferably between 0.5 and 0.7, more preferably between 0.55 and 0.7, even more preferably between 0.6 and 0.7, most preferred is CMC with a degree of substitution between 0.6 and 0.65.

[0041] The detergent compositions may also comprise an anionic cellulose derivative such as, but not limited to, carboxymethyl hydroxyethylcellulose, and carboxymethyl hydroxylpropyl cellulose (HPC).

[0042] Any further reference to ultra-low molecular weight carbohydrate polymer is to include the aforementioned polysaccharides selected from a carboxymethyl cellulose component, an anionic cellulose derivative, or mixtures thereof.

[0043] The ultra-low molecular weight polysaccharides may have an average molecular weight of no greater than from about 1,000 Da to 80,000 Da. For example, the ultra-low molecular weight polysaccharide has an average molecular weight of from about 1,000 Da to about 40,000 Da., from about 1,000 Da to about 30,000 Da. or from about 1,000 Da to about 15,000 Da. For example, the ultra-low molecular weight polysaccharide may have an average molecular weight of 1,000 Da, 1,500 Da, 2,000 Da, 2,500 Da, 3,000 Da, 4,000 Da, 5,000 Da, 6,000 Da, 7,000 Da, 8,000 Da, 9,000 Da, 10,000 Da, 11,000 Da, 12,000 Da, 13,000 Da, 14,000 Da, 15,000 Da, 16,000 Da, 17,000 Da, 18,000 Da, 19,000 Da, 20,000 Da, 21,000 Da, 22,000 Da, 23,000 Da, 24,000 Da, 25,000 Da, 26,000 Da, 27,000 Da, 28,000 Da, 29,000 Da, 30,000 Da, 31,000 Da, 32,000 Da, 33,000 Da, 34,000 Da, 35,000 Da, 36,000 Da, 37,000 Da, 38,000 Da, 39,000 Da, 40,000 Da, 41,000 Da, 42,000 Da, 43,000 Da, 44,000 Da, 45,000 Da, 46,000 Da, 47,000 Da, 48,000 Da, 49,000 Da, 50,000 Da, 51,000 Da, 52,000 Da, 53,000 Da, 54,000 Da, 55,000 Da, 56,000 Da, 57,000 Da, 58,000 Da, 59,000 Da, 60,000 Da, 61,000 Da, 62,000 Da, 63,000 Da, 64,000 Da, 65,000 Da, 66,000 Da, 67,000 Da, 68,000 Da, 69,000 Da, 70,000 Da, 71,000 Da, 72,000 Da, 73,000 Da, 74,000 Da, 75,000 Da, 76,000 Da, 77,000 Da, 78,000 Da, 79,000 Da, or 80,000 Da. The ultra-low molecular weight polysaccharides of this disclosure can also have an average molecular weight between any of these recited molecular weights.

[0044] The ultra-low molecular weight polysaccharides and, in particular, the ultra-low molecular weight CMC component may have a molecular weight distribution that is unimodal, bimodal or multimodal and in each case the molecular weight peaks (Mr) are no greater than 80,000 Da. For example, the molecular weight peaks may be from about 750 to 60,000 Da.

[0045] Optionally, the ultra-low molecular weight polysaccharide and, in particular, the ultra-low molecular weight CMC component is present in the detergent composition at a concentration from about 0.005 percent to about 10 percent by weight of the detergent composition, from about 0.01 percent to about 5 percent or from about 0.05 percent to about 2 percent by weight of the detergent composition. For example, the ultra-low molecular weight polysaccharide is present in the detergent composition at a concentration of about 0.005 percent, 0.01 percent, 0.02 percent, 0.03 percent, 0.04 percent, 0.05 percent, 0.06 percent, 0.07 percent, 0.08 percent, 0.09 percent, 0.1 percent, 0.2 percent, 0.3 percent, 0.4 percent, 0.5 percent, 0.6 percent, 0.7 percent, 0.8 percent, 0.9 percent, 1 percent, 1.1 percent, 1.2 percent, 1.3 percent,

1.4 percent 1.5 percent, 1.6 percent, 1.7 percent, 1.8 percent, 1.9 percent, 2 percent, 2.1 percent, 2.2 percent, 2.3 percent, 2.4 percent 2.5 percent, 2.6 percent, 2.7 percent, 2.8 percent, 2.9 percent, 3 percent, 3.1 percent, 3.2 percent, 3.3 percent, 3.4 percent 3.5 percent, 3.6 percent, 3.7 percent, 3.8 percent, 3.9 percent, 4 percent, 4.1 percent, 4.2 percent, 4.3 percent, 4.4 percent 4.5 percent, 4.6 percent, 4.7 percent, 4.8 percent, 4.9 percent, 5 percent, 5.1 percent, 5.2 percent, 5.3 percent, 5.4 percent 5.5 percent, 5.6 percent, 5.7 percent, 5.8 percent, 5.9 percent, 6 percent, 6.1 percent, 6.2 percent, 6.3 percent, 6.4 percent 6.5 percent, 6.6 percent, 6.7 percent, 6.8 percent, 6.9 percent, 7 percent, 7.1 percent, 7.2 percent, 7.3 percent, 7.4 percent 7.5 percent, 7.6 percent, 7.7 percent, 7.8 percent, 7.9 percent, 8 percent, 8.1 percent, 8.2 percent, 8.3 percent, 8.4 percent 8.5 percent, 8.6 percent, 8.7 percent, 8.8 percent, 8.9 percent, 9 percent, 9.1 percent, 9.2 percent, 9.3 percent, 9.4 percent 9.5 percent, 9.6 percent, 9.7 percent, 9.8 percent, 9.9 percent, or 10 percent by weight of the detergent composition. The ultra-low molecular weight polysaccharide can also be present in the detergent composition at a concentration between any of these recited percentages.

[0046] In US 2019/0390140 A it is described that such ultra-low molecular weight polysaccharides and, in particular, ultra-low molecular weight CMC components have increased solubility within a wash liquor provided by a detergent composition. This increase in solubility is advantageous because incorporating the ultra-low molecular weight polysaccharide with the ability to partially or completely dissolve quickly allows for the ultra-low molecular weight polysaccharide to become functional soon after use initiates, which therefore enables the ultra-low molecular weight polysaccharide to function earlier in the wash cycle, as compared to conventional polysaccharides. Thus, by incorporating an ultra-low molecular weight polysaccharide into a detergent composition, the wash cycle time therefore can be beneficially decreased.

[0047] Nonetheless, it is also possible to include CMC components having a MG above 80,000 Da., i.e. conventional CMC components known for addition in detergent compositions, even if not particularly preferred.

[0048] Carboxymethylinulin is a carboxyl-containing fructan where the carboxyl is carboxymethyl and the fructan has a beta -2,1 bond. The carboxymethylinulin is typically supplied as an alkali metal salt such as sodium carboxymethylinulin. Preferred carboxymethylinulin types available on the market are provided as Carboxy*line*® CMI e.g. the types 20 LS D powder, 25-40 D or 25 D powder, available by Cosun Beet Company. A further suitable source of the carboxymethylinulin are the Dequest PB polymers, like Dequest PB11620 or 11625, from Italmatch Chemicals. The carboxymethylinulin may have a degree of substitution ranging from about 0.15 to about 3, preferably from about 1 to about 3, preferably from about 1 to about 2.5, more preferably from about 1.5 to about 2.5, and most preferably ranges from about 1.8 to about 2.2. The carboxymethylinulin preferably has a degree of substitution of about 2. A low degree of substitution lacks performance, a high degree of substitution lacks a good biodegradability. The carboxymethylinulin can be present in an amount of 0.01 percent to 30 percent, preferably of 0.01 percent to 20 percent, preferably of 0.01 percent to 10 percent, preferably from 0.01 percent to 5 percent, more preferably of 0.01 percent to 3 percent, typically from 0.05 percent to 2.5 percent, and may be present in an amount of from 0.1 percent to 2 percent, or from 0.2 to 1.5 percent of the weight of the detergent composition.

[0049] In addition to polymer(s) (b) the composition of the invention can also comprise further polymers (c) free of itaconic monomers. Such further polymers (c) can be used in any suitable total amount from about 0.1 to about 15 percent, preferably from 0.2 to about 10 percent, more preferably from 0.3 to 8 percent by weight of the composition. It is, however, particularly preferred that the composition does not comprise acrylic, methacrylic or maleic acid homo- or copolymers besides polymer (b) In particular, it is preferred that the composition does not comprise sulphonated acrylic, methacrylic or maleic acid copolymers having no itaconic acid monomers as polymers (c).

[0050] The further polymers (c) may include polyaspartic acid polymers, modified polyaspartic acid polymers, other biodegradable sulfonated polymers of polycarboxylic acids (except acrylic, methacrylic or maleic acid) and may comprise two, three, four or more different monomer units. Polyaspartic acid polymers are preferred.

[0051] The further polymer (c) is preferably at least inherently biodegradable, more preferably readily biodegradable according to the OECD guidelines (status April 2022).

[0052] The further polymer (c) is at least 50% from a renewable source, preferably at least 60%, more preferably at least 70%, more preferably at least 80%, even more preferably at least 90%, most preferably is 100% from a renewable source. The percentage is based on the amount of carbon atoms that are from renewable source compared to all carbon atoms in the polymeric compound.

[0053] The composition may further comprise a further monomeric complexing agent, preferably an, according to the OECD guidelines (status April 2022) readily or inherently, biodegradable complexing agent in an amount of up to 6 wt.%, like 0.2 to 5 wt.% or 0.5 to 4 wt.%.

[0054] A "complexing agent" is a compound capable of binding polyvalent ions such as calcium, magnesium, lead, copper, zinc, cadmium, mercury, manganese, iron, aluminium and other cationic polyvalent ions to form a water-soluble complex.

[0055] Said monomeric complexing agent preferably is selected from the group consisting of methylglycine-diacetic acid (MGDA), its salts and derivatives thereof, glutamic-N,N- diacetic acid (GLDA), its salts and derivatives thereof, iminodisuccinic acid (IDS), its salts and derivatives thereof, aspartic acid diacetic acid (ASDA), its salts and derivatives

thereof, dipicolinic acid (DPA), its salts and derivatives thereof, ethylenediamine-N,N'-disuccinic acid (EDDS), its salts and derivatives thereof, and mixtures of the mentioned. A preferred complexing agent for use herein is MGDA and salts thereof, especially preferred for use herein is the three sodium salt of MGDA. Another preferred complexing agent for use herein is GLDA and salts thereof, preferred for use herein is the three sodium salt of GLDA, more preferred is the four sodium salt of GLDA.

[0056] However, MGDA-containing formulations may display a yellow discoloration and a distinct ammonia smell after storage and therefore often contain further additives or ingredients to mitigate the detrimental effects of MGDA degradation. Strong aminocarboxylate chelating ligands may also decrease the in-wash stability of other metal-containing formula ingredients. For example, MGDA is capable to extract the central metal ion(s) from manganese complexes commonly used in ADWformulations. Thus, the absence of MGDA may have certain beneficial effects in the present invention. In a preferred embodiment the composition comprises MGDA in an amount of less than 3 wt.%, less than 2 wt.%, less than 1 wt.% or is free of MGDA.

[0057] In a very preferred embodiment, complexing agent does not comprise ethylenediaminetetraacetic acid (EDTA) or its derivates.

[0058] According to the invention the detergent composition has a low phosphonate(s) content, i.e. in a total amount of less than 3 wt.% of the detergent composition. In particular, "phosphonates" according to the present disclosure comprise aminopolyphosphonates or bisphosphonates.

[0059] Aminopolyphosphonates comprise aminotris(methylenephosphonic acid) (ATMP), hydroxyethylamino bis(methylene phosphonic acid) (HEMPA), ethylenediamine tetra(methylene phosphonic acid) (EDTMP), hexamethylenediamine-tetra(methylene phosphonic) acid (HDTMP), polyamino polyether methylene phosphonic acid (PAPEMP), bis(hexamethylene triamine penta(methylenephosphonic acid)) (BHMTMP), DTPMP (diethylenetriamine penta(methylene phosphonic acid) (DTPMP), lysine tetra(methylene phosphonates) (LTMP).

[0060] Bisphosphonates are e.g. 1-hydroxyethane 1,1-diphosphonic acid (HEDP), also known as 1-hydroxyethylidine 1,1-diphosphonic acid in a neutral or partially neutralized form.

[0061] It is preferred that phosphonates are present in the detergent composition of the present invention in a total amount of less than 3 wt.%, preferably less than 2 wt.%, even more preferred less than 1 wt.%, even more preferred less than 0.5 wt.% referring to the weight of the total weight of the composition. This should be understood in a way, that any of the mentioned phosphonates can be present in an amount of less than 3 wt.%, but if more than one phosphonate is present, the total amount of said phosphonates does not summarize and does not exceed the "less than 3 wt.%". In a particularly preferred embodiment, the detergent composition comprises no phosphonate(s).

[0062] The detergent composition can be a dish washing composition, preferably an automatic dishwashing detergent (ADD) composition, a laundry composition, a hard surface cleaning composition, a water softener composition or any water additive in water circulating systems, but is preferably an automatic dishwashing composition or a laundry composition. Most preferred it is an ADD composition.

[0063] The detergent composition preferably is provided for domestic of professional use. The detergent compositions can be used in domestic or professional appliances. Preferred is that the detergent composition is used at domestic level, preferably in domestic appliances, more preferably in automatic dishwashing machines and laundry machines. The detergent composition can be in any physical form. It can be a powder, a gel, paste, liquid, granulate, compacted granulate or provided in unit dose form. Preferably it is in unit dose form, wherein unit dose forms include pressed tablets and water-soluble packages comprising the detergent. The composition of the invention can be provided in the form of a multi-compartment pack, e.g. a multi-compartment pack comprising compartments with compositions having different ingredients or which are in different physical forms, for example a compartment comprising a composition in solid form and another compartment comprising a composition in liquid or gel form. Another preferred unit dose form is a tablet.

[0064] The detergent composition according to the invention comprises at least one further ingredient, selected from builder(s), surfactant(s), bleaching agent(s), bleach activator(s), bleach catalyst, dyes, corrosion inhibitors, silver-protecting agents, anti-redeposition agents, perfumes, process aids, enzymes, and combinations thereof, without being restricted to the mentioned.

[0065] One common ingredient of cleaning compositions, in particular ADD and laundry compositions are builders. Thus, to include at least one builder is preferred for the detergent composition of the present invention.

[0066] The detergent composition of the present invention is free of phosphates, however comprises a builder system of other builders.

[0067] The term "builder" as used herein includes sequestering (e.g. polycarboxylic acids like citrate) and precipitating builders (e.g., carbonates) but excludes materials that function primarily as alkalis such as NaOH, KOH and alkaline silicates such as sodium metasilicate and amorphous silicates having an SiO_2 to Na_2O ratio of greater than 1. The compositions of the invention may however comprise alkali metal silicates in order to provide protection against corrosion of metals and against attack on dishware, including china and glassware, and for pH control, although the compositions can also be free of metal silicates. Silicates give rise to high pH compositions which can be aggressive, producing corrosion and attacking the dishware/tableware. Preferably, the detergent composition has a pH in the wash liquor of

from about 5 to 13, preferably 7 to about 11, and more preferably from about 8 to about 10.8.

[0068] Builders suitable for use in detergent and cleaning compositions herein include builder which forms water-soluble hardness ion complexes (sequestering builder) such as polycarboxylic acids, e.g. citric acid or citrates, and builder which forms hardness precipitates (precipitating builder) such as carbonates, e.g. sodium carbonate. The alkali metal nonphosphate detergent builder salts include sodium or potassium carbonate, sodium or potassium citrate, sodium or potassium nitrilotriacetate, and the like, wherein sodium carbonate and sodium citrate are preferred.

[0069] The builder component(s) is/are typically present at a level of from about 20 to about 80 percent, preferably from about 25 to about 70 percent, more preferred from about 30 to 60 percent by weight of the detergent composition (as the sum of the builder components). It can also be suitable that the ratio of sequestering builder to precipitating builder is from about 10:1 to about 1:2, preferably from about 8:1 to 1:1.

[0070] The preferred compositions herein comprise a pH-adjusting component selected from water-soluble alkaline inorganic salts and water-soluble organic or inorganic builders. The pH-adjusting components are selected so that when the detergent composition is dissolved in water at a concentration of 1,000 - 5,000 ppm, the pH remains in the range from about 5 to 13, preferably 7 to about 12, and more preferably from about 8 to about 11 like e.g. from about 9 to about 10.8. The preferred non-phosphate pH-adjusting component(s) of the invention (partially also representing builder components) is/are selected from the group consisting of:

(i) sodium carbonate or sesquicarbonate;
(ii) sodium silicate, preferably hydrous sodium silicate having SiO_2:Na_2O ratio of from about 1:1 to about 2:1, and mixtures thereof with limited quantites of sodium metasilicate;
(iii) sodium citrate;
(iv) citric acid;
(v) sodium bicarbonate;
(vi) sodium borate, preferably borax;
(vii) sodium hydroxide
(viii) L-glutamic acid N,N-diacetic acid, tetrasodium salt
(ix) L-glutamic acid N,N-diacetic acid; and
(x) mixtures of (i)-(ix).

[0071] Preferred embodiments contain low levels of silicate (i.e. from about 0.5% to about 5% SiO_2) or no silicate.

[0072] For compositions herein having a pH between about 7 and about 12 of the initial wash solution, particularly preferred non-phosphate ADD embodiments comprise, by weight of ADD, from about 5% to about 50%, preferably from about 10% to about 45%, most preferably from about 15% to about 40%, of sodium citrate with from about 5% to about 50%, preferably from about 7% to 40%, most preferably from about 8% to about 30% sodium carbonate. Also preferred non-phosphate ADD embodiments may comprise, by weight of ADD, from about 10% to about 38%, preferably from about 15% to about 34%, most preferably from about 20% to about 30%, of L-glutamic acid N,N-diacetic acid, tetrasodium salt with from about 5% to about 50%, preferably from about 7% to 40%, most preferably from about 8% to about 30% sodium carbonate.

[0073] The builder system can be complemented (i.e. for improved sequestration in hard water) by other optional detergency builder salts selected from non-phosphate detergency builders known in the art, which include the various water-soluble, alkali metal, ammonium or substituted ammonium borates, hydroxysulfonates, polyacetates, and polycarboxylates. Preferred are the alkali metal, especially sodium, salts of such materials. Alternate water-soluble, non-phosphorus organic builders can be used for their sequestering properties. Examples of polyacetate and polycarboxylate builders are the sodium, potassium, lithium, ammonium and substituted ammonium salts of nitrilotriacetic acid, tartrate monosuccinic acid, tartrate disuccinic acid, oxydisuccinic acid, carboxymethyloxysuccinic acid, mellitic acid, and sodium benzene polycarboxylate salts.

[0074] When present, sodium and potassium, especially sodium, silicates are preferred. A particularly preferred alkali metal silicate is a granular hydrous sodium silicate having a SiO_2:Na_2O ratio of about 2.0 or about 2.4 available from PQ Corporation, named Britesil H20 and Britesil H24. Most preferred is a granular hydrous sodium silicate having a SiO_2:Na_2O ratio of 2.0. Typical forms, i.e., powder and granular, of hydrous silicate particles are suitable.

[0075] Alternate silicate-containing materials which can be used as builders include zeolites, such as zeolites A and P, including "maximum aluminium" variants; or, more preferably, layer silicates such as SKS-6, a wide variety of such silicates are available from Hoechst Corp. or from PQ Corp. When used in the instant compositions for pH-adjusting, aluminium anticorrosion or surfactant-absorbing effects, the levels of any limited water-solubility silicates should not be such as to result in deposition on dishware.

[0076] The detergent composition preferably includes one or more surfactants. Any of nonionic, anionic, cationic, gemini surfactants, amphoteric or zwitterionic surfactants or suitable mixtures thereof may plausibly be used. Many such suitable surfactants are described in Kirk Othmer's Encyclopedia of Chemical Technology, 3rd Ed., Vol. 22, pp. 360-379,

"Surfactants and Detersive Systems", incorporated by reference herein. In general, bleach-stable surfactants are preferred according to the present invention.

[0077] In the case of automatic dishwashing compositions, it is preferred to minimise the amount of anionic surfactant. Accordingly, preferably an ADD composition comprises no more than 2 wt.%, no more than 1 wt.%, or no anionic surfactant.

[0078] ADD compositions preferably comprise nonionic surfactants, preferably in a total amount of from 0.5 to 15 percent by weight, such as from 0.5 to 10 percent, from 1 to 8 percent, from 1.5 to 7 percent, from 2 to 6 percent, or from 2.5 to 5.5 percent, or from 3 to 5 percent (e.g. when the product is in the form of a multi-chamber water-soluble pouch or a tablet), of one or more nonionic surfactants. Laundry compositions as well can comprise nonionic surfactants, but usually in the amount of from 1 to 10 percent by weight.

[0079] It is preferred that the composition of the present invention comprises at least a nonionic surfactant. Nonionic surfactants are commonly known and comprise e.g. modified alcohol polyglycol ether, fatty alcohols, fatty alcohol glycol ether (alkoxylated fatty alcohols), like fatty alcohol ethoxylates and fatty alcohol propoxylates, alkylglucosides, alkylpolyglucosides and phenolethoxylates, like octyl- or nonyl phenolethoxylates.

[0080] Preferred nonionic surfactants are modified alcohol polyglycol ether, modified alcohol poly-(ethylenglycol)-ether, alkoxylated fatty alcohols, alkoxylated fatty acids or combinations thereof. The relative hydrophilic alkoxy-chain comprises or essentially consists of ethylene oxide, propylene oxide or butylene oxide or combinations thereof. The length of this chain can vary between averagely 1 and averagely 200 ethylene oxide-, propylene oxide- or butylene oxide-groups or combinations thereof, including 4, 6, 8, 10, 13, 15, 20, 25, 30, 40, 50, 80, 100 and the ranges between the particularly mentioned.

[0081] The relative hydrophobic hydrocarbon-chain from the fatty alcohol or fatty acid can be saturated, mono-unsaturated or poly-unsaturated and linear or branched. The length of this hydrocarbon-chain varies between 4 and 30 carbon molecules, including 6, 8, 10, 11, 12, 14, 16, 18, 20, 22, 24, 26 or 28.

[0082] Preferred surfactants of this type may be represented by the formula $R^1O\ (CH_2CH_2O)_x$, $(CH_2CH(CH_3)O)_y\ H$, wherein R^1 is a linear or branched, saturated or unsaturated hydrocarbon residue having 4 to 30 C atoms, preferably 6 to 26, even more preferred 10 to 24 C atoms, x preferably is an integer of from 8 to 200, preferably from 20 or from 25 to 200, y preferably is an integer of at most 100 and x+y is below 200. In a preferred embodiment in at least one of the "carry over" surfactants x is at least 26, preferably at least 30, and even more preferred at least or more than 40, however, below 200. R^1 preferably is a linear, saturated hydrocarbon residue.

[0083] Particularly preferred are alcohol ethoxylates that can be prepared by ethoxylation of a fatty chain alcohol. The preferred alcohol ethoxylates have a hydrocarbon-chain that ranges from 4 up to 26 carbon molecules, including 4, 6, 8, 10, 12, 14, 16, 18, 20, 22 and between averagely 1 and averagely 200 ethylene oxide-groups, including averagely 4, 6, 8, 10, 13, 15, 20, 25, 30, 40, 50, 80, 100 ethylene oxide-groups.

[0084] Also preferred are fatty acid ethoxylates that can be prepared by a reaction of fatty acid with ethylene oxide or a polyglycol with the general formula $RCOO^-(CH_2CH_2O)_nH$. When a polyglycol is used a mixture of mono- and di-esters ($RCOO^-(CH_2CH_2O)_n$-OCOR) is produced. The preferred fatty acid has a hydrocarbon-chain R that varies from 4 up to 26 carbon molecules, including 4, 6, 8, 10, 12, 14, 16, 18, 20, 22. The number of ethylene oxide-groups in the fatty acid ethoxylate is between averagely 1 and averagely 200 ethylene oxide-groups, including averagely 4, 6, 8, 10, 13, 15, 20, 25, 30, 40, 50, 80, 100 ethylene oxide-groups.

[0085] Preferred are ethylene oxide-propylene oxide co-polymers which may be prepared with a starting material that reacts with ethylene oxide (EO) or propylene oxide (PO) or a mixture of EO and PO (resulting in block copolymers). The starting materials that can be used are (difunctional) poly(oxypropylene glycol) or (difunctional) poly(oxyethylene glycol) or glycerol (for trifunctional products) or ethylene diamine (for tetrafunctional products).

[0086] Further preferred are sucrose esters that may be produced by esterification of sucrose with fatty acids or fatty glycerides. Alkyl polyglucosides (APG) may be produced by a reaction of a fatty alcohol with a glucose. Preferred APGs can have averagely one to averagely four glucose units and has a hydrocarbon-chain that varies from 4 up to 26 carbon molecules, including 4, 6, 8, 10, 12, 14, 16, 18, 20, 22.

[0087] Nonionic surfactants can be "end-capped" by a methyl or a ethyl group at the end of the alkoxy-chain. This affects the properties of the surfactant, e.g. it decreases the foaming behaviour. It is also known that nonionic surfactants can be "end-capped" with a fatty alcohol or a fatty acid where the hydrocarbon-chain varies from 4 up to 26 carbon molecules, including 4, 6, 8, 10, 11, 12, 14, 16, 18, 20, 22. The structure of the surfactants than is "hydrocarbon chain - alkoxy chain - hydrocarbon chain".

[0088] The cleaning composition, in particular the ADD compositions of the present invention can preferably comprise low foaming nonionic surfactants (LFNIs). LFNI can be present in amounts from 0 to about 30% by weight, preferably from about 0.01 to 20% by weight, more preferred from about 0.25% to about 10% by weight and most preferred from about 1 to 6 % by weight. LFNIs are most typically used in ADDs on account of the improved water-sheeting action (especially from glass) which they confer to the ADD product. They also encompass non-silicone, nonphosphate polymeric materials further illustrated hereinafter which are known to defoam food soils encountered in automatic dishwashing.

[0089] Preferred LFNIs include nonionic alkoxylated surfactants, especially ethoxylates derived from primary alcohols, and blends thereof with more sophisticated surfactants, such as the polyoxypropylene/polyoxyethylene/polyoxypropylene reverse block polymers. The PO/EO/PO polymer-type surfactants are well-known to have foam suppressing or defoaming action, especially in relation to common food soil ingredients such as egg.

[0090] The invention encompasses preferred embodiments wherein LFNI is present, and wherein this component is solid at about 35°C, more preferably solid at about 25°C. For ease of manufacture, a preferred LFNI has a melting point between about 25°Cand about 60°C, more preferably between about 27°C and 45°C.

[0091] In a preferred embodiment, the LFNI is an ethoxylated surfactant derived from the reaction of a monohydroxy alcohol containing from about 8 to about 20 carbon atoms with from about 6 to about 80 moles of ethylene oxide per mole of alcohol on an average basis.

[0092] A particularly preferred LFNI is derived from a straight chain fatty alcohol containing from about 16 to about 20 carbon atoms (C_{16}-C_{20} alcohol), preferably a C_{18} alcohol, condensed with an average of from about 6 to about 15 moles, preferably from about 7 to about 12 moles, and most preferably from about 7 to about 9 moles of ethylene oxide per mole of alcohol. Preferably the ethoxylated nonionic surfactant so derived has a narrow ethoxylate distribution relative to the average.

[0093] The LFNI can optionally contain propylene oxide in an amount up to about 15% by weight. Other preferred LFNI surfactants can be prepared by the processes described in U.S. Patent 4,223,163.

[0094] ADDs described herein wherein the LFNI is present can make use of ethoxylated monohydroxy alcohol or alkyl phenol and additionally comprise a polyoxyethylene, polyoxypropylene block polymeric compound; the ethoxylated monohydroxy alcohol or alkyl phenol fraction of the LFNI comprising from about 20% to about 80%, preferably from about 30% to about 70%, of the total LFNI.

[0095] Suitable block polyoxyethylene-polyoxypropylene polymeric compounds may include those based on ethylene glycol, propylene glycol, glycerol, trimethylolpropane and ethylenediamine as initiator reactive hydrogen compound. Polymeric compounds made from a sequential ethoxylation and propoxylation of initiator compounds with a single reactive hydrogen atom, such as $C_{12\text{-}18}$ aliphatic alcohols, do not generally provide satisfactory suds control in the instant ADDs. Certain of the block polymer surfactant compounds designated PLURONIC® and TETRONIC® by the BASF-Wyandotte Corp., Wyandotte, Michigan, are suitable in ADD compositions of the invention.

[0096] A particularly preferred LFNI contains from about 40% to about 70% of a polyoxypropylene/polyoxyethylene/polyoxypropylene block polymer blend comprising about 75%, by weight of the blend, of a reverse block co-polymer of polyoxyethylene and polyoxypropylene containing 17 moles of ethylene oxide and 44 moles of propylene oxide; and about 25%, by weight of the blend, of a block copolymer of polyoxyethylene and polyoxypropylene initiated with trimethylolpropane and containing 99 moles of propylene oxide and 24 moles of ethylene oxide per mole of trimethylolpropane.

[0097] Suitable for use as LFNI in the ADD compositions are those LFNI having relatively low cloud points and high hydrophilic-lipophilic balance (HLB). Cloud points of 1% solutions in water are typically below about 32°C and preferably lower, e.g., 0°C, for optimum control of sudsing throughout a full range of water temperatures.

[0098] LFNIs which may also be used include a C_{18} alcohol polyethoxylate, having a degree of ethoxylation of about 8, commercially available as SLF18 from Olin Corp., and any biodegradable LFNI having the melting point properties discussed hereinabove.

[0099] The use of a mixture of any of the aforementioned nonionic surfactants is suitable in compositions of the present invention.

[0100] In laundry compositions the inclusion of anionic surfactants is preferred.

[0101] Preferred anionic surfactants comprise or consist of a hydrophobic chain and an anionic hydrophilic group. The hydrophilic group can be a carboxylate, $C_nH_{2n+1}COO^-$ X, a sulphate, $CnH_2n\text{-}_10(SO_3)^-$ X, a sulphonate, $C_nH_{2n+1}(SO_3)^-$ X, phosphate, $C_nH_{2n+1}OPO(OH)O^-$ X, a sulphosuccinate, an isethionate, a taurate or any other anionic hydrophilic group.

[0102] Particularly preferred anionic surfactants are sulphates and sulphonates. Sulphate surfactants can be produced by a reaction of an alcohol with sulphuric acid, chlorosulphonic or sulphur dioxide and are esters of sulphuric acid. The surfactant properties can optionally be modified by, for example, introducing ethylene oxide units in the chain so it becomes an alcohol ether sulphate.

[0103] Suitable examples of preferred surfactants are alkyl benzene sulfonates, alkanesulfonates, fatty alcohol sulfates or similar suitable anionic surfactants. Common types of sulphonate surfactants are alkyl aryl sulphonates (e.g. sodium alkyl benzene sulphonate, naphthalene sulphonate, alkyl naphthalene sulphonate), paraffin sulphonates, linear alkyl benzene sulphonates (LABS), alpha-olefin sulphonates, sulphosuccinates (as mono- or di-esters or a mixture thereof). Alpha-olefin sulphonates can be prepared by reacting linear alpha-olefin with sulphur trioxide, yielding in a mixture of alkene sulphonates, 3- and 4-hydroxyalkane sulphonates, di-sulphonates and other species. The properties of sulphonate surfactants can optionally be modified by introducing ethylene oxide units in the chain.

[0104] Preferred alkyl phosphates and alkyl ether phosphates can be made by treating fatty alcohols or alcohol ethoxylates with a phosphorylating agent which yields in a mixture of mono- and di-esters of phosphoric acid.

[0105] Preferably, the total amount of anionic surfactant(s) present in a laundry detergent composition according to

the invention ranges from 0.5 to 40 wt.-%, preferably from 1 to 20 wt.-%, more preferably from 2 to 10 wt.-% based on the total weight of the composition.

[0106] The composition may include one or more enzymes. For ADDs it is preferred that the one or more enzymes are selected from proteases, lipases, amylases, cellulases and peroxidases, with proteases and amylases being preferred, most preferred are proteases and alpha-amylases. It is most preferred that protease and/or amylase enzymes are included in the compositions according to the invention as such enzymes are especially effective in ADD compositions. More than one species may be used. For Laundry compositions preferably at least one enzyme is selected from the group of proteases, amylases, lipases, cellulases, mannanase, peroxidase, oxidase, xylanase, pullulanase, glucanase, pectinase, cutinase, hemicellulases, glucoamylases, phospholipases, esterases, keratanases, reductases, phenoloxidase, lipoxygenases, ligninases, tannases, pentosanases, malanases, arabinosidases, hyalurodindase, chondroitinase, laccase or mixtures thereof. The enzymes can for example be used as a granulate and/or liquid in commonly used amounts.

[0107] The total quantity of active enzyme(s) is preferably from 0.5 to 5 percent by weight, such as from 1 to 4 percent by weight of the detergent composition.

[0108] The composition may include one or more bleaching agent(s), preferably in combination with one or more bleach activators and/or one or more bleach catalysts. The bleaching agent is preferably selected from the group consisting of an oxygen-releasing bleaching agent, a chlorine-releasing bleaching agent and mixtures of two or more thereof. More preferably, the bleaching agent is or comprises an oxygen-releasing bleaching agent. The bleaching agent may comprise the active bleach species itself or a precursor to that species. Preferably, the bleaching agent is selected from the group consisting of an inorganic peroxide, an organic peracid and mixtures of two or more thereof. The terms "inorganic peroxide" and "organic peracid" encompass salts and derivatives thereof. Inorganic peroxides include percarbonates, perborates, persulphates, hydrogen peroxide and derivatives and salts thereof. The sodium and potassium salts of these inorganic peroxides are suitable, especially the sodium salts. Sodium percarbonate is particularly preferred, even more preferred is coated sodium percarbonate.

[0109] The active bleaching agent(s) is/are preferably present in a total amount of from 5 to 28 percent by weight, such as from 7 to 25 percent, from 9 to 22 percent, or from 10 to 20 percent by weight of the detergent composition.

[0110] The composition may further comprise one or more bleach activators and/or bleach catalysts. Any suitable bleach activator may be included, for example TAED (tetraacetyl-ethylenediamine), if this is desired for the activation of the bleaching agent. Any suitable bleach catalyst may be used, for example a manganese-containing bleach catalyst like MnTACN. MnTACN is a dinuclear manganese complex, e.g. a complex of manganese(IV) with 1,4,7-trimethyl-1,4,7-triazacyclononane or a complex of manganese(IV) with 1,2,4,7-tetramethyl-1,4,7-triazacyclononane. The organic peracids such as perbenzoic acid and peroxycarboxylic acids e.g. phthalimidoperoxyhexanoic acid (PAP) do not require the use of a bleach activator or catalyst as these bleaches are active at relatively low temperatures such as about 30 degrees centigrade. A preferred composition contains a bleach activator and a bleach catalyst, more preferred is that the composition contains TAED and MnTACN. Another preferred composition contains a bleach activator and is free of a manganese-containing bleach catalyst, more preferred is that the composition contains TAED and is free of MnTACN. Jet another preferred composition contains a manganese containing bleach catalyst and doesn't contain a bleach activator, more preferred is that the composition contains MnTACN as a bleach catalyst and is free of TAED.

[0111] Dyes may be used to color the detergent composition, parts of the composition or provide speckles in the composition to render it more attractive to the consumer.

[0112] Perfume can be added to improve the sensorial properties of the composition or of the target surface after cleaning, such as the load of a dishwashing or laundry machine. Also perfumes that have a deodorizing effect can be applied.

[0113] The main function of anticorrosion agents is to minimize the amount of material damage caused on glass, metal and metal alloy, as well as the colors of and prints or decorations on these materials, during automatic dishwashing.

[0114] The types of anti-corrosion agents that commonly are used in detergent compositions include, but are not limited to, triazole-based compounds (like tolyltriazole and 1,2,3-benzotriazole), polymers with an affinity to attach to glass or metal surfaces, strong oxidizers (like permanganate), cystine, silicates, metal oxides, organic or inorganic metal salts, or metal salts of biopolymers.

[0115] The metal of these metal salts can be selected from the group aluminium, strontium, barium, titanium, zirconium, manganese, lanthanum, bismuth and zinc, wherein the latter two are most commonly applied for the prevention of glass corrosion. Of the group of metal oxides is zinc oxide commonly applied for the prevention of glass corrosion. Preferred for the use of anti-corrosion agents are bismuth citrate, zinc oxide, zinc sulphate, zinc hydroxy carbonate and zinc stearate.

[0116] The preferred composition contains zinc salts or oxides, or bismuth salts, or any combination of these. Another preferred composition contains bismuth salts and is free of zinc salts or oxides. Another preferred composition is free of zinc salts or oxides.

[0117] Process aids can be added for example to optimize compressibility, friability, toughness, elasticity, disintegration speed, hygroscopicity, density, free flowing properties, stickiness, viscosity, rheology of a detergent composition in a

certain physical shape.

Examples

Example 1

[0118] A build-up test has been performed in Miele GSL dishwashers. The used washing-program cleans at 65°C and has a rinsing phase of 65°C. The used water hardness is 21°dH. A total of thirty washing cycles have been performed where for each washing cycle the detergent and an amount of ballast soil are dosed.

[0119] After all thirty washing cycles the build-up performance of the detergent composition is determined by visually assessing the individual items in the dishwasher on spotting and filming. The performance of spotting and filming is expressed in a score from 1 to 10, where 1 means a very poor performance on spotting or filming, and 10 means a very good performance on spotting or filming. The scores on spotting are the average of the scores on the number of spots and the intensity of the spots. For gaining a well-balanced score for the build-up performance of the detergent composition the scores from the filming and the spotting are multiplied by each other. The overall build-up performance is expressed in a scale from 1 to 100, where 1 means the worst possible performance and 100 means the best possible performance.

[0120] The detergent base in this example contains builder, surfactants, sodium percarbonate, bleach activator, amylase and protease enzymes, anti-corrosion agents and process aids.

[0121] Detergent compositions in percent by weight:

	V1	E1	E2	E3	E4
Detergent base	93	93	93	93	93
(a) PESA	5	3	3	3	3
(b1) IA/AMPS copolymer	-	-	-	3	2
(b2) CMI	-	0.24	0.24	0.24	0.24
(b2) CMC	0.7	0.7	0.7	0.7	0.7
(b2) Polysacharide copolymer	-	3	2	-	-
(c) AA/AMPS copolymer	1	-	-	-	-
Phosphonate	0.4	-	-	-	-

[0122] The dose of these detergent is 19.0 gram.

Filming performance

[0123]

Detergent composition	V1	E1	E2	E3	E4
Glasses (average)	4.5	4.5	4.5	4.8	4.5
Plastic (Tupperware and melamine)	5.0	5.0	5.0	4.5	4.5
Black Ceramic	4.0	4.0	4.0	4.0	4.0
Black Glass	4.0	4.0	4.0	4.0	4.0
Knives	4.0	4.0	5.0	4.0	4.0

Spotting performance

[0124]

Detergent composition	V1	E1	E2	E3	E4
Glasses (average)	5.3	6.8	6.5	6.8	6.8
Plastic (Tupperware and melamine)	4.0	4.0	4.0	4.5	5.0
Black Ceramic	5.0	6.0	6.0	6.0	6.0
Black Glass	5.0	6.0	6.0	7.0	7.0
Knives	4.0	7.0	7.0	7.0	7.0

Build-up performance

[0125]

Detergent composition	V1	E1	E2	E3	E4
Glasses (average)	24	30	29	32	30
Plastic (Tupperware and +melamine)	20	20	20	20	23
Black Ceramic	20	24	24	24	24
Black Glass	20	24	24	28	28
Knives	16	28	35	28	28
Average build-up performance	20	25	26	26	27

[0126] The results show that the detergent compositions which are according to the invention (E1 to E4) result in a similar filming performance as detergent composition according to the state of the art, however, show a better spotting result and give a better build-up performance compared to a state-of-the-art detergent composition (V1).

Example 2

[0127] A build-up test has been performed in Miele GSL2 dishwashers. The used washing-program cleans at 65°C and has a rinsing phase of 65°C. The used the water hardness is 21°dH. A total of thirty washing cycles are performed where for each washing cycle the detergent and an amount of ballast soil are dosed.

[0128] After all thirty washing cycles the build-up performance of the detergent composition is determined by visually assessing the individual items in the dishwasher on build-up performance. The performance on build-up is expressed in a score from 1 to 10, where 1 means a very poor performance and 10 means a very good performance on build-up.

[0129] The detergent base in this example contains builder, surfactants, sodium percarbonate, bleach activator, amylase and protease enzymes, anti-corrosion agents and process aids.

[0130] Detergent compositions in percent by weight:

	V2	E5	V3	E6
Detergent base	92	92	92	92
(a) PESA	5	3	3.4	3.4
(b1) IA/AMPS copolymer	-	3	-	2.8
(b2) CMI	-	0.3	-	0.3
(b2) CMC	0.6	1	0.8	0.8
(c) polyacrylic homopolymer	-	-	1.7	-
(c) AA/AMPS copolymer	1.3	-	1	-
Phosphonate	0.4	-	0.4	-

[0131] The dose of detergents V2 and E5 is 19.0 gram, the dose of detergents V3 and E6 is 21.0 gram.

Build-up performance

[0132]

Detergent compositions	V2	E5	V3	E6
Glass	5.0	5.3	5.3	5.1
Plastic	7.1	6.9	7.4	6.8
Porcelain	5.8	7.0	6.0	6.5
Stainless steel	5.3	5.6	5.8	6.1
Average build up performance	5.8	6.2	6.1	6.1

[0133] When V2 and E5 are compared to each other, the results show that the detergent composition which is according

to the invention (E5) has a better build-up performance compared to a state-of-the-art detergent compositions (V2).

[0134] When V3 and E6 are compared to each other, the results show that the detergent composition which is according to the invention (E6) has a comparable build-up performance compared to a state-of-the-art detergent compositions (V3).

Example 3

[0135] The rinse-aid performance is tested in Miele GSL2 dishwashers. The used washing-program cleans at 50°C and has a rinsing phase of 65°C. The used the water hardness is 21°dH. A total of six washing cycles have been performed where for each washing cycle the detergent is dosed and an amount of ballast soil.

[0136] After the fourth, fifth and sixth washing cycle the rinse-aid performance of the detergent composition is determined by visually assessing the individual items in the dishwasher on spotting and filming. For the assessment of spotting the number of spots and the intensity of the spots are taken in to account. The spotting and filming are expressed in a score from 1 to 10, where 1 means a very poor performance and 10 means a very good performance. The average scores of the assessments after the fourth, fifth and sixth cleaning cycle are the overall scores of spotting and filming.

[0137] For gaining a well-balanced score for the overall rinse-aid performance of the detergent composition, the overall scores of spotting and filming are multiplied by each other. The overall rinse-aid performance is expressed in a scale from 1 to 100, where 1 means the worst possible performance and 100 means the best possible performance.

Detergent compositions in percent by weight:

[0138]

	V4	E7	V5	E8
ADD base	93	93	93	93
(a) PESA	5.5	3.0	5.0	3.5
(b1) IA/AMPS	-	3.0	-	2.5
(b2) CMI	-	0.25	-	0.25
(b2) CMC	0.30	1.10	0.35	0.50
(c) polyacrylic homopolymer	-	-	1.0	-
(c) AA/AMPS copolymer	1.1	-	-	-
Phosphonate	0.45	-	0.40	-

[0139] The dose of detergents V4 and E7 is 19 gram, the dose of detergents V5 and E8 is 20 gram.

[0140] The ADD base, used for V4 and E7, contains builder, surfactants, sodium percarbonate, bleach activator, amylase and protease enzymes, anti-corrosion agents and process aids.

[0141] The ADD base, used for V5 and E8, contains builder, surfactants, sodium percarbonate, bleach activator, bleach catalyst, amylase and protease enzymes, anti-corrosion agents and process aids.

Spotting performance

[0142]

Detergent composition	V4	E7	V5	E8
Glasses	6.4	7.0	6.3	6.5
Plastics	5.0	5.5	4.7	4.3
Black Ceramic	5.7	6.3	6.3	6.7
Black glass	5.7	7.0	6.0	6.7
Knives	7.0	7.0	7.0	7.0

Filming performance

[0143]

Detergent composition	V4	E7	V5	E8
Glasses	5.0	4.9	5.0	5.0

(continued)

Detergent composition	V4	E7	V5	E8
Plastics	5.2	5.0	5.5	4.5
Black Ceramic	5.3	4.3	5.3	5.0
Black Glass	5.0	4.3	5.0	5.0
Knives	4.3	5.3	4.7	5.3

Rinse-aid performance

[0144]

Detergent composition	V4	E7	V5	E8
Glasses	32	34	31	33
Plastics	26	28	26	20
Black Ceramic	30	27	34	33
Black Glass	28	30	30	33
Knives	30	37	33	37
Sum of all items	146	156	154	156

[0145] The results show that when V4 and E7 (both dosed with 19 grams per wash) are compared to each other, composition E7 (which is according to the invention) shows the better rinse-aid performance compared to composition V4 (which is state of the art).

[0146] The results show that when V5, which is state of the art, and E8, which is according to the invention (and both are dosed with 20 grams per wash), are compared to each other, both have a comparable rinse-aid performance.

Claims

1. Phosphate-free detergent comprising

(a) polyepoxysuccinic acid (PESA) or derivatives thereof,
(b) at least one additional polymeric compound, said polymeric compound is selected from

(b1) a copolymer comprising

(i) itaconic acid monomers and
(ii) at least one type of sulphonated monomer(s),
(iii) optionally any further monomer,
and / or

(b2) carbohydrate polymers,
wherein said composition comprises less than 3 wt.% of any phosphonate.

2. Detergent composition according to claim 1, wherein said copolymer (b1) comprises (ii) styrene sulphonic acid and/or 2- acrylamido-2-methyl-propanesulphonic acid monomers.

3. Detergent composition according to at least one of the preceding claims, wherein said carbohydrate polymer(s) (b2) is/are selected from carboxymethylcellulose (CMC), carboxymethylinulin (CMI), carboxymethyl dextran (CM-Dextran), carboxymethyl sucrose (CMSU), carboxymethyl polysucrose (CM-polysucrose), carboxymethyl starch (CMS), and polysaccharide copolymers.

4. Detergent composition according to claim 3, wherein the carboxymethylcellulose has a degree of substitution of from 0.4 to 0.8, preferably 0.45 to 0.75, more preferably 0.5 to 0.7, more preferably 0.55 to 0.7, even more preferably 0.6 to 0.7, most preferred from 0.6 to 0.65 and / or the carboxymethylinulin has a substitution degree of from about 0.15 to about 3, preferably from about 1 to about 3, preferably from about 1 to about 2.5, more preferably from about

1.5 to about 2.5, and most preferably from about 1.8 to about 2.2.

5. Detergent composition according to at least one of the preceding claims, wherein the composition besides polymer (b) does not comprise a further polymer comprising acrylic, methacrylic, methyl methacrylic or maleic acid monomers.

6. Detergent composition according to at least one of the preceding claims, wherein phosphonates are present in the detergent composition in a total amount of less than 2 wt.%, more preferred less than 1 wt.%, even more preferred less than 0.5 wt.% referring to the weight of the total weight of the composition.

7. Detergent composition according to at least one of the preceding claims, wherein the PESA (a) is present in an amount of from 0.01 to 52 percent by weight, like 0.1 to 20 percent by weight, preferably from 0.2 to 18 percent, from 0.3 to 15 percent, from 0.4 to 12 percent, from 0.5 to 10 percent, from 0.6 to 9 percent, from 0.7 to 8 percent, or from 0.8 to 7 percent by weight of the detergent composition.

8. Detergent composition according to at least one of the preceding claims, wherein the itaconic acid / sulphonic copolymer (b1) is present in an amount of from 0.1 to 15 percent by weight, like 0.5 to 15 percent by weight of the detergent composition, more preferred in an amount of from 0.8 to 10 percent, or from 1 to 8 percent, even more preferred from 1.5 to 6 percent or from 2 to 4 percent by weight of the detergent composition

9. Detergent composition according to any of claims 3 to 8, wherein the CMC component is present in the detergent composition in an amount of from 0.005 percent to 10 percent by weight of the detergent composition, preferably from about 0.01 percent to about 5 percent or from about 0.05 percent to about 2 percent by weight of the detergent composition and / or the CMI is present in an amount of 0.01 percent to 30 percent, preferably of 0.01 percent to 20 percent, preferably of 0.01 percent to 10 percent, preferably from 0.01 percent to 5 percent, more preferably of 0.01 percent to 3 percent of the weight of the detergent composition, preferably from 0.05 percent to 2.5 percent, from 0.1 percent to 2 percent, or from 0.2 to 1.5 percent of the weight of the detergent composition.

10. Detergent composition according to at least one of the preceding claims, wherein the copolymer (b1) comprises a further monomer (iii) selected from acrylic, methacrylic, methyl methacrylic or maleic acid monomers.

11. Detergent composition according to at least one of the preceding claims, wherein the composition comprises MGDA in an amount of less than 3 wt.%, less than 2 wt.%, less than 1 wt.% or is free of MGDA.

12. Detergent composition according to at least one of the preceding claims, wherein the composition is provided as a powder, a gel, paste, liquid, granulate, compacted granulate or in unit dose form, wherein said unit dose form includes pressed tablets and water-soluble packages.

13. Detergent composition according to at least one of the preceding claims, being an automatic dishwashing detergent composition or a laundry composition, preferably an automatic dishwashing composition.

14. Use of a detergent composition of any of the preceding claims in an automatic dishwashing device or a laundry machine, preferably for preventing scale formation.

15. Use of a combination of

(a) polyepoxysuccinic acid (PESA) or derivatives thereof,
(b) at least one additional polymeric compound, said polymeric compound is selected from
(b1) a copolymer comprising (i) itaconic acid monomers and (ii) at least one type of sulphonated monomer(s), optionally (iii) any further monomer,
and / or
(b2) carbohydrate polymers,
for decreasing or inhibiting scale formation in water systems, in particular when no phosphates and/or phosphonates are present.

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 22 17 0164

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	CN 108 165 376 B (SHANDONG TAIHE WATER TREAT TECH CO LTD) 12 March 2021 (2021-03-12) * claims 1-3; examples *	1,3,5-7, 11-13,15	INV. C11D3/22 C11D3/37 C11D3/20
X	US 4 846 650 A (BENEDICT JAMES J [US] ET AL) 11 July 1989 (1989-07-11) * column 9, line 56 - line 68; examples I, II *	1,3-7,9, 11,12	
X	EP 3 623 456 A1 (CLARO PRODUCTS GMBH [AT]) 18 March 2020 (2020-03-18) * paragraph [0035]; examples GM4, GM6; table 1 *	1,5-7, 11-14	
Y	US 2021/238503 A1 (GORDON JAMES WILLIAM [GB] ET AL) 5 August 2021 (2021-08-05) * claims 1, 2, 8; tables *	1,2,5-13	
Y,D	WO 2021/213807 A1 (RECKITT BENCKISER FINISH BV [NL]) 28 October 2021 (2021-10-28) * claim 1 *	1,2,5-9, 11-13	TECHNICAL FIELDS SEARCHED (IPC) C11D
T	US 4 654 159 A (BUSH RODNEY D [US] ET AL) 31 March 1987 (1987-03-31) * column 6, line 54 - column 7, line 8 * * column 1, line 48 - line 62 * * column 3, line 44 - line 48; claims 1-5; example 1 *		
Y,D	WO 2014/143773 A1 (LUBRIZOL ADVANCED MAT INC [US]) 18 September 2014 (2014-09-18) * samples 19-22, 45, 46; paragraphs [0251], [0257]; table 3 *	10	
A	EP 3 418 366 A1 (PROCTER & GAMBLE [US]) 26 December 2018 (2018-12-26) * claims 1-9; example 2 *	1-4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	30 September 2022	Loiselet-Taisne, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 22 17 0164

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

30-09-2022

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 108165376 B	12-03-2021	NONE	
US 4846650 A	11-07-1989	NONE	
EP 3623456 A1	18-03-2020	EP 3623456 A1	18-03-2020
		EP 3850072 A1	21-07-2021
		WO 2020053316 A1	19-03-2020
US 2021238503 A1	05-08-2021	CA 3170119 A1	12-08-2021
		US 2021238503 A1	05-08-2021
		WO 2021159146 A1	12-08-2021
WO 2021213807 A1	28-10-2021	NONE	
US 4654159 A	31-03-1987	GB 2183633 A	10-06-1987
		US 4654159 A	31-03-1987
WO 2014143773 A1	18-09-2014	BR 112015023790 A2	18-07-2017
		CN 105209508 A	30-12-2015
		CN 110105480 A	09-08-2019
		EP 2970542 A1	20-01-2016
		ES 2744403 T3	25-02-2020
		JP 6742234 B2	19-08-2020
		JP 7065135 B2	11-05-2022
		JP 2016519697 A	07-07-2016
		JP 2018104720 A	05-07-2018
		JP 2020090687 A	11-06-2020
		KR 20150133237 A	27-11-2015
		US 2016068620 A1	10-03-2016
		US 2018223016 A1	09-08-2018
		US 2021355253 A1	18-11-2021
		WO 2014143773 A1	18-09-2014
EP 3418366 A1	26-12-2018	EP 3418366 A1	26-12-2018
		US 2018362890 A1	20-12-2018
		WO 2018236841 A1	27-12-2018

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2021213807 A1 **[0005]**
- EP 3092294 B1 **[0005]**
- EP 3050953 B1 **[0005]**
- EP 3850072 A **[0005]**
- EP 3674386 A **[0005]**
- WO 2018236810 A1 **[0005]**
- WO 2018191326 A1 **[0023]**
- WO 2014143773 A1 **[0029]**
- WO 2015138872 A1 **[0029]**
- US 20190390140 A **[0036] [0046]**
- EP 2302025 B1 **[0039]**
- US 6600033 B **[0039]**
- US 4223163 A **[0093]**

Non-patent literature cited in the description

- Surfactants and Detersive Systems. **KIRK OTHMER'S.** Encyclopedia of Chemical Technology. vol. 22, 360-379 **[0076]**