



(11) **EP 4 428 217 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
11.09.2024 Bulletin 2024/37

(51) International Patent Classification (IPC):
C11D 3/00 ^(2006.01) **C11D 3/37** ^(2006.01)
C11D 11/00 ^(2006.01)

(21) Application number: **23160371.3**

(52) Cooperative Patent Classification (CPC):
C11D 3/3788; C11D 3/0078; C11D 3/3796;
C11D 2111/14

(22) Date of filing: **07.03.2023**

(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 ME MK MT NL
NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA
Designated Validation States:
KH MA MD TN

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(54) **GRAFT COPOLYMERS FOR CORROSION INHIBITION IN AN AUTOMATIC DISHWASHING PROCESS**

(57) The present invention relates to the use of a graft copolymer having a permanent cationic charge, for reducing surfaces corrosion in an automatic dishwashing process. Moreover, the present invention relates to a method for reducing corrosion, in particular surfaces corrosion in an automatic dishwashing process in the presence of said graft copolymer.

The graft copolymers comprise:

a) at least one graft base A selected from nonionic mono-,

di-, oligo- and polysaccharides,

b) and polymeric side chains P obtainable by grafting ethylenically unsaturated monomers M onto the graft base, where the monomers M comprise

b1) at least one monomer b1 selected from monoethylenically unsaturated mono- and dicarboxylic acids; and
b2) at least one monomer b2 selected from ethylenically unsaturated monomers having a permanent cationic charge.

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Description

[0001] The present invention relates to the use of a graft copolymer having a permanent cationic charge, for reducing surfaces corrosion in an automatic dishwashing process. Moreover, the present invention relates to a method for reducing surfaces corrosion in an automatic dishwashing process in the presence of said graft copolymer.

[0002] Cleaning compositions as such, especially for being used within automatic dishwashing processes, are known to a person skilled in the art. Modern cleaning compositions for automatic dishwashing processes need to meet many requirements. They need to work under various conditions, for example various temperatures. They need to yield excellent results in the case of hard surface cleaners and in particular automatic dish-washing formulations they need to provide excellent results with respect to spotting and filming. In case glass to be cleaned, glass corrosion needs to be inhibited or at least strongly reduced. Cleaning compositions need to be environmentally friendly, and they have to work even under conditions where only so-called "hard water" is available, for example water with a comparatively high content of Mg^{2+} and Ca^{2+} salts.

[0003] Typically automatic dishwashing formulations contain complexing agents for reducing water hardness. While previously phosphates and polyphosphates, e. g. sodium tripolyphosphate, were used for reducing water-hardness, such phosphates and polyphosphates have to be replaced by non-phosphate complexing agents for ecological reasons.

[0004] Depending on the non-phosphate complexing agents, automatic dishwashing compositions, also referred to herein as ADW compositions and ADW detergents, can lead to corrosion of machine parts (metal corrosion), corrosion of metal dishes and of the surface of glasses. While (poly)aminocarboxylates are powerful complexing agents, they cause or at least contribute to surface corrosion of glass and metal surfaces under the condition of automatic dishwashing. Typical (poly)aminocarboxylates which cause corrosion of glass and metal surfaces include methylglycine *N,N*-diacetic acid (MGDA), glutamic acid *N,N*-diacetic acid (GLDA), ethylenediamine-*N,N*-disuccinic acid (EDDS), iminodisuccinic acid (IDS), ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA) and the salts thereof. These chelating agents show detrimental effects on metal and glass. Moreover the problem of metal corrosion could become even more severe when commonly used phosphate and phosphonate co-builders, e. g. hydroxyalkyl phosphonates such as 1-hydroxyethane 1,1-diphosphonate, have to be replaced and/or reduced in formulations due to ecological reasons. Surface corrosion, in particular corrosion of glass surfaces, including decorated glass, and ceramic surfaces, such as porcelain and decorated porcelain surfaces, may also be caused by the high alkalinity of the machine dishwashing compositions.

[0005] Some widely used chemistry for inhibition of metal corrosion are benzotriazoles (BTA). However, triazole-based components such as BTA, are now known to have a potential risk in respect of an endocrine disruptor, which might lead to a ban of BTA and derivatives thereof.

[0006] WO 2021/170637 A1 suggests replacing benzotriazoles in ADW compositions by imidazole-based compounds selected from the group consisting of unsubstituted or at least monosubstituted imidazole compounds and unsubstituted or at least monosubstituted benzimidazole compounds, or a salt of such imidazole-based compounds.

[0007] WO 2013/160132 A1 describes solid detergent compositions, in particular to ADW compositions, containing at least one (poly)aminocarboxylate, such as GLDA or MGDA, at least one cationic (co)polymer based on a polyalkylene imine with a specific cationic charge density and at least one silicate, such as sodium silicates. The compositions provide for low glass corrosion in automatic dishwashing.

[0008] There is an ongoing need to provide means for corrosion inhibition that are non-toxic, environmentally safe and effective in inhibiting corrosion of both metal and glass surfaces in automatic dishwashing, in particular of corrosion caused by non-phosphate complexing agents, in particular complexing agents from the group of (poly)aminocarboxylates.

[0009] It was found that this objective is achieved by graft copolymers as described herein, where the graft copolymers comprise:

- a) at least one graft base A selected from nonionic mono-, di-, oligo- and polysaccharides,
- b) and polymeric side chains P obtainable by grafting ethylenically unsaturated monomers M onto the graft base, where the monomers M comprise

- b1) at least one monomer b1 selected from monoethylenically unsaturated mono- and dicarboxylic acids; and
- b2) at least one monomer b2 selected from ethylenically unsaturated monomers having a permanent cationic charge;

[0010] Therefore, a first aspect of the present invention relates to the use of the graft copolymers as described herein for reducing surfaces corrosion in an automatic dishwashing process, in particular for reducing surface corrosion of glass surfaces, including decorated glass surfaces and non-decorated glass surfaces, ceramic surfaces, such as porcelain and decorated porcelain surfaces, and/or metal surfaces, in particular of both metal and glass surfaces.

[0011] Here and in the following, the term "metal surface" relates in particular to copper surfaces, copper alloy surfaces,

silver surfaces, steel surfaces, stainless steel surfaces and aluminium or aluminum alloy surfaces.

[0012] In a second aspect, the present invention relates to a method for reducing surfaces corrosion in an automatic dishwashing process which comprises carrying out the process in the presence of a graft copolymer. In particular, the second aspect of the present invention relates to a method for reducing surfaces corrosion of metal and/or glass surfaces, especially of both metal and glass surfaces, in an automatic dishwashing process.

[0013] In particular, the first and second aspect of the present invention relate to uses and methods for reducing surfaces corrosion in an automatic dishwashing process where the surfaces corrosion is caused by non-phosphate complexing agents, in particular by non-phosphate complexing agents of the group of (poly)aminocarboxylates.

[0014] Especially, the first and second aspect of the present invention relate to uses and methods for reducing surfaces corrosion of metal and/or glass surfaces, in particular of both metal and glass surfaces, in an automatic dishwashing process where the surfaces corrosion is caused by non-phosphate complexing agents, in particular by non-phosphate complexing agents of the group of (poly)aminocarboxylates.

[0015] Here the term "non-phosphate complexing agent" refers to a complexing agent, in particular to a non-polymeric complexing agent, which does not contain phosphate groups.

[0016] Generally, the meaning of the term "comprising" is to be interpreted as encompassing all the specifically mentioned features as well optional, additional, unspecified ones, whereas the term "consisting of" includes only those features as specified. All percentages indicated are given in percent by weight, calculated on the total weight of the respective formulation. It is moreover intended that in each actual case the sum of all of the percentages of the specified and unspecified constituents of a formulation is always 100%.

[0017] In the context of the present invention, the term "ADW formulation" refers to a cleaning formulation for automatic dishwashing. The terms "cleaning formulation" and "cleaning composition" are used synonymously and may refer to single dose formulations/compositions and free dosage formulations/compositions.

[0018] The graft copolymers as used according to the present invention and their preparation by graft copolymerization are known, e. g. from EP 2138560 A1, WO 2015/197378, WO 2015/197379 and WO 2017/186524. Although these graft copolymers have also been used in ADW compositions for improving filming, their use as corrosion inhibitors remained unrecognized.

[0019] The graft copolymers are generally obtainable by copolymerization of the ethylenically unsaturated monomers M in the presence of the graft base and a polymerization initiator, which forms free radicals under the polymerization conditions. Thereby polymer side chains of polymerized monomers M are formed which are grafted onto the graft base, i. e. which are covalently bound to the graft base. Without wishing to be bound to theory, it may be assumed that the polymerization initiator creates free radicals on the graft base which react with the ethylenically unsaturated double bond of a monomer M and thereby start the polymerization of the monomers M.

[0020] Nonionic monosaccharides suitable as graft base A may, for example, be aldopentoses, pentuloses (ketopentoses), aldohexoses and hexuloses (ketohexoses). Suitable aldopentoses are, for example, D-ribose, D-xylose and L-arabinose. Aldohexoses include D-glucose, D-mannose and D-galactose; examples of hexuloses (ketohexoses) particularly include D-fructose and D-sorbose. In the context of the present invention, deoxy sugars, for example L-fucose and L-rhamnose, should also be counted among the nonionic monosaccharides.

[0021] In the context of the graft base A examples of nonionic disaccharides include, for example, cellobiose, lactose, maltose and sucrose.

[0022] Nonionic oligosaccharides in the context of the graft base A refer to nonionic carbohydrates having at least three and preferably up to ten nonionic monosaccharide units per molecule, for example glycans. Nonionic polysaccharides in the context of the present invention refer to nonionic carbohydrates having more than ten nonionic monosaccharide units per molecule. Nonionic oligo- and polysaccharides may, for example, be linear, branched or cyclic.

[0023] Examples of nonionic polysaccharides include, for example, starch, cellulose, dex-transes, inulin as a polycondensate of D-fructose (fructans) and chitin. Further examples of nonionic oligo and polysaccharides are nonionic starch degradation products, for example products which can be obtained by enzymatic or what is called chemical degradation of starch. One example of the chemical degradation of starch is acid-catalyzed hydrolysis.

[0024] Preferred examples of nonionic starch degradation products are maltodextrins and glucose syrups. Maltodextrins and glucose syrups are obtained by hydrolysis of starch. Maltodextrins as well as glucose syrups are typically mixtures of glucose, diglucose as well as oligomers and polymers of glucose. The relative amounts of the components of maltodextrins differs according to the degree of hydrolysis. The composition of such starch degradation products is defined in terms of the dextrose equivalent DE, which is typically in the range of 3 and 40 in the case of maltodextrins and glucose syrups. Here the, dextrose equivalent DE is the reducing power of the starch degradation product relative to pure dextrose which has a DE of 100%, while pure starch has a DE < 1. As a rule of thumb, the DE value and the number average degree of polymerization DP of the starch degradation product is such that $DE \times DP = 120$. The DE value can be determined by the Lane-Eynon method (a titration based on the reduction of copper(II) sulfate in an alkaline tartrate solution as described in Dziedzic, S. Z.; Kearsley, M. W. (1995). Handbook of starch hydrolysis products and their derivatives. London: Blackie Academic & Professional. p. 230.

[0025] Preferably, the graft base A is selected from nonionic polysaccharides and nonionic oligosaccharides, especially from starch which has preferably not been chemically modified, for example wherein the hydroxyl groups have preferably been neither esterified nor etherified, and starch degradation products of non-modified starches. In one embodiment of the present invention, starch is selected from those nonionic polysaccharides having in the range from 20% to 30% by weight of amylose and in the range from 70% to 80% amylopectin. Examples are corn starch, rice starch, potato starch and wheat starch.

[0026] In particular, the graft base A is selected from starch degradation products, especially from starch degradation products of non-modified starches. Especially the graft base A is selected from maltodextrins and glucose sirups, in particular from maltodextrins and glucose syrups having a DE value in the range of 3 to 40, especially in the range from 3 to 20.

[0027] The relative amount of the graft base A in the graft copolymer is typically in the range of 40 to 95% by weight, in particular in the range of 50 to 90% by weight, based on the total weight of the graft base A and the polymer side chains P. Consequently, the total amount of the side chains B is typically in the range of 5 to 60% by weight, in particular in the range of 10 to 50% by weight, based on the total weight of the graft base A and the polymer side chains P.

[0028] The polymeric side chains P are formed by the monomers M which comprise the monomers b1 selected from monoethylenically unsaturated mono- and dicarboxylic acids and the monomers b2 selected from ethylenically unsaturated monomers having a permanent cationic charge. Typically, the total amount of monomers b1 and b2 is at least 90% by weight, in particular at least 95% and may be 100% by weight, based on the total amount of monomers M which form the side chains P.

[0029] Examples of monomers b1 are monoethylenically unsaturated monocarboxylic acids having typically from 3 to 10 carbon atoms, in particular 3 to 6 carbon atoms, and monoethylenically unsaturated dicarboxylic acids having typically from 4 to 10 carbon atoms, in particular 4 to 6 carbon atoms. Preferred monocarboxylic acids are acrylic acid and methacrylic acid and mixtures thereof. Examples of monoethylenically unsaturated dicarboxylic acids are maleic acid, fumaric acid, itaconic acid and citraconic acid. In the preparation of the graft copolymers, the monomers b1 may be used in the form of the acid or as a salt, in particular in the form of the ammonium or alkalimetal salts, such as the sodium or potassium salts. The monoethylenically unsaturated dicarboxylic acids may also be used in the form of their anhydrides, such as maleic anhydride and itaconic anhydride. In one embodiment, the monomers b1 comprises at least one monoethylenically unsaturated monocarboxylic acid and at least one monoethylenically unsaturated dicarboxylic acid. In a preferred groups of embodiments of the present invention, the monomers b1 comprise exclusively monoethylenically unsaturated monocarboxylic acids.

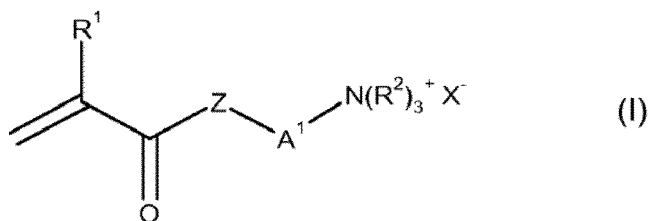
[0030] Examples of monomers b2 are ethylenically unsaturated N-containing compounds with a permanent cationic charge on the nitrogen atom, i.e. those ethylenically unsaturated N-containing compounds which form ammonium salts with anions such as sulfate, C₁-C₄-alkyl sulfates, such as methylsulfate (methosulfate), ethylsulfate, n-propylsulfate, isopropylsulfate or n-butylsulfate, and halides, in particular with chloride, sulfate (SO₄²⁻) and methosulfate (CH₃-OSO₃⁻), and independently of the pH. Any desired mixtures of two or more monomers b2 are also suitable.

[0031] Suitable monomers b2 are e. g. quaternized vinyl- and allyl-substituted nitrogen heterocycles such as quaternized 2-vinylpyridine and quaternized 4-vinylpyridine, quaternized 2-allyl- pyridine and quaternized 4-allylpyridine, and also quaternized N-vinylimidazole, e.g. 1-vinyl-3-methylimidazolium salts. Also of suitability are quaternized N,N-dialkylamines and N,N-diallyl-N-alkylamines, such as e.g. N,N-diallyl-N,N-dimethylammonium chloride (DADMAC). Preferred monomers b2 are

- quaternized amides of monoethylenically unsaturated mono- and dicarboxylic acids with diamines which have at least one primary or secondary amino group. Preference is given here to those diamines which have one tertiary and one primary or secondary amino group, and
- quaternized esters of monoethylenically unsaturated mono- and dicarboxylic acids with C₂-C₁₂-amino alcohols which are mono- or dialkylated on the amine nitrogen.

[0032] Typical acid components of the aforementioned esters and amides are e.g. acrylic acid, methacrylic acid, fumaric acid, maleic acid, itaconic acid, crotonic acid, monobutyl maleate and mixtures thereof. As acid component, preference is given to using acrylic acid, methacrylic acid and mixtures thereof.

[0033] The above-mentioned monomer b2 is preferably selected from monomers of the formula (I)



where

Z is O or NH,

A¹ is C₂-C₄-alkandiyl, such as ethane-1,2-diyl, propane-1,3-diyl or butane-1,4-diyl, in particular ethane-1,2-diyl or propane-1,3-diyl,

R¹ is H or methyl

R² are identical or different and selected from C₁-C₄-alkyl, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, 2-butyl, tert.-butyl or isobutyl, in particular methyl or ethyl, especially methyl,

X is a counter ion, which is in particular selected from halide, mono-C₁-C₄-alkyl sulfate and sulfite, in particular from chloride, sulfate and methosulfate.

[0034] Examples of preferred monomers b2 are those of the formula (I), where Z, R¹, A¹ and R² are as defined in rows 1 to 8 of the following table and where X is Cl⁻.

	Z	R ¹	A ¹	R ²
1	O	H	-CH ₂ -CH ₂ -	CH ₃
2	O	CH ₃	-CH ₂ -CH ₂ -	CH ₃
3	O	H	-CH ₂ -CH ₂ -CH ₂ -	CH ₃
4	O	CH ₃	-CH ₂ -CH ₂ -CH ₂ -	CH ₃
5	NH	H	-CH ₂ -CH ₂ -	CH ₃
6	NH	CH ₃	-CH ₂ -CH ₂ -	CH ₃
7	NH	H	-CH ₂ -CH ₂ -CH ₂ -	CH ₃
8	NH	CH ₃	-CH ₂ -CH ₂ -CH ₂ -	CH ₃

[0035] Further examples of preferred monomers b2 are those of the formula (I), where Z, R¹, A¹ and R² are as defined in rows 1 to 8 of the above table and where X is ½ SO₄²⁻. Further examples of preferred monomers b2 are those of the formula (I), where Z, R¹, A¹ and R² are as defined in rows 1 to 8 of the above table and where X is CH₃OSO₃⁻.

[0036] Generally, the graft copolymer as used according to the present invention comprises, based on the total weight of the graft copolymer,

a) 40 to 95% by weight, in particular 60 to 90% by weight of the graft base;

b.1) 2 to 40% by weight, in particular 5 to 30% by weight especially 5 to 25% by weight of the at least one polymerized monomer b1; and

b.2) 3 to 50% by weight, in particular 5 to 40% by weight especially 5 to 30% by weight of the at least one polymerized monomer b2;

where the weight ratio of the monomer b2 to the monomer b1 is preferably > 1, e. g. in the range of 1,1:1 to 5:1. Preferably, the molar ratio of monomers b1 to monomers b2 is in the range of 1.1:1 to 5:1, in particular in the range of 1.5:1 to 4:1.

[0037] The side chains may contain further polymerized ethylenically unsaturated monomers b3 which are different from the aforementioned monomers b1 and b2. Frequently, the amount said monomers b3 will not exceed 10% by weight, based on the total amount of monomers M which form the side chains P and is preferably 5% by weight or less or 0% by weight, based on the total amount of monomers M which form the side chains P. Examples of monomers b3 include e. g. hydroxyalkyl esters of monoethylenically unsaturated monocarboxylic acids such as 2-hydroxyethyl

(meth)acrylate or 3-hydroxypropyl (meth)acrylate, or esters of monoethylenically unsaturated monocarboxylic acids with polyalkyleneoxides or with alkoxylated fatty alcohols, and anionic monoethylenically unsaturated monomers containing sulfonic acid groups, for example 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and its alkali metal salts.

[0038] One suitable graft copolymer as used according to the present invention is the copolymer obtainable according to WO 2015/197379, graft copolymer B.4, wherein the graft base is maltodextrin, the monomer b1) is acrylic acid and the monomer b2) is a compound of formula (I) wherein Z is O, A¹ is -CH₂-CH₂-, R¹ and R² are methyl, and X is Cl-. Another suitable graft copolymer as used according to the present invention is the copolymer obtainable according to WO 2015/197378, graft copolymer B.4, wherein the graft base is maltodextrin, the monomer b1) is acrylic acid and the monomer b2) is a compound of formula (I) wherein Z is NH, A¹ is -CH₂-CH₂-CH₂-, R¹ and R² are methyl, and X is Cl-.

[0039] The graft copolymers according to the present invention generally have a weight average molecular weight (M_w) in the range of 1500 to 200000 g/mol, preferably in the range of 2000 to 150000 and especially in the range of 3000 to 100000 g/mol. The molecular weight M_w is preferably measured by gel permeation chromatography in aqueous KCl/formic acid solution.

[0040] As mentioned before, the graft copolymers used according to the present invention are obtained by copolymerization of the ethylenically unsaturated monomers M in the presence of the graft base and a polymerization initiator, which forms free radicals under the polymerization conditions. The process is described in EP 2138560 A1, WO 2015/197378, WO 2015/197379 and WO 2017/186524, to which full reference is made.

[0041] Frequently, the copolymerization of the ethylenically unsaturated monomers M, hereinafter grafting, is carried out in water or a mixture of water and water-miscible organic solvents such as alkanols, ketones, and polar aprotic solvents, such as dimethylsulfoxide, N-methyl-2-pyrrolidone and dimethylformamide. The grafting is preferably carried out at temperatures in the range of 50 to 120°C, in particular in the range of 60 to 100°C and at pressure in the range of 1 bar to 20 bar. Preferably, an aqueous solution of the graft base is charged to a reaction vessel and the monomers M are added to the solution in the presence of the initiator, which is preferably a free radical initiator. For example, the monomers M and at least the major amount of the initiator, which is preferably a free radical initiator, are metered to the aqueous solution of the graft base under polymerization conditions. During the metering of the monomers the relative amounts of monomers b1 and b2 may vary. For example, it may be possible to initially start with a high ratio b1/b2 and decrease the ratio stepwise or continuously during the addition of the monomers M. Alternatively, one may initially start with a low ratio of b1/b2 and increase the ratio stepwise or continuously during the addition of the monomers M. Examples of such free radical initiators include azo compounds, such as azodiisobutyronitrile (AIBN), peroxide compounds and hydroperoxides, in particular peroxodisulfates, alkylhydroperoxides and H₂O₂. It may also be possible to add a ferrous(II)salt to the polymerization reaction, in particular when a hydroperoxide is used as an initiator.

[0042] The graft copolymer is usually obtained as aqueous solution from which it can be isolated, e.g. by spray drying, spray granulation or freeze drying. If desired, the solution of the graft copolymer or a solution of the dried graft copolymer can be used for producing ADW formulations according to the invention.

[0043] It is preferred to stabilize graft copolymer by at least one biocide. Examples of suitable biocides are isothiazolinones, for example 1,2-benzisothiazolin-3-one (BIT), octylisothiazolinone (OIT), dichlorooctylisothiazolinone (DCO-IT), 2-methyl-2H-isothiazolin-3-one ("MIT") and 5-chloro-2-methyl-2H-isothiazolin-3-one (CIT), phenoxyethanol, alkylparabens such as methylparaben, ethylparaben, propylparaben, benzoic acid and its salts such as e.g. sodium benzoate, benzyl alcohol, alkali metal sorbates such as sodium sorbate, and (substituted) hydantoins such as 1,3-bis(hydroxymethyl)-5,5-dimethylhydantoin (DMDM hydantoin). Further examples are 1,2-dibromo-2,4-dicyanobutane, iodo-2-propynyl butylcarbamate, iodine and iodophores.

[0044] Needless to say, the graft copolymer is present during automatic dishwashing to reduce the surface corrosion. The graft copolymer may be dosed separately from the ADW composition or it can be included into the ADW composition. In particular, the graft copolymer as used according to the present invention is included into the automatic dishwashing composition.

[0045] As mentioned above, the graft copolymers reduce surface corrosion of glass and/or metal surfaces caused by non-phosphate complexing agents, in particular by (poly)amino carboxylates, especially by methylglycine *N,N*-diacetic acid (MGDA), glutamic acid *N,N*-diacetic acid (GLDA), ethylenediamine-*N,N*-disuccinic acid (EDDS) or iminodisuccinic acid (IDS).

[0046] Therefore, the invention relates in particular to methods and uses of the graft copolymers as described herein in ADW formulations or in combination with ADW formulations which comprise a non-phosphate complexing agent selected from (poly)amino carboxylates. More particularly, the invention relates to methods and uses of the graft copolymers as described herein in ADW formulations or in combination with ADW formulations which comprise a non-phosphate complexing agent selected from the group consisting of methylglycine *N,N*-diacetic acid (MGDA), glutamic acid *N,N*-diacetic acid (GLDA), ethylenediamine-*N,N*-disuccinic acid (EDDS), iminodisuccinic acid (IDS), ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA) and combinations thereof and the salts thereof. Especially, the invention relates to methods and uses of the graft copolymers as described herein in ADW formulations or in combination with ADW formulations which comprise a non-phosphate complexing agent selected from the group consisting of methylglycine

N,N-diacetic acid (MGDA), *N,N*-diacetic acid (GLDA), ethylenediamine-*N,N*-disuccinic acid (EDDS), iminodisuccinic acid (IDS) and combinations thereof and the salts thereof, in particular the alkalimetal salts thereof and especially the sodium salts thereof.

[0047] Suitable salts of (poly)amino carboxylates are in particular their alkali metal salts, more preferably their sodium salts. Particularly preferred salts are the trisodium salt of MGDA, the tetrasodium salt of GLDA, the tetrasodium salt of EDDS and the tetrasodium salt of IDS and combinations thereof.

[0048] It may also be possible to use the (poly)amino carboxylates in combination with citric acid or a salt thereof, in particular in combination with an alkalimetal salt of citric acid, such as the trisodium salts of citric acid.

[0049] The weight ratio of the complexing agent to the graft copolymer is generally at least 2:1, e.g. in the range of 2:1 to 100:1.

[0050] The effect of reduction of surface corrosion achieved by the graft copolymers is pronounced, if the automatic dishwashing is carried out in the absence or essential absence of a phosphate complexing agent. The graft copolymer may of course be used in the presence of a phosphate complexing agent. However, as mentioned above, phosphates and phosphonates are problematic due to environmental concerns. Preferably, the graft copolymer is therefore used in the absence of phosphate complexing agents. Thus, it is preferred to use the graft copolymer in an ADW formulation or in combination with an ADW formulation which is essentially free of phosphate compounds. In the context of the present invention, the term "essentially free of phosphate compounds" refers to a combined phosphate and polyphosphate content of 0.01% by weight or less, based on the ADW formulation.

[0051] In one embodiment of the present invention, the graft copolymers as described herein are used in ADW formulations or in combination with ADW formulations which contain one or more cobuilders from the group of phosphonates, which themselves may have an anti-corrosive effect on metal surfaces. Examples of cobuilders from the group of phosphonates include hydroxyalkanephosphonates and aminoalkanephosphonates. Among the hydroxyalkanephosphonates, 1-hydroxyethane-1,1-diphosphonate (HEDP) is of particular importance as a cobuilder. It is preferably used as the sodium salt, the disodium salt giving a neutral reaction and the tetrasodium salt an alkaline reaction (pH 9). Suitable aminoalkanephosphonates are preferably ethylenediaminetetramethylenephosphonate (EDTMP), diethylenetriaminepentamethylenephosphonate (DTPMP) and higher homologs thereof. They are preferably used in the form of the neutrally reacting sodium salts, e.g. as hexasodium salt of EDTMP or as hepta- and octasodium salt of DTPMP.

[0052] The effect of reduction of surface corrosion achieved by the graft copolymers is pronounced, if the automatic dishwashing is carried out in the absence or essential absence of a phosphonate cobuilder. The graft copolymer may of course be used in the presence of a phosphonate cobuilder. However, as mentioned above, phosphonates are problematic due to environmental concerns. Therefore, in a preferred group of embodiments, the graft copolymer is used in the absence of phosphonate cobuilder. Thus, it is preferred to use the graft copolymer in an ADW formulation or in combination with an ADW formulation which is essentially free of phosphonate cobuilders. In the context of the present invention, the term "essentially free of phosphonate cobuilders" refers to a phosphonate cobuilder content of 0.01% by weight or less, based on the ADW formulation.

[0053] It was surprisingly found that the effect of reduction of surface corrosion achieved by the graft copolymers is still present, if the automatic dishwashing is carried out in the presence of conventional compounds that inhibit the corrosion of metal in automatic dishwashing, which are referred to as conventional metal corrosion inhibitors. The use of the graft copolymers as defined herein in automatic dishwashing applications and ADW formulations allow for reducing the amount of these conventional metal corrosion inhibitors in ADW formulations.

[0054] Examples of suitable conventional metal corrosion inhibitors are

- triazoles, including in particular benzotriazoles, such as benzotriazole, tolutriazoles and bisbenzotriazoles, amino-triazoles and alkylaminotriazoles,
- imidazoles, and
- phenol derivatives such as, for example, hydroquinone, pyrocatechol, hydroxyhydroquinone, gallic acid, phloroglucinol or pyrogallol.

[0055] Example of triazoles include triazole, aminotriazole, alkyltriazole, benzotriazole, tolyltriazole, also referred to as methyl-1H-benzotriazole or tolutriazole (CAS-Nummer: 29385-43-1) and dibenzotriazole. Example of imidazole compounds include imidazole, 2-ethyl-imidazole, 2-propyl-imidazole, 8-octyl-imidazole, 1-ethyl-4-methyl-imidazole, 2-ethyl-4-methyl-imidazole, 2-amino-3-(1H-imidazol-4-yl)propanoic acid (histidine), 4-methyl-1-p-tolylimidazole, 2-methyl-benzimidazole, benzimidazole and 5-nitro-benzimidazole.

[0056] Amongst conventional metal corrosion inhibitors preference is given to the aforementioned triazoles and imidazoles, in particular to benzotriazoles, such as benzotriazole or tolyltriazole, and imidazoles, such as benzimidazole.

[0057] Generally, the amount of conventional metal corrosion inhibitors may be contained in ADW formulation used in combination with the graft copolymers defined herein in an amount in the range of 0.001 to 2.0% by weight, in particular in the range of 0.01 to 1.0% by weight or 0.01 to 0.5% by weight, based on the total weight of the ADW formulation.

Frequently, the presence of the graft copolymers in the automatic dishwashing allows for reducing the amount of conventional metal corrosion inhibitors by an amount of at least 10% in particular at least 20% or at least 40%, based on the amount of conventional metal corrosion inhibitors typically present in the ADW composition, without significant deterioration of corrosion inhibition.

[0058] For the use and methods of the graft copolymers defined herein in automatic dishwashing, the graft copolymers may be dosed separately to the automatic dishwashing process, i. e. the automatic dishwashing formulation and the graft copolymer are dosed in separate dosage forms.

[0059] Preferably, the graft copolymers are included into the automatic dishwashing formulation used for automatic dishwashing. The amount of the graft copolymer in the ADW formulation is typically in the range of 0.1 to 5% by weight, in particular in the range of 0.2 to 4% by weight and especially in the range of 0.5 to 3% by weight, based on the total weight of the ADW formulation.

[0060] In addition to the graft copolymer, the automatic dishwashing formulations contain the conventional ingredients typically contained in automatic dishwashing formulations. Typical ingredients of ADW formulations are complexing agents, in particular non-phosphate complexing agents,

[0061] The automatic dishwashing formulations typically contain one or more complexing agents. Typically, the complexing agents comprise at least one non-phosphate complexing agent, in particular at least one complexing agent selected from the group of (poly)amino carboxylates. It is also preferred that the ADW formulations contain a combination of at least one non-phosphate complexing agent selected from the group of (poly)amino carboxylates and citric acid. In particular, the (poly)amino carboxylates contained in the ADW formulation are selected from methylglycine *N,N*-diacetic acid (MGDA), glutamic acid *N,N*-diacetic acid (GLDA), ethylenediamine-*N,N*-disuccinic acid (EDDS), iminodisuccinic acid (IDS) and combinations thereof and the salts thereof, in particular the alkalimetal salts thereof and especially the sodium salts thereof. Especially, the ADW formulation contains the (poly)amino carboxylates in the form of their alkalimetal salts, in particular their sodium salts, such as the trisodium salt of MGDA, the tetrasodium salt of GLDA, the tetrasodium salt of EDDS and the tetrasodium salt of IDS and combinations thereof. It is also preferred that the ADW formulation contains a combination of at least one (poly)amino carboxylate in the form of its alkalimetal salt, in particular its sodium salt, such as the trisodium salt of MGDA, the tetrasodium salt of GLDA, the tetrasodium salt of EDDS and the tetrasodium salt of IDS and citric acid or a salt thereof, in particular in combination with an alkalimetal salt of citric acid, such as the trisodium salts of citric acid.

[0062] The amount of the non-phosphate complexing agent in the ADW formulation is typically in the range of 2 to 60% by weight, in particular in the range of 5 to 45% by weight, based on the total weight of the ADW formulation.

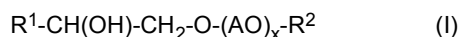
[0063] The weight ratio of the complexing agent to the graft copolymer in the ADW formulation is generally at least 2:1, in particular at least 5:1, e.g. in the range of 2:1 to 100:1 or in the range of 5:1 to 100:1.

[0064] Typically, the automatic dishwashing formulation contains at least one surfactant. The surfactant may be non-ionic, zwitterionic/amphoteric or anionic. In particular, the automatic dishwashing formulation contains at least one non-ionic surfactant or at least one non-ionic surfactant in combination with one or more surfactants selected from anionic and zwitterionic surfactants.

[0065] The amount of the surfactant in the ADW formulation is typically in the range of 0.1 to 60% by weight, in particular in the range of 0.5 to 25% by weight and especially in the range of 1 to 10% by weight, based on the total weight of the ADW formulation.

[0066] Examples of suitable non-ionic surfactants are alkoxyated alcohols, di- and multiblock copolymers of ethylene oxide and propylene oxide and reaction products of sorbitan with ethylene oxide or propylene oxide, alkyl polyglycosides (APG), hydroxyalkyl mixed ethers and amine oxides.

[0067] Preferred non-ionic surfactants to be employed in ADW formulations within the context of the present invention are disclosed within WO 2019/197315. Such non-ionic surfactants are also called mixed hydroxymethylethers or "HME" or "HME ethers". The non-ionic surfactant according to general formula (I) is defined as follows



wherein:

- R^1 selected from C_4 - C_{30} -alkyl, straight-chain or branched, and from C_4 - C_{30} -alkylene, straight-chain or branched, with at least one C-C double bond,
- R^2 selected from C_1 - C_{30} -alkyl, straight-chain or branched, and from C_2 - C_{30} -alkylene, straight-chain or branched, with at least one C-C double bond,
- x being in the range of 1 to 100,
- AO identical or different alkylene oxides, selected from CH_2-CH_2-O , $(CH_2)_3-O$, $(CH_2)_4-O$, $CH_2CH(CH_3)-O$, $CH(CH_3)-CH_2-O$ and $CH_2CH(n-C_3H_7)-O$.

[0068] Within the above-mentioned definition of the HME ethers according to general formula (I), it is preferred that the respective variables/substituents are defined as follows

- R^1 is selected from C_4 - C_{30} -alkyl, straight-chain or branched, and from C_4 - C_{30} -alkylene, straight-chain or branched, with at least one C-C double bond, preferred is C_4 - C_{30} -alkyl, straight-chain or branched, more preferred is straight-chain C_4 - C_{30} -alkyl and even more preferred is n - C_{10} - C_{12} -alkyl,
- R^2 is selected from C_1 - C_{30} -alkyl, straight-chain or branched, and from C_2 - C_{30} -alkylene, straight-chain or branched, with at least one C-C double bond, preferred is C_6 - C_{20} -alkyl, more preferred is C_8 - C_{11} -alkyl,
- x is in the range of 1 to 100, preferably in the range of 5 to 60, more preferably in the range of 10 to 50, and even more preferably in the range of 20 to 40,
- AO is selected from identical or different alkylene oxides, selected from CH_2 - CH_2 -O, $(CH_2)_3$ -O, $(CH_2)_4$ -O, $CH_2CH(CH_3)$ -O, $CH(CH_3)$ - CH_2 -O- and $CH_2CH(n-C_3H_7)$ -O. Preferred example of AO is CH_2 - CH_2 -O (EO).

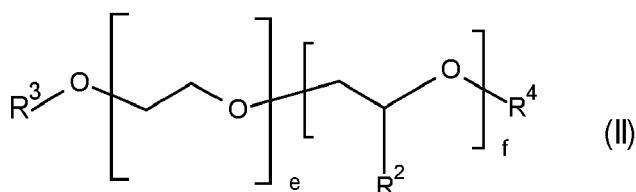
[0069] In one embodiment of the present invention, $(AO)_x$ is selected from $(CH_2CH_2O)_{x1}$, $x1$ being in the range of 1 to 50.

[0070] In one embodiment of the present invention, $(AO)_x$ is selected from $-(CH_2CH_2O)_{x2}-(CH_2CH(CH_3)-O)_{x3}$ and $-(CH_2CH_2O)_{x2}-(CH(CH_3)CH_2-O)_{x3}$, $x2$ and $x3$ being identical or different and in the range of 1 to 30.

[0071] In one embodiment of the present invention, $(AO)_x$ is selected from $-(CH_2CH_2O)_{x4}$, $x4$ = being in the range of 10 to 50, AO being EO, and R^1 and R^2 each being independently selected from C_8 - C_{14} -alkyl.

[0072] In the context of the present invention, x or $x1$ or $x2$ or $x3$ or $x4$ are to be understood as average values, the number average being preferred. Therefore, each x or $x1$ or $x2$ or $x3$ or $x4$ - if applicable - can refer to a fraction although a specific molecule can only carry a whole number of alkylene oxide units.

[0073] Preferred examples of alkoxyated alcohols and alkoxyated fatty alcohols are, for example, compounds of the general formula (II)



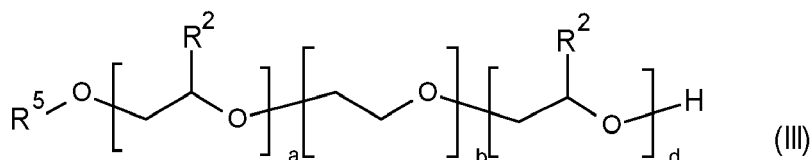
in which the variables are defined as follows:

- R^2 is identical or different and selected from hydrogen and linear C_1 - C_{10} -alkyl, preferably in each case identical and ethyl and particularly preferably hydrogen or methyl,
- R^3 is selected from C_8 - C_{22} -alkyl, branched or linear, for example n - C_8H_{17} , n - $C_{10}H_{21}$, n - $C_{12}H_{25}$, n - $C_{14}H_{29}$, n - $C_{16}H_{33}$ or n - $C_{18}H_{37}$,
- R^4 is selected from C_1 - C_{10} -alkyl, methyl, ethyl, n -propyl, isopropyl, n -butyl, isobutyl, sec-butyl, tert-butyl, n -pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, isoamyl, n -hexyl, isohexyl, sec-hexyl, n -heptyl, n -octyl, 2-ethylhexyl, n -nonyl, n -decyl or isodecyl,

[0074] The variables e and f are in the range of zero to 300, where the sum of e and f is at least one, preferably in the range of 3 to 50. Preferably, e is in the range of 1 to 100 and f is in the range of 0 to 30.

[0075] In one embodiment, compounds of the general formula (I) may be block copolymers or random copolymers, preference being given to block copolymers.

[0076] Other preferred examples of alkoxyated alcohols are, for example, compounds of the general formula (III)



in which the variables are defined as follows:

- R^2 is identical or different and selected from hydrogen and linear C_1 - C_4 -alkyl, preferably identical in each case and

ethyl and particularly preferably hydrogen or methyl,

R^5 is selected from C_6 - C_{20} -alkyl, branched or linear, in particular n - C_8H_{17} , n - $C_{10}H_{21}$, n - $C_{12}H_{25}$, n - $C_{13}H_{27}$, n - $C_{15}H_{31}$, n - $C_{14}H_{29}$, n - $C_{16}H_{33}$, n - $C_{18}H_{37}$,

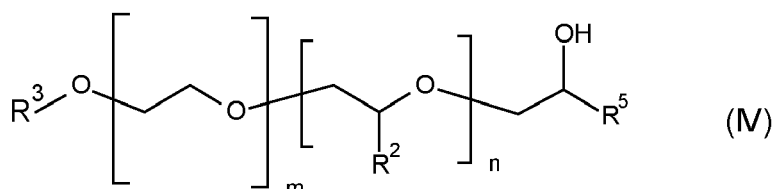
a is a number in the range of zero to 10, preferably in the range of 1 to 6,

b is a number in the range of 1 to 80, preferably in the range of 4 to 20,

d is a number in the range of zero to 50, preferably 4 to 25.

[0077] The sum $a + b + d$ is preferably in the range of 5 to 100, even more preferably in the range of 9 to 50.

[0078] Preferred examples for hydroxyalkyl mixed ethers are compounds of the general formula (IV)



[0079] in which the variables are defined as follows:

R^2 is identical or different and selected from hydrogen and linear C_1 - C_{10} -alkyl, preferably in each case identical and ethyl and particularly preferably hydrogen or methyl,

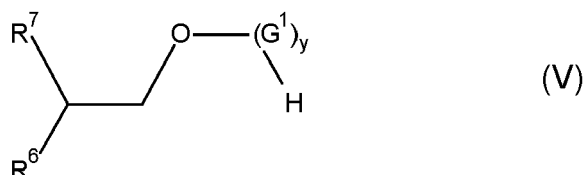
R^3 is selected from C_8 - C_{22} -alkyl, branched or linear, for example iso- $C_{11}H_{23}$, iso- $C_{13}H_{27}$, n - C_8H_{17} , n - $C_{10}H_{21}$, n - $C_{12}H_{25}$, n - $C_{14}H_{29}$, n - $C_{16}H_{33}$ or n - $C_{18}H_{37}$,

R^5 is selected from C_6 - C_{20} -alkyl, for example n -hexyl, isohexyl, sec-hexyl, n -heptyl, n -octyl, 2-ethylhexyl, n -nonyl, n -decyl, isodecyl, n -dodecyl, n -tetradecyl, n -hexadecyl, and n -octadecyl.

[0080] The variables m and n are in the range of zero to 300, where the sum of n and m is at least one, preferably in the range of 5 to 50. Preferably, m is in the range of 1 to 100 and n is in the range of 0 to 30.

[0081] Compounds of the general formula (III) and (IV) may be block copolymers or random copolymers, preference being given to block copolymers.

[0082] Further suitable non-ionic surfactants are selected from di- and multiblock copolymers, composed of ethylene oxide and propylene oxide. Further suitable nonionic surfactants are selected from ethoxylated or propoxylated sorbitan esters. Amine oxides or alkyl polyglycosides, especially linear C_4 - C_{16} -alkyl polyglucosides and branched C_8 - C_{14} -alkyl polyglycosides such as compounds of general average formula (V) are likewise suitable.



wherein:

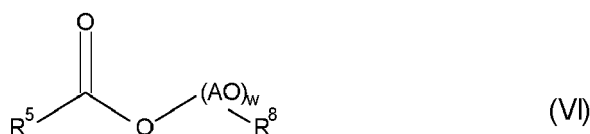
R^6 is C_1 - C_4 -alkyl, in particular ethyl, n -propyl or isopropyl,

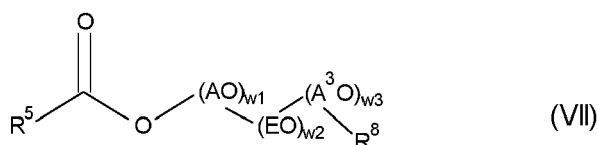
R^7 is $-(CH_2)_2-R^6$,

G^1 is selected from monosaccharides with 4 to 6 carbon atoms, especially from glucose and xylose,

y in the range of 1.1 to 4, y being an average number,

[0083] Further examples of non-ionic surfactants are compounds of general formula (VI) and (VII)





- AO is selected from ethylene oxide, propylene oxide and butylene oxide,
 EO is ethylene oxide, $\text{CH}_2\text{CH}_2\text{-O}$,
 R^8 selected from $\text{C}_8\text{-C}_{18}$ -alkyl, branched or linear, and R^5 is defined as above.
 A^3O is selected from propylene oxide and butylene oxide,
 w is a number in the range of 15 to 70, preferably 30 to 50,
 w1 and w3 are numbers in the range of 1 to 5, and
 w2 is a number in the range of 13 to 35.

[0084] An overview of suitable further nonionic surfactants can be found in EP-A 0 851 023 and in DE-A 198 19 187.

[0085] Mixtures of two or more different non-ionic surfactants selected from the foregoing may also be present.

[0086] Other surfactants that may be present are selected from amphoteric (zwitterionic) surfactants and anionic surfactants and mixtures thereof.

[0087] Examples of amphoteric surfactants are those that bear a positive and a negative charge in the same molecule under use conditions. Preferred examples of amphoteric surfactants are so-called betaine-surfactants. Many examples of betaine-surfactants bear one quaternized nitrogen atom and one carboxylic acid group per molecule. A particularly preferred example of amphoteric surfactants is cocamidopropyl betaine (lauramidopropyl betaine).

[0088] Examples of amine oxide surfactants are compounds of the general formula (VIII)



wherein R^9 , R^{10} , and R^{11} are selected independently from each other from aliphatic, cycloaliphatic or $\text{C}_2\text{-C}_4$ -alkylene $\text{C}_{10}\text{-C}_{20}$ -alkylamido moieties. Preferably, R^9 is selected from $\text{C}_8\text{-C}_{20}$ -alkyl or $\text{C}_2\text{-C}_4$ -alkylene $\text{C}_{10}\text{-C}_{20}$ -alkylamido and R^{10} and R^{11} are both methyl.

[0089] A particularly preferred example is lauryl dimethyl aminoxide, sometimes also called lauramine oxide. A further particularly preferred example is cocamidylpropyl dimethylaminoxide, sometimes also called cocamidopropylamine oxide.

[0090] Examples of suitable anionic surfactants are alkali metal and ammonium salts of $\text{C}_8\text{-C}_{18}$ -alkyl sulfates, of $\text{C}_8\text{-C}_{18}$ -fatty alcohol polyether sulfates, of sulfuric acid half-esters of ethoxylated $\text{C}_4\text{-C}_{12}$ -alkylphenols (ethoxylation: 1 to 50 mol of ethylene oxide/mol), $\text{C}_{12}\text{-C}_{18}$ sulfo fatty acid alkyl esters, for example of $\text{C}_{12}\text{-C}_{18}$ sulfo fatty acid methyl esters, furthermore of $\text{C}_{12}\text{-C}_{18}$ -alkylsulfonic acids and of $\text{C}_{10}\text{-C}_{18}$ -alkylarylsulfonic acids. Preference is given to the alkali metal salts of the aforementioned compounds, particularly preferably the sodium salts.

[0091] Further examples for suitable anionic surfactants are soaps, for example the sodium or potassium salts of stearic acid, oleic acid, palmitic acid, ether carboxylates, and alkylether phosphates.

[0092] In a preferred embodiment of the present invention, the surfactant contained in the ADW formulation comprises at least one nonionic surfactant in an amount of at least 95% by weight, based on the total weight of the surfactant contained in the ADW formulation.

[0093] In a particular preferred embodiment of the present invention, the surfactant contained in the ADW formulation comprises at least one nonionic surfactant in an amount of at least 95% by weight, based on the total weight of the surfactant contained in the ADW formulation, wherein the non-ionic surfactant is selected from the non-ionic surfactants of the formula (VII).

[0094] The ADW formulations typically comprise a further component, which is at least one bleaching agent. Bleaching agents as such are known to a person skilled in the art. Bleaching agents are also referred to as bleach. The bleaching agent may comprise besides the bleach as such at least one bleach catalyst and/or at least one bleach activator. The total amount of bleaching agents in the ADW formulation, i. e. the total amount of bleach and the optional bleach activator and/or bleaching agent, is typically in the range of 0.1 to 30% by weight, in particular in the range of 2 to 20% by weight, based on the total weight of the ADW formulation.

[0095] Bleaches include e. g. chlorine bleach and peroxide bleach. Peroxide bleach may be for example inorganic peroxide bleach and organic peroxide bleach. Preferred are inorganic peroxide bleaches, in particular inorganic peroxide bleaches selected from alkali metal percarbonate, alkali metal perborate and alkali metal persulfate. Liquid peroxide bleaches preferably do not contain both bleaching agent and enzyme.

[0096] Examples of organic peroxide bleaches are organic percarboxylic acids, especially organic percarboxylic acids.

[0097] Alkali metal percarbonates, especially sodium percarbonates, are preferably used in coated form. Such coatings

may be of organic or inorganic nature. Examples are glycerol, sodium sulfate, silicate, sodium carbonate, and combinations of at least two of the foregoing, for example combinations of sodium carbonate and sodium sulfate.

[0098] Suitable chlorine-containing bleaches are, for example, 1,3-dichloro-5,5-dimethylhydantoin, N-chlorosulfamide, chloramine T, chloramine B, sodium hypochlorite, calcium hypochlorite, magnesium hypochlorite, potassium hypochlorite, potassium dichloroisocyanurate and sodium dichloroisocyanurate.

[0099] The ADW formulations may comprise, for example, in the range from 1 to 10% by weight of chlorine-containing bleach and/or a peroxide bleach.

[0100] The ADW formulations may comprise one or more bleach catalysts. Bleach catalysts include e. g. bleach-boosting transition metal salts or transition metal complexes such as, for example, manganese-, iron-, cobalt-, ruthenium- or molybdenum-salen complexes or carbonyl complexes. Manganese, iron, cobalt, ruthenium, molybdenum, titanium, vanadium and copper complexes with nitrogen-containing tripod ligands and also cobalt-, iron-, copper- and ruthenium-amine complexes can also be used as bleach catalysts.

[0101] The ADW formulations may comprise one or more bleach activators, for example N-methylmorpholinium-acetonitrile salts ("MMA salts"), trimethylammonium acetonitrile salts, N-acylimides such as, for example, N-nonanoyl-succinimide, 1,5-diacetyl-2,2-dioxohexahydro-1,3,5-triazine ("DADHT") or nitrile quats (trimethylammonium acetonitrile salts). Further examples of suitable bleach activators are tetraacetythylenediamine (TAED) or tetraacetylhexylenediamine.

[0102] It is preferred that the ADW formulation contains at least one bleaching agent comprising

- i) a chlorine bleach and/or preferably a peroxide bleach, where the peroxide bleach in particular comprises at least one inorganic peroxide bleach, most preferably, at least one alkali metal percarbonate,
- ii) a bleach catalyst, and/or
- iii) at least one bleach activator, the at least one bleach activator is preferably selected from tetraacetythylenediamine (TAED) and tetraacetylhexylenediamine.

[0103] The weight ratio of bleach to bleach catalyst and/or bleach activator is preferably in the range of 100:1 to 2:1.

[0104] The ADW composition may contain one or more polymeric carboxylic acids. These polymeric carboxylic acids are frequently used as organic polymeric builders in ADW formulations and improve the cleaning activity, e. g. by acting as dispersants and/or by inhibiting scaling.

[0105] The total amount of polymeric carboxylic acids in the ADW formulation is typically in the range of 0.1 to 10% by weight, in particular in the range of 2 to 7% by weight, based on the total weight of the ADW formulation.

[0106] The polymeric carboxylic acids are in particular selected from the group consisting of homo- and copolymers of acrylic acid, polyaspartic acid, modified polyaspartic acid, polyepoxy succinic acid (Cas No. 51274-37-4) and combinations thereof and the salts thereof, in particular the alkalimetal salts thereof, e. g. the sodium salts thereof.

[0107] In one embodiment of the present invention, the polymeric carboxylic acids comprises at least one homo- or copolymer of acrylic acid. Examples of suitable comonomers are methacrylic acid, monoethylenically unsaturated dicarboxylic acids such as maleic acid, fumaric acid, maleic anhydride, itaconic acid and citraconic acid, monoethylenically unsaturated sulfonic acids and monoethylenically unsaturated phosphonic acids and the salts thereof, in particular their alkalimetal salts, e. g. the sodium salts thereof. Examples of monoethylenically unsaturated sulfonic acids are 1-acrylamido-1-propanesulfonic acid, 2-acrylamido-2-propanesulfonic acid, 2-acrylamido-2-methylpropane-1-sulfonic acid (AMPS), 2-methacrylamido-2-methylpropanesulfonic acid, 3-methacrylamido-2-hydroxypropanesulfonic acid, allylsulfonic acid, methallylsulfonic acid, allyloxybenzenesulfonic acid, methallyloxybenzenesulfonic acid, 2-hydroxy-3-(2-propenyloxy)propanesulfonic acid, 2-methyl-2-propene-1-sulfonic acid, styrenesulfonic acid, vinylsulfonic acid, 3-sulfopropyl acrylate, 2-sulfoethyl methacrylate, 3-sulfopropyl methacrylate, sulfomethacrylamide, sulfomethylmethacrylamide, and salts of said acids, such as sodium, potassium or ammonium salts thereof. An example of a monoethylenically unsaturated phosphonic acid is vinylphosphonic acid and its salts.

[0108] Preferred polymeric carboxylic acid from the group of homo- and copolymers generally have a weight average molecular weight M_w in the range of 2000 to 100000 g/mol, preferably in the range of 2500 to 80000 g/mol, in particular in the range of 3000 to 70000 g/mol.

[0109] In one further embodiment of the present invention, the polymeric carboxylic acids comprises at least one of polyaspartic acid and modified polyaspartic acid. Suitable modified polyaspartic acids and modified polyaspartic acids and their use in dishwashing formulations have been described in WO 2011/001170, WO 2015/036325 and WO 2019/211231. The preparation of such (modified) polyaspartic acids is also described, by way of example in DE 4221875.6.

[0110] Further suitable polymeric carboxylic acids are copolymers of at least one monomer from the group consisting of monoethylenically unsaturated C_3 - C_{10} -mono- or C_4 - C_{10} -dicarboxylic acids or anhydrides thereof, such as maleic acid, maleic anhydride, acrylic acid, methacrylic acid, fumaric acid, itaconic acid and citraconic acid, with at least one hydrophilic or hydrophobic monomer as listed below. Suitable hydrophobic monomers are, for example, isobutene, diisobutene,

butene, pentene, hexene and styrene, olefins with 10 or more carbon atoms or mixtures thereof, such as, for example, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, 1-docosene, 1-tetracosene and 1-hexacosene, C₂₂- α -olefin, a mixture of C₂₀-C₂₄- α -olefins and polyisobutene having on average 12 to 100 carbon atoms per molecule. Suitable hydrophilic monomers are monoethylenically unsaturated sulfonic acids, their salts, monoethylenically unsaturated phosphonic acids and their salts, and also nonionic monomers with hydroxyl function or alkylene oxide groups. By way of example, mention may be made of: allyl alcohol, isoprenol, methoxypolyethylene glycol (meth)acrylate, methoxypolypropylene glycol (meth)acrylate, methoxypolybutylene glycol (meth)acrylate, methoxypoly(propylene oxide-co-ethylene oxide) (meth)acrylate, ethoxypolyethylene glycol (meth)acrylate, ethoxypolypropylene glycol (meth)acrylate, ethoxypolybutylene glycol (meth)acrylate and ethoxypoly(propylene oxide-co-ethylene oxide) (meth)acrylate. Polyalkylene glycols here may comprise 3 to 50, in particular 5 to 40 and especially 10 to 30 alkylene oxide units per molecule.

[0111] Carboxymethyl inulin is a further example of a polymeric carboxylic acid which is suitable as an organic polymeric builder.

[0112] Moreover, amphoteric polymers can also be used as organic polymeric builders instead or in combination with polymeric carboxylic acids.

[0113] The ADW formulation typically contains least one inorganic builder. Suitable inorganic builders include sodium sulfate, sodium carbonate and silicates.

[0114] Suitable silicates are in particular sodium silicate, e. g. sodium disilicate and sodium metasilicate, potassium silicates and aluminosilicates, e. g. zeolithes, with preference given to sodium disilicates, most preferably α -Na₂Si₂O₅, β -Na₂Si₂O₅ or δ -Na₂Si₂O₅. Suitable examples of such silicates are disclosed, for example, in WO 2013/160132.

[0115] The sodium sulfate and the sodium carbonate may be used in their anhydrate form or their hydrate forms.

[0116] The total amount of inorganic builder in the ADW formulation is typically in the range of 5 to 80% by weight, in particular in the range of 5 to 50% by weight, based on the total weight of the ADW formulation.

[0117] The ADW formulations may comprise one or more enzymes. Enzymes are often used to aid the removal of stains. In most cases the enzymes react with the soiling and break it down into particles that have increased water solubility or are better dispersible in the washing liquid. The enzymes that can be used in ADW formulations include, but are not limited to, hydrolases, proteases, amylases, lipases, cellulases, mannanases, peroxidases, oxidases, xylanases, pullulanases, glucanases, pectinases, cutinases, hemicellulases, glucoamylases, phospholipases, esterases, keratanases, reductases, phenoloxidases, lipoxigenases, ligninases, tannases, pentosanases, malanases, arab-inosidases, hyaluronidases, chondroitinases, lactases or mixtures thereof. The ADW formulations may contain, for example, up to 20% by weight of one or more enzymes, preference being given to 0.1 to 10% by weight, in particular 0.2 to 5% by weight, based on the total weight of the ADW formulation. Said enzyme may be stabilized, for example with the sodium salt of at least one C₁-C₃-carboxylic acid or C₄-C₁₀-dicarboxylic acid. Preferred are formates, acetates, adipates, and succinates.

[0118] In one group of embodiments, the ADW formulations contain one or more cobuilders from the group of phosphonates as described above, in particular a hydroxyalkanephosphonate especially 1-hydroxyethane-1,1-diphosphonate (HEDP). The amount of the cobuilders from the group of phosphonates. If present in the ADW formulation, the total amount of cobuilders from the group of phosphonates is in the range of 0.01 to 12% by weight, based on the weight of the ADW formulation. In another embodiment of the invention, the total amount of the cobuilders from the group of phosphonates in the ADW formulation is less than 0.01% by weight, based on the weight of the ADW formulation.

[0119] In one group of embodiments, the ADW formulations contain one or more conventional metal corrosion inhibitor as described herein. In this group of embodiments, the conventional metal corrosion inhibitors is preferably selected from the aforementioned triazoles and imidazoles, in particular from benzotriazoles, such as benzotriazole or tolutriazoles, and imidazoles, such as benzimidazole, and combinations thereof. If present in the ADW formulation, the total amount of conventional metal corrosion inhibitors is generally in the range of 0.001 to 2% by weight, preferably in the range of 0.01 to 1% by weight, in particular in the range of 0.01 to 0.5% by weight, based on the total weight of the ADW formulation. In another embodiment of the invention, the total amount of conventional metal corrosion inhibitors in the ADW formulation is 0.01% by weight or less, based on the weight of the ADW formulation.

[0120] ADW formulations may comprise one or more alkali carriers. Alkali carriers ensure, for example, a pH of at least 8 if an alkaline pH is desired. Of suitability are, for example, the alkali metal carbonates, the alkali metal hydrogen carbonates, and alkali metal meta silicates mentioned above, and, additionally, alkali metal hydroxides. A preferred alkali metal is in each case potassium, particular preference being given to sodium.

[0121] Together with enzymes ADW formulations may comprise also enzyme stabilizing systems which may be used such as for example calcium ions, boric acid, boronic acids, propylene glycol and short chain carboxylic acids. In the context of the present invention, short chain carboxylic acids are selected from monocarboxylic acids with 1 to 3 carbon atoms per molecule and from dicarboxylic acids with 2 to 6 carbon atoms per molecule. Preferred examples are formic acid, acetic acid, propionic acid, oxalic acid, succinic acid, or adipic acid.

[0122] ADW formulations may comprise one or more further additives, such as fragrances, dyestuffs, organic solvents,

buffers and/or disintegrants for tabs.

[0123] The ADW formulations may comprise at least one zinc salt. Zinc salts may be selected from water-soluble and water-insoluble zinc salts. In this connection, within the context of the present invention, water-insoluble is used to refer to those zinc salts which, in distilled water at 25°C, have a solubility of 0.1 g/l or less. Zinc salts which have a higher solubility in water are accordingly referred to within the context of the present invention as water-soluble zinc salts.

[0124] Suitable zinc salts include e. g. zinc benzoate, zinc gluconate, zinc lactate, zinc formate, ZnCl_2 , ZnSO_4 , zinc acetate, zinc citrate, zinc glycinate, $\text{Zn}(\text{NO}_3)_2$, $\text{Zn}(\text{CH}_3\text{SO}_3)_2$ and zinc gallate, preferably ZnCl_2 , ZnSO_4 , zinc acetate, zinc citrate, $\text{Zn}(\text{NO}_3)_2$, $\text{Zn}(\text{CH}_3\text{SO}_3)_2$ and zinc gallate. In another embodiment of the present invention, the zinc salt is selected from ZnO , ZnO-aq , $\text{Zn}(\text{OH})_2$ and ZnCO_3 . Preference is given to ZnO-aq . In one embodiment of the present invention, the zinc salt is selected from zinc oxides with an average particle diameter (weight-average) in the range from 10 nm to 100 μm .

[0125] The cation in zinc salt can be present in complexed form, for example complexed with ammonia ligands or water ligands, and in particular be present in hydrated form. To simplify the notation, within the context of the present invention, ligands are generally omitted if they are water ligands.

[0126] Depending on how the pH is adjusted, zinc salt can change. Thus, it is for example possible to use zinc acetate or ZnCl_2 for preparing formulation according to the invention, but this converts at a pH of 8 or 9 in an aqueous environment to ZnO , $\text{Zn}(\text{OH})_2$ or ZnO-aq , which can be present in non-complexed or in complexed form.

[0127] In ADW formulations which are solid at room temperature the zinc salt is preferably present in the form of particles which have for example an average diameter (number-average) in the range from 10 nm to 100 μm , preferably 100 nm to 5 μm , determined for example by X-ray scattering.

[0128] Zinc salt may be present in those ADW formulations that are liquid at room temperature in dissolved or in solid or in colloidal form.

[0129] In one embodiment of the present invention, the ADW formulations comprise the zinc salt in total amount in the range of 0.05 to 0.4% by weight of, based in each case on the solids content of the formulation. Here, the fraction of zinc salt is given as zinc or zinc ions. From this, it is possible to calculate the counterion fraction.

[0130] The ADW formulations may comprise one or more antifoams such as silicone oils and paraffin oils. In one embodiment of the present invention, the ADW formulations comprise antifoam in an amount in the range 0.05 to 0.5% by weight, based on the weight of the ADW formulation.

[0131] The ADW formulations may have any product form suitable for automatic dishwashing. Suitable product forms include, but are not limited to solids forms, such as granules, powders and tablets, semi-solids, gels, pastes, liquids, water-soluble pouches, and combinations thereof. In one embodiment of the present invention the composition forms part of a multi-phase unit dose product, preferably a dual compartment water-soluble pouch, wherein one of the phases preferably comprises a main wash detergent composition or a multiphase tablet or a shaped body. Shaped bodies may be disk-like, spherical, or cuboids, especially with rounded corners. Preferred shaped bodies are tablets. Shaped are solid ADW compositions, preferably as mono-dose. Such a mono-dose may have a weight of from 8 to 30 g, preferably 10 to 20 g.

[0132] The ADW formulations may be solid, and in such embodiments they may contain some residual humidity, such as 0.01 to 10 % by weight, water. In other embodiments, ADW formulations may be liquids or gels and stored in a container made from a water-soluble polymer, for example in a pouch. Preferred water-soluble polymers are polyvinylalcohols (PVA), for example with an average molecular weight M_w in the range of from 50,000 to 150,000 g/mol and with a degree of saponification in the range of from 87 to 89 mole-%. The degree of saponification can be determined in accordance with the determination of the ester value, for example according to DIN EN ISO 3681 (2007-10).

[0133] Preferred compositions and manufacturing methods for unit dose executions are described in WO 02/42408. Any water-soluble film-forming polymer which is compatible with the compositions of the invention and which allows the delivery of the composition into the rinse cycle can be employed in the unit dose embodiment. The film should remain intact during the wash cycle and only dissolves at the beginning of or during the rinse cycle. This can be achieved by modifying the thickness of the film and/or the solubility of the film material. The solubility of the film material can be delayed by for example cross-linking the film as described in WO 02/102,955 at pages 17 and 18. Other water-soluble films designed for rinse release are described in U.S. Pat. No. 4,765,916.

[0134] The ADW formulations composition suitable herein can be dispensed from any suitable device, including but not limited to: dispensing baskets or cups, bottles (pump assisted bottles, squeeze bottles, etc.), mechanic pumps, multi-compartment bottles, capsules, multi-compartment capsules, paste dispensers, and single- and multi-compartment water-soluble pouches, and combinations thereof. For example, a multi-phase tablet, a water-soluble or water-dispersible pouch, and combinations thereof, may be used to deliver the graft copolymer to the desired substrate. The ADW formulations may take the form of an additive that is used in addition to one or more other ADW formulations. The graft copolymer may also be delivered in a rinse aid.

[0135] The graft copolymer may also be delivered to the automatic dishwashing process through solutions including but are not limited to: hot and/or cold water, wash and/or rinse liquor, and combinations thereof.

[0136] The invention also relates to methods for cleaning dishware in an automatic dishwasher, wherein said method is performed under use of at least one graft copolymer or an ADW formulation as defined above.

[0137] By consequence, the graft copolymer as defined herein and the ADW formulations containing such a graft copolymer can be employed within a process for cleaning hard surfaces, e.g., dishware, in an automatic dishwasher, hereinafter also referred to as automatic dishwashing process. The automatic dishwashing process is characterized in that it is performed under use of a graft copolymer as defined herein or an ADW formulation containing such graft copolymer.

[0138] Dishware as used hereunder includes china, polymer, metal, clay, and glassware. A process to clean dishware includes removal of all sorts of soil, like fat, proteins, starch, dyes, and more. More specifically, the term "dishware" includes articles used in the preparation, serving, consumption, and disposal of food stuffs including pots, pans, trays, pitchers, bowls, plates, saucers, cups, glasses, forks, knives, spoons, spatulas, and other glass, metal, ceramic, plastic composite articles commonly available in the institutional or household kitchen or dining room. In general, such dishware can be referred to as food or beverage contacting articles because they have surfaces which are provided for contacting food and/or beverage. When used in these automatic dishwashing process, the ADW formulations should provide effective sheeting action and low foaming properties. In addition to having the desirable properties described above, it may also be useful for ADW formulations to be biodegradable, environmentally friendly, and generally nontoxic. An ADW formulation of this type may be described as being "food grade".

[0139] The automatic dishwashing process is preferably carried out at a temperature in the range of from 30 to 65°C, more preferably 40 to 60°C. Said temperature refers to the temperature of the water being used in the automatic dishwashing process.

[0140] The automatic dishwashing process is carried out using water. The amount of water is influenced by the type of machine used and by the choice of the program. The water used may have a German hardness in the range of from zero to 25° dH, referring to the permanent hardness.

[0141] The automatic dishwashing process may be performed with a combination of two compositions of which one is an ADW formulation, and the other composition comprises a rinse-aid containing, for example, at least one non-ionic surfactant and at least one inorganic salt selected from alkali metal sulfates and alkali metal (bi)carbonates.

[0142] The present invention will now be explained in further detail with reference to the following non-limiting Examples.

EXAMPLES

[0143] The following materials were used to prepare ADW formulations:

Protease: BLAZE® EVITY® 100 T (Novozymes)

Amylase: STAINZYME® PLUS EVITY® 12 T (Novozymes)

Nonionic surfactant: $n\text{-C}_5\text{H}_{11}\text{-CH}(\text{n-C}_3\text{H}_7)\text{-CH}_2\text{-O}(\text{CH}_2\text{-CH}_2\text{-O})_{21}\text{-CH}_2\text{-CH}(\text{OH})\text{-n-C}_{10}\text{H}_{21}$, commercial product

Polyacrylic acid Na: M_w 4.000 g/mol, as a completely neutralized sodium salt, commercial product (granules)

Polyaspartic acid Na: polyaspartic acid sodium salt obtained according to WO 2019/211231 A1, Example 1 (granules).

Polymeric Carboxylate: Copolymer of 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid (sodium salt), commercial product (granules);

Sodium percarbonate: $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, commercial product

Graft copolymer 1: graft copolymer B.4 obtained according to Example I.4 of EP 3157901 (granules, may also be dosed as aqueous solution)

Graft copolymer 2: graft copolymer obtained according to EP 2138560 A1, Example 4 (granules, may also be dosed as aqueous solution)

TAED: tetraacetyl ethylene diamine (bleach activator)

$\text{Na}_2\text{Si}_2\text{O}_5$: commercial product Britesil® H 265 LC

Sodium carbonate: Na_2CO_3 (anhydrate), commercial product

MGDA- Na_3 : methylglycine diacetic acid trisodium salt (granules, active content 78 wt.-%)

Sodium sulfate: Na_2SO_4 (anhydrate, inorganic builder)

Zinc sulfate Heptahydrate

Example 1: ADW formulations F1-F5 (invention) and C1-C3 (comparative)

[0144] For each ADW formulation, the solid components were mixed. The nonionic surfactant was heated and added as a liquid onto the solid mixture. The composition of the ADW formulation is given in table 1 below:

Table 1

Example	C1	F1	F2	C2	F3	C3	F4	F5
Protease	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Amylase	1	1	1	1	1	1	1	1
Nonionic surfactant	4	4	4	4	4	4	4	4
Polyacrylic acid Na	5	5	5	-	-	-	-	-
Polyaspartic acid Na	-	-	-	5	5	-	-	-
Polymeric carboxylate	-	-	-	-	-	5	5	5
Sodium percarbonate	15	15	15	15	15	15	15	15
Graft copolymer 1	-	1	-	-	1	-	1	-
Graft copolymer 2	-	-	1	-	-	-	-	1
TAED	4	4	4	4	4	4	4	4
Na ₂ Si ₂ O ₅	2	2	2	2	2	2	2	2
Sodium carbonate	23.7	23.7	23.7	23.7	23.7	23.7	23.7	23.7
MGDA-Na ₃	40	40	40	40	40	40	40	40
Sodium sulfate	2.8	1.8	1.8	2.8	1.8	1.8	1.8	1.8
	100	100	100	100	100	100	100	100

Legend:

[0145]

C1 - C3 are comparative Examples

F1 - F5 are working Examples according to the invention

[0146] The following automatic dishwashing experiments were carried out in Miele automatic dish wash machines, type G1223 GSL2. The program R65°-55'-KI65° (65°C in the main cycle, 55 min for washing, and 65° for rinsing) was selected. No separate rinsing agent was added, no regenerating salt was used. The dish-washing experiments were carried out with demineralized water, 0°dH (German hardness). There was no dish load in the dishwasher and no ballast soil used. The metal coupons were placed in the upper rack.

[0147] Each experiment was carried out with two different types of metal (brass) coupons (Cu63-Zn37 and Cu85-Zn15). One coupon of each type was used. Before starting the test in the machine, the coupons were marked with numbers and cleaned with ethyl acetate. After drying, the weight was determined on an analytical balance. Afterwards the coupons were stored in a desiccator until the test was started.

[0148] 18 g of each ADW formulation was added in the dosage chamber of the machine. No rinse aid was used. Ten cycles were carried out for each experiment. After the 10th cycle, the coupons were taken out, rinsed with demineralized water, cleaned again with ethyl acetate and dried. Directly after drying, the weight was determined. An average weight loss per cycle was calculated (weight before test - weight after test) / 10. The contents of the components are indicated in Table 1 in [%]. The results of the experiments are summarized in table 2 below.

Table 2

Weight loss [mg / cycle]	C1	F1	F2	C2	F3	C3	F4	F5
Cu63-Zn37	40.2	25.4	21.8	43.7	28.4	42.4	33.0	29.2
Cu85-Zn15	17.4	12.4	10.7	18.5	13.2	20.6	16.5	14.5

[0149] It can be seen from Table 2 that the formulations F1 - F5 according to the invention (containing 1% of graft copolymer 1 or 2) caused less corrosion on metal surfaces than the comparative formulations C1 - C3.

Example 2: Simulation of Automatic Dishwashing

[0150] The following experiments were carried out to simulate the conditions in an automatic dishwashing process. The following materials and equipments were used:

Polymeric Carboxylate: Copolymer of 2-acrylamido-2-methylpropane sulfonic acid and acrylic acid (sodium salt), commercial product;
Complexing agent: MGDA- Na_3 (granules, active content 78 wt.-%)
Sodium carbonate: Na_2CO_3 anhydrate, commercial product
Graft copolymer 1: graft copolymer B.4 obtained according to Example I.4 of EP 3157901
Graft copolymer 2: graft copolymer obtained according to EP 2138560 A1, Example 4
Corrosion Inhibitor 1: Benzotriazole, Irgamet BTZ
Corrosion Inhibitor 2: Tolutriazole, Irgamet TTZ
Corrosion Inhibitor 3: Benzimidazole

[0151] The experiments were carried out in 100 ml glass beakers placed in a stirrable block thermostate. Brass coupons (Cu63-Zn37) were used.

[0152] The test solutions were prepared by dissolving the respective ingredients in the following amounts in 0.5 dH water.

1 g/L complexing agent
0.6g/L sodium carbonate
0.05g/L polymeric Carboxylate
0.02g/L graft copolymer 1 or 2
0.01g/L or 0.005g/L corrosion inhibitor 1, 2 or 3

[0153] The brass coupons were cleaned/degreased in an ethyl acetate bath for 30 minutes at 22°C. Afterwards they were rubbed dry. Before starting the experiment, the coupons were weighed with the analytical balance. The brass coupons were placed in the center of the 100ml glass beaker and 80ml of test solution was poured over them. The beakers were then placed in the block thermostat at 50°C and stirred at 600 rpm for 5h. Then, the brass coupons were rinsed with deionized water and dried with compressed air. The completely dried coupons were then weighed on the analytical balance and the removal in mg is determined with the tare weight. The results are summarized in the following table 3:

Table 3:

Exp.	graft-copolymer	Corrosion inhibitor	Weight loss of Coupon		
			[g/L]	[mg]	[%]
C4*	-	-	-	0.56	0.069
F6	1	-	-	0.36	0.044
F7	2	-	-	0.37	0.046
F8	1	1	0.01	0.11	0.014
F9	2	1	0.01	0.06	0.007
F10	1	2	0.01	0.00	0.000
F11	2	2	0.01	0.01	0.001
F12	1	3	0.01	0.05	0.006
F13	2	3	0.01	0.04	0.005
F14	1	1	0.005	0.12	0.015
F15	2	1	0.005	0.12	0.015
F16	1	2	0.005	0.02	0.002

(continued)

Exp.	graft-copolymer	Corrosion inhibitor	Weight loss of Coupon		
			[g/L]	[mg]	[%]
F17	2	2	0.005	0.02	0.002
* Comparative experiment					

Example 3: ADW compositions F19-F22 (invention) and C5-C6 (comparative)

[0154] The ADW compositions F19-F22 and C5-C6 were prepared as described for example 1. The recipe is given in the following table 4.

Table 4:

Example	C5	F19	F20	C6	F21	F22
Protease	2.5	2.5	2.5	2.5	2.5	2.5
Amylase	1	1	1	1	1	1
Nonionic surfactant	4	4	4	4	4	4
Polyacrylic acid Na	5	5	5	5	5	5
Zinc sulfate-Heptahydrate	-	-	-	0,2	0,2	0,2
Sodium percarbonate	15	15	15	15	15	15
Graft copolymer 1	-	1	-	-	1	-
Graft copolymer 2	-	-	1	-	-	1
TAED	4	4	4	4	4	4
Na ₂ Si ₂ O ₅	2	2	2	2	2	2
HEDP	0.8	0.8	0.8	0.8	0.8	0.8
Sodium carbonate	23.7	23.7	23.7	23.7	23.7	23.7
MGDA-Na ₃	40	40	40	40	40	40
Sodium sulfate	1	1	1	1	1	1

[0155] For the glass corrosion experiments three types of glasses were used: Champagne glass Gilde, shot glass Intermezzo (not decorated) and decorated glass "Die Maus", all of Fa. Libbey, Netherlands. The glasses were precleaned in a Miele GSL 2 machine with the program R50°-8'-KI65° one cycle with 1 g Plurafac SLF 18 (nonionic surfactant) and second cycle with 30 g of citric acid monohydrate both with soft water (0°dH).

[0156] The glass corrosion experiments were carried out in Miele automatic dish wash machines, type G1223 GSL2. The program R65°-30'-KI65° (65°C in the main cycle, 30 min for washing, and 65° for rinsing) was selected. No separate rinsing agent was added, no regenerating salt was used. The dish-washing experiments were carried out with demineralized water, 0°dH (German hardness). The glasses (three of each type) were placed in the upper basket of the machine. The machines were started with 18 g formulation per cycle for 50 times. Between cycles the machine doors were opened for 50 min. After drying after the last cycle the glasses were weighed again to determine the weight loss of the glass. The results are summarized in the following tables 5 and 6.

Table 5: Weight loss after 50 automatic dishwashing cycles ¹⁾

	shot glass "Intermezzo" (mg)	champagne glass "Gilde" (mg)	decor glass "Die Maus" (mg)
C5	79.7	140.0	388.0
F19	46.3	79.3	217.0
F20	42.7	77.0	197.1

(continued)

	shot glass "Intermezzo" (mg)	champagne glass "Gilde" (mg)	decor glass "Die Maus" (mg)
C6	78.0	138.7	403.0
F21	42.3	73.7	203.0
F22	41.3	69.0	169.0
1) The given weight loss is the average of the differences in weight between before and after test per glass type.			

[0157] Inventive ADW formulation F19-F22 show clearly less weight loss than comparative ADW formulations C5 and C6.

[0158] The decor of glasses "Die Maus" were evaluated visually after 50 cycles with a rating from 1 to 5 (1 = strong discoloration / fading, 5 = no discoloration / fading). The results are the average visual appearance of the three glasses used in the respective experiment. The results are summarized in table 6.

Table 6: Results of visual evaluation of decorated glass

	Rating
C1	2.0
F1	3.5
F2	4.5
C5	2.0
F19	4.5
F20	4,5

Claims

1. The use of a graft copolymer comprising:

a) at least one graft base selected from nonionic mono-, di-, oligo- and polysaccharides,
b) and polymeric side chains P obtainable by grafting ethylenically unsaturated monomers M onto the graft base, where the monomers M comprise

b1) at least one monomer b1 selected from monoethylenically unsaturated mono- and dicarboxylic acids; and
b2) at least one monomer b2 selected from ethylenically unsaturated monomers having a permanent cationic charge;

for reducing surfaces corrosion in an automatic dishwashing process.

2. A method for reducing surfaces corrosion in an automatic dishwashing process which comprises carrying out the process in the presence of a graft copolymer comprising:

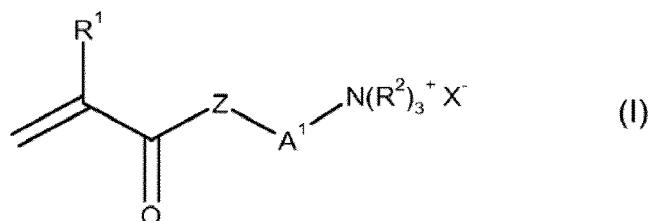
a) at least one graft base selected from nonionic mono-, di-, oligo- and polysaccharides,
b) and polymeric side chains P obtainable by grafting ethylenically unsaturated monomers M onto the graft base, where the monomers M comprise

b1) at least one monomer b1 selected from monoethylenically unsaturated mono- and dicarboxylic acids; and
b2) at least one monomer b2 selected from ethylenically unsaturated monomers having a permanent cationic charge.

3. The use of claim 1 or the method of claim 2, wherein the graft base is selected from starch and starch degradation products, and where the graft base is in particular a maltodextrin.

4. The use or method of any one of the preceding claims where the monomer b.1 is selected from monoethylenically unsaturated monocarboxylic acids having 3 to 6 carbon atoms and in particular from acrylic acid, methacrylic acid and combinations thereof.

5. The use or method of any one of the preceding claims where the monomer b.2 is selected from monomers of the formula (I)



where

Z is O or NH,

A¹ is C₂-C₄-alkandiyl

R¹ is H or methyl

R² are identical or different and selected from C₁-C₄-alkyl

X is a counter ion, which is in particular selected from halide, mono-C₁-C₄-alkyl sulfate and sulfate.

6. The use or method of any one of the preceding claims where the graft copolymer comprises, based on the total weight of the graft copolymer,

a) 40 to 95% by weight of the graft base;

b1) 2 to 40% by weight of at least one monomer b1; and

b2) 3 to 50% by weight of at least one monomer b2;

where the weight ratio of the monomer b2 to the monomer b1 is preferably > 1.

7. The use or method of any one of the preceding claims where the polymer P of the graft copolymer contains the polymerized monomers b1 and b2 in an amount of at least 95% by weight, based on the total amount of polymerized monomers M.

8. The use or method of any one of the preceding claims where the graft copolymer is used in combination with a formulation for automatic dishwashing which comprises a complexing agent selected from the group consisting of methylglycine *N,N*-diacetic acid (MGDA), glutamic acid *N,N*-diacetic acid (GLDA), ethylenediamine-*N,N*-disuccinic acid (EDDS), iminodisuccinic acid (IDS), ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA) and combinations thereof and the salts thereof.

9. The use or method of claim 8, where the graft copolymer is used in such an amount that the weight ratio of the complexing agent to the graft copolymer is at least 2:1, e. g. in the range of 2:1 to 100.

10. The use or method any one of the preceding claims, where the graft copolymer is used in the absence of phosphates and phosphonates.

11. The use or method of any of any one of the preceding claims, where the graft copolymer is contained in the formulation for automatic dishwashing.

12. The use or method of any of claims 9 to 11, where the formulation for automatic dishwashing contains at least one polymeric carboxylic acid, which is in particular selected from the group consisting homo- and copolymers of acrylic acid, polyaspartic acid, modified polyaspartic acid, polyepoxy succinic acid and combinations thereof and the salts thereof, in particular the alkalimetal salts thereof, e. g. the sodium salts thereof.

13. The use or method of any one of claims 9 to 12, where the formulation for automatic dishwashing contains a bleach

and optionally a bleach activator.

14. The use or method of any one of claims 9 to 13, where the formulation for automatic dishwashing contains at least one non-ionic surfactant.

15. The use or method of any one of claims 9 to 14, where the formulation for automatic dishwashing contains, based on the total weight of the formulation,

- (i) 0.1 to 5% by weight of at least one of the graft copolymers;
- (ii) 2 to 60% by weight of at least one non-phosphate complexing agent;
- (iii) 0.1 to 60% by weight of at least one nonionic surfactant;
- (iv) 0.1 to 30% by weight of at least one bleaching agent;
- (v) 0.1 to 10% by weight of at least one of the polymeric carboxylic acids;
- (vi) 5 to 80% of at least one inorganic builder; and
- (vii) 0 to 20% by weight of one or more enzymes.

16. The use or method of any one of claims 9 to 15, where the formulation for automatic dishwashing contains an anti-corrosive compound from the group of triazoles and imidazoles in an amount of 0.01 to 1.0% by weight, based on the total weight of the formulation.

17. The use or method of any one of claims 9 to 16, where the formulation for automatic dishwashing is essentially free of phosphates and phosphonates.



EUROPEAN SEARCH REPORT

Application Number

EP 23 16 0371

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EPO FORM 1503 03.82 (P04C01)

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	US 2021/238504 A1 (DETERING JUERGEN [DE] ET AL) 5 August 2021 (2021-08-05) * examples 2-3; tables 1-3 * * paragraphs [0177] - [0179], [0202] - [0229] *	1-17	INV. C11D3/00 C11D3/37 C11D11/00
X	US 8 674 021 B2 (RODRIGUES KLIN A [US]; SANDERS JANNIFER [US]; AKZO NOBEL NV [NL]) 18 March 2014 (2014-03-18) * examples 1, 18 * * column 9, line 2 - line 16 * * column 12, line 32 - line 43 * * column 21, line 3 - line 23 * * column 24, line 29 - column 25, line 4 * * column 32, line 1 - line 16 *	1-7, 9-13,17	
A	EP 0 725 093 A2 (BASF AG) 7 August 1996 (1996-08-07) * page 3, line 1 - line 10 *	1-17	
			TECHNICAL FIELDS SEARCHED (IPC)
			C11D
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 4 August 2023	Examiner Agra-Gutierrez, C
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	

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 23 16 0371

5 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.

04-08-2023

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2021238504 A1	05-08-2021	BR 112020021882 A2	26-01-2021
		CN 112074589 A	11-12-2020
		EP 3788125 A1	10-03-2021
		JP 7292309 B2	16-06-2023
		JP 2021522393 A	30-08-2021
		KR 20210006389 A	18-01-2021
		US 2021238504 A1	05-08-2021
		WO 2019211231 A1	07-11-2019

US 8674021 B2	18-03-2014	CA 2594195 A1	21-01-2008
		CN 103467657 A	25-12-2013
		EP 1881017 A2	23-01-2008
		US 2008020948 A1	24-01-2008

EP 0725093 A2	07-08-1996	CA 2168594 A1	04-08-1996
		DE 19503546 A1	08-08-1996
		EP 0725093 A2	07-08-1996
		JP H08239433 A	17-09-1996
		US 5658993 A	19-08-1997

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2021170637 A1 [0006]
- WO 2013160132 A1 [0007]
- EP 2138560 A1 [0018] [0040] [0143] [0150]
- WO 2015197378 A [0018] [0038] [0040]
- WO 2015197379 A [0018] [0038] [0040]
- WO 2017186524 A [0018] [0040]
- WO 2019197315 A [0067]
- EP 0851023 A [0084]
- DE 19819187 A [0084]
- WO 2011001170 A [0109]
- WO 2015036325 A [0109]
- WO 2019211231 A [0109]
- DE 4221875 [0109]
- WO 2013160132 A [0114]
- WO 0242408 A [0133]
- WO 02102955 A [0133]
- US 4765916 A [0133]
- WO 2019211231 A1 [0143]
- EP 3157901 A [0143] [0150]

Non-patent literature cited in the description

- **DZIEDZIC, S. Z. ; KEARSLEY, M. W.** Handbook of starch hydrolysis products and their derivatives. Blackie Academic & Professional, 1995, 230 [0024]
- *CHEMICAL ABSTRACTS*, 29385-43-1 [0055]