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(54) **New use of sulfonated polymers**

(57) Use of a sulfonated polymer in an automatic dishwashing detergent composition for the removal of bleachable stains from dishware in automatic dishwashing.

EP 3 050 954 A1

Description

TECHNICAL FIELD

[0001] The present invention is in the field of automatic dishwashing. In particular, it relates to the use of sulfonated polymers to provide bleaching benefits.

BACKGROUND OF THE INVENTION

[0002] The automatic dishwashing detergent formulator is continuously looking for ways to improve the performance of detergents. Items placed in a dishwasher to be washed are usually stained with different kinds of stains. Tea and coffee stains are particularly difficult to remove. The problem is more acute when the detergent is phosphate free.

[0003] Sulfonated polymers are used in automatic dishwashing to avoid filming and spotting on the washed items thereby improving the shine of the washed items.

SUMMARY OF THE INVENTION

[0004] The present invention is based on the use of a sulfonated polymer in an automatic dishwashing detergent composition. Unexpectedly, the sulfonated polymer improves the removal of bleachable stains from dishware. In particular tea stains. Preferably the composition comprises more than 1 gram of sulfonated polymer. For the purpose of this invention "dishware" means all the eaten and cooking utensils, including tableware and cookware.

[0005] For the purpose of this invention a "sulfonated polymer" is a polymer comprising sulphur in any of its forms.

[0006] The composition for the use of the invention is sometimes herein referred to as "the composition of the invention".

[0007] The composition herein is preferably phosphate free. By "phosphate-free" is herein understood that the composition comprises less than 1%, preferably less than 0.1% by weight of the composition of phosphate.

[0008] Preferably, the composition comprises an organic complexing agent. It comprises greater than about 3 to about 10, preferably greater than about 3.5 to about 9 and especially greater than about 4 to about 8 grams of complexing agent. This level of complexing agent favours the removal of bleachable stains. For the purpose of this invention 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. The complexing agent has a logarithmic stability constant ([log K]) for Ca^{2+} of at least 5, preferably at least 6. The stability constant, log K, is measured in a solution of ionic strength of 0.1, at a temperature of 25° C.

[0009] The complexing agent is preferably selected from the group consisting of methyl-glycine-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, carboxy methyl inulin, its salts and derivatives thereof and mixtures thereof. Especially preferred complexing agent for use herein is selected from the group consisting of MGDA and salts thereof, especially preferred for use herein is the sodium salt of MGDA.

[0010] Preferably the composition of the invention comprises from about 1 to about 3 grams of bleach, preferably sodium percarbonate. Preferably the composition also comprises a bleach activator, in particular TAED, and a metal bleach catalyst, in particular a manganese bleach catalyst. Also preferred are compositions comprising a crystal growth inhibitor, in particular HEDP and preferably a non-ionic surfactant.

[0011] It has been observed that some phosphate-free automatic dishwashing compositions can leave a coloured film on stainless steel items. This problem is avoided when the composition of the invention is free of citrate, thus preferred for use herein are citrate free compositions.

[0012] Preferably, the composition of the invention has a pH equal or greater than 9 to 12, more preferably equal or greater than about 10 to about 11.5 as measured in 1% weight/volume aqueous solution in distilled water at 20°C.

[0013] Preferably the composition of the present invention has a reserve alkalinity of 10 or greater, preferably 12 or greater, most preferably 14 or greater. "Reserve alkalinity", as used herein refers to, the ability of an automatic dishwashing composition to maintain an alkali pH in the presence of acid. This is relative to the ability of an automatic dishwashing composition to have sufficient alkali in reserve to deal with any added acid -coming from the water and/or the soils on the dishware- while maintaining the pH.

[0014] Preferably, the composition of the invention is in unit-dose form. By "unit-dose form" is herein meant that the composition is provided in a form sufficient to provide enough detergent for one wash. Suitable unit dose forms include tablets, sachets, capsules, pouches, etc. Preferred for use herein are compositions in unit-dose form wrapped in water-soluble material, for example polyvinyl alcohol. The detergent composition of the invention weighs from about 8 to about 25 grams, preferably from about 10 to about 20 grams. This weight range fits comfortable in a dishwasher dispenser. Even although this range amount to a low amount of detergent, the detergent has been formulated in a way that provides all the benefits mentioned herein above.

[0015] More specifically, it is defined as the grams of NaOH per 100 cc's, exceeding pH 9.5, in product. The reserve alkalinity for a solution is determined in the following manner.

[0016] A pH meter (for example An Orion Model 720A) with a Ag/AgCl electrode (for example an Orion sure flow Electrode model 9172BN) is standardized using pH 7 and pH 10 buffers. A 1% solution of the composition to be tested is prepared in distilled water. The weight of the sample is noted. The pH of the 1% solution is measured and the solution is titrated down to pH 9.5 using a solution of 0.2N HCL. The reserve alkalinity is calculated in the following fashion:

$$\text{Reserve Alkalinity} = \%\ \text{NaOH} \times \text{Specific Gravity.}$$

$$\%\ \text{NaOH} = \text{ml HCl} \times \text{Normality of HClx4'} / \text{Weight of Sample Aliquot Titrated}$$

* Equivalent weight of NaOH in the % NaOH equation,
derived from:

$$\%\ \text{NaOH} = \text{ml HCl} \times \text{Normality of HCl} \times \text{Equiv. Weight NaOH} \times 100 / 1000 \times \text{Weight of Sample Aliquot Titrated}$$

SUMMARY OF THE INVENTION

[0017] The present invention relates to the use of a sulfonated polymer in an automatic dishwashing composition to provide bleaching benefits, i.e., the removal of bleachable stains, such as tea and coffee and other coloured stains.

Detergent composition

[0018] The detergent composition of the invention can be presented in unit-dose form and it can be in any physical form including solid, liquid and gel form. The composition of the invention is very well suited to be presented in the form of a multi-compartment pack, more in particular a multi-compartment pack comprising compartments with compositions in different physical forms, for example a compartment comprising a composition in solid form and another compartment comprising a composition in liquid form. The composition is preferably enveloped by a water-soluble film such as polyvinyl alcohol. The composition comprises a sulfonated polymer and optionally a complexing agent, bleach, crystal growth inhibitor, non-ionic surfactant, etc.

[0019] The composition of the invention preferably has a pH as measured in 1% weight/volume aqueous solution in distilled water at 20°C of from about 9 to about 12, more preferably from about 10 to less than about 11.5 and especially from about 10.5 to about 11.5.

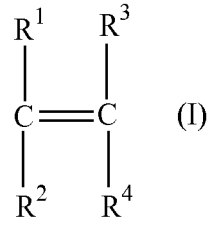
[0020] The composition of the invention preferably has a reserve alkalinity of from about 10 to about 20, more preferably from about 12 to about 18 at a pH of 9.5 as measured in NaOH with 100 grams of product at 20°C.

Sulfonated polymer

[0021] The polymer is used in any suitable amount from about 0.1% to about 30%, preferably from 0.5% to about 20%, more preferably from 1% to 10% by weight of the composition. The composition of the invention comprises preferably at least 1 gram, more preferably at least 1.5 grams of sulfonated polymer and preferably less than 5 grams of sulfonated polymer. Sulfonated/carboxylated polymers are particularly suitable for the composition of the invention.

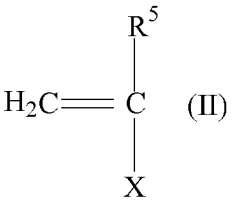
[0022] Suitable sulfonated/carboxylated polymers described herein may have a weight average molecular weight of less than or equal to about 100,000 Da, or less than or equal to about 75,000 Da, or less than or equal to about 50,000 Da, or from about 3,000 Da to about 50,000, preferably from about 5,000 Da to about 45,000 Da.

[0023] As noted herein, the sulfonated/carboxylated polymers may comprise (a) at least one structural unit derived from at least one carboxylic acid monomer having the general formula (I):



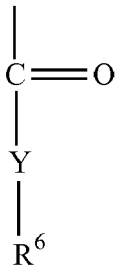
(I)

wherein R^1 to R^4 are independently hydrogen, methyl, carboxylic acid group or CH_2COOH and wherein the carboxylic acid groups can be neutralized; (b) optionally, one or more structural units derived from at least one nonionic monomer having the general formula (II):



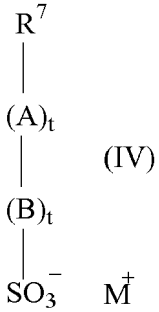
(II)

wherein R^5 is hydrogen, C_1 to C_6 alkyl, or C_1 to C_6 hydroxyalkyl, and X is either aromatic (with R^5 being hydrogen or methyl when X is aromatic) or X is of the general formula (III):



(III)

wherein R^6 is (independently of R^5) hydrogen, C_1 to C_6 alkyl, or C_1 to C_6 hydroxyalkyl, and Y is O or N; and at least one structural unit derived from at least one sulfonic acid monomer having the general formula (IV):



(IV)

wherein R7 is a group comprising at least one sp2 bond, A is O, N, P, S or an amido or ester linkage, B is a mono- or polycyclic aromatic group or an aliphatic group, each t is independently 0 or 1, and M+ is a cation. In one aspect, R7 is a C2 to C6 alkene. In another aspect, R7 is ethene, butene or propene.

[0024] Preferred carboxylic acid monomers include one or more of the following: acrylic acid, maleic acid, itaconic acid, methacrylic acid, or ethoxylate esters of acrylic acids, acrylic and methacrylic acids being more preferred. Preferred sulfonated monomers include one or more of the following: sodium (meth) allyl sulfonate, vinyl sulfonate, sodium phenyl (meth) allyl ether sulfonate, or 2-acrylamido-methyl propane sulfonic acid. Preferred non-ionic monomers include one or more of the following: methyl (meth) acrylate, ethyl (meth) acrylate, t-butyl (meth) acrylate, methyl (meth) acrylamide, ethyl (meth) acrylamide, t-butyl (meth) acrylamide, styrene, or α-methyl styrene.

[0025] Preferably, the polymer comprises the following levels of monomers: from about 40 to about 90%, preferably from about 60 to about 90% by weight of the polymer of one or more carboxylic acid monomer; from about 5 to about 50%, preferably from about 10 to about 40% by weight of the polymer of one or more sulfonic acid monomer; and optionally from about 1% to about 30%, preferably from about 2 to about 20% by weight of the polymer of one or more non-ionic monomer. An especially preferred polymer comprises about 70% to about 80% by weight of the polymer of at least one carboxylic acid monomer and from about 20% to about 30% by weight of the polymer of at least one sulfonic acid monomer.

[0026] The carboxylic acid is preferably (meth)acrylic acid. The sulfonic acid monomer is preferably one of the following: 2-acrylamido methyl-1-propanesulfonic acid, 2-methacrylamido-2-methyl-1-propanesulfonic acid, 3-methacrylamido-2-hydroxypropanesulfonic acid, allysulfonic acid, methallysulfonic acid, allyloxybenzenesulfonic acid, methallyloxybenzensulfonic acid, 2-hydroxy-3-(2-propenyloxy)propanesulfonic acid, 2-methyl-2-propene-1-sulfonic acid, styrene sulfonic acid, vinylsulfonic acid, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate, sulfomethylacrylamid, sulfomethylmethacrylamide, and water soluble salts thereof. The unsaturated sulfonic acid monomer is most preferably 2-acrylamido-2-propanesulfonic acid (AMPS).

[0027] Preferred commercial available polymers include: Alcosperse 240, Aquatreat AR 540 and Aquatreat MPS supplied by Alco Chemical; Acumer 3100, Acumer 2000, Acusol 587G and Acusol 588G supplied by Rohm & Haas; Goodrich K-798, K-775 and K-797 supplied by BF Goodrich; and ACP 1042 supplied by ISP technologies Inc. Particularly preferred polymers are Acusol 587G and Acusol 588G supplied by Rohm & Haas.

[0028] In the polymers, all or some of the carboxylic or sulfonic acid groups can be present in neutralized form, i.e. the acidic hydrogen atom of the carboxylic and/or sulfonic acid group in some or all acid groups can be replaced with metal ions, preferably alkali metal ions and in particular with sodium ions.

Complexing agent

[0029] A complexing agent is a material capable of sequestering hardness ions, particularly calcium and/or magnesium. The composition of the invention comprises greater than about 2 to about 10 grams, preferably greater than about 2 to about 8 grams of a complexing agent. The complexing agent agent is preferably selected from the group consisting of methyl-glycine-diacetic acid, its salts and derivatives thereof, glutamic-N,N-diacetic acid, its salts and derivatives thereof, iminodisuccinic acid, its salts and derivatives thereof, carboxy methyl inulin, its salts and derivatives thereof and mixtures thereof. Especially preferred complexing agent for use herein is a salt of MGDA, in particular the three sodium salt of MGDA.

Bleach

[0030] The composition of the invention preferably comprises from 1 to 3, preferably from 1.2 to 2.8 and especially from 1.5 to 2.5 grams of bleach.

[0031] Inorganic and organic bleaches are suitable for use herein. Inorganic bleaches include perhydrate salts such as perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts. The inorganic perhydrate salt may be included as the crystalline solid without additional protection. Alternatively, the salt can be coated. Suitable coatings include sodium sulphate, sodium carbonate, sodium silicate and mixtures thereof. Said coatings can be applied as a mixture applied to the surface or sequentially in layers.
Alkali metal percarbonates, particularly sodium percarbonate is the preferred bleach for use herein. The percarbonate is most preferably incorporated into the products in a coated form which provides in-product stability.
Potassium peroxymonopersulfate is another inorganic perhydrate salt of utility herein.

[0032] Typical organic bleaches are organic peroxyacids, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid, and diperoxyhexadecanedioc acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid are also suitable herein. Diacyl and Tetraacylperoxides, for instance dibenzoyl peroxide and dilauroyl peroxide, are other organic peroxides that can be used in the context of this invention.

[0033] Further typical organic bleaches include the peroxyacids, particular examples being the alkylperoxy acids and the arylperoxy acids. Preferred representatives are (a) peroxybenzoic acid and its ring-substituted derivatives, such as alkylperoxybenzoic acids, but also peroxy-α-naphthoic acid and magnesium monoperphthalate, (b) the aliphatic or substituted aliphatic peroxy acids, such as peroxylauric acid, peroxystearic acid, ε-phthalimidoperoxycaproic acid[phthaloiminoperoxyhexanoic acid (PAP)], o-carboxybenzamidoperoxycaproic acid, N-nonenylamidoperadipic acid and N-nonenylamidopersuccinates, and (c) aliphatic and araliphatic peroxydicarboxylic acids, such as 1,12-diperoxycarboxylic acid, 1,9-diperoxyazelaic acid, diperoxysebacic acid, diperoxybrassylic acid, the diperoxyphthalic acids, 2-decyldiperoxybutane-1,4-dioic acid, N,N-terephthaloyldi(6-aminopercaproic acid).
Preferably, the level of bleach in the composition of the invention is from about 0 to about 10%, more preferably from about 0.1 to about 5%, even more preferably from about 0.5 to about 3% by weight of the composition.

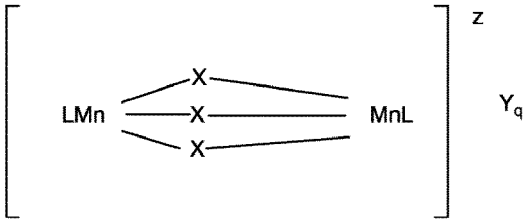
Bleach Activators

[0034] Bleach activators are typically organic peracid precursors that enhance the bleaching action in the course of cleaning at temperatures of 60° C and below. Bleach activators suitable for use herein include compounds which, under perhydrolysis conditions, give aliphatic peroxoycarboxylic acids having preferably from 1 to 12 carbon atoms, in particular from 2 to 10 carbon atoms, and/or optionally substituted perbenzoic acid. Suitable substances bear O-acyl and/or N-acyl groups of the number of carbon atoms specified and/or optionally substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, in particular tetraacetylethylenediamine (TAED), acylated triazine derivatives, in particular 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, in particular tetraacetylglycoluril (TAGU), N-acylimides, in particular N-nonanoylsuccinimide (NOSI), acylated phenolsulfonates, in particular n-nonanoyl- or isononanoyloxybenzenesulfonate (n- or iso-NOBS), decanoyloxybenzoic acid (DOBA), carboxylic anhydrides, in particular phthalic anhydride, acylated polyhydric alcohols, in particular triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran and also triethylacetyl citrate (TEAC). If present the composition of the invention comprises from 0.1 to 2, preferably from 0.2 to 1 grams of bleach activator, preferably TAED.

Bleach Catalyst

[0035] The composition herein preferably contains a bleach catalyst, preferably a metal containing bleach catalyst. More preferably the metal containing bleach catalyst is a transition metal containing bleach catalyst, especially a manganese or cobalt-containing bleach catalyst.
Bleach catalysts preferred for use herein include the manganese triazacyclononane and related complexes (US-A-4246612, US-A-5227084); Co, Cu, Mn and Fe bispyridylamine and related complexes (US-A-5114611); and pentamine acetate cobalt(III) and related complexes(US-A-4810410). A complete description of bleach catalysts suitable for use herein can be found in WO 99/06521, pages 34, line 26 to page 40, line 16.

[0036] Manganese bleach catalysts are preferred for use in the composition of the invention. Especially preferred catalyst for use here is a dinuclear manganese-complex having the general formula:



wherein Mn is manganese which can individually be in the III or IV oxidation state; each x represents a coordinating or bridging species selected from the group consisting of H2O, 022-, 02-, OH-, HO2-, SH-, S2-, >SO, Cl-, N3-, SCN-, RCOO-, NH2- and NR3, with R being H, alkyl or aryl, (optionally substituted); L is a ligand which is an organic molecule containing a number of nitrogen atoms which coordinates via all or some of its nitrogen atoms to the manganese centres; z denotes the charge of the complex and is an integer which can be positive or negative; Y is a monovalent or multivalent counter-ion, leading to charge neutrality, which is dependent upon the charge z of the complex; and q = z/[charge Y].

[0037] Preferred manganese-complexes are those wherein x is either CH_3COO^- or O^2 or mixtures thereof, most preferably wherein the manganese is in the IV oxidation state and x is O^{2-}. Preferred ligands are those which coordinate via three nitrogen atoms to one of the manganese centres, preferably being of a macrocyclic nature. Particularly preferred ligands are:

(1) 1,4,7-trimethyl-1,4,7-triazacyclononane, (Me-TACN); and
(2) 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, (Me-Me TACN).

[0038] The type of counter-ion Y for charge neutrality is not critical for the activity of the complex and can be selected from, for example, any of the following counter-ions: chloride; sulphate; nitrate; methylsulphate; surfactant anions, such as the long-chain alkylsulphates, alkylsulphonates, alkylbenzenesulphonates, tosylate, trifluoromethylsulphonate, perchlorate (ClO_4^-), BPh_4^-, and PF_6^-' though some counter-ions are more preferred than others for reasons of product property and safety.

[0039] Consequently, the preferred manganese complexes useable in the present invention are:

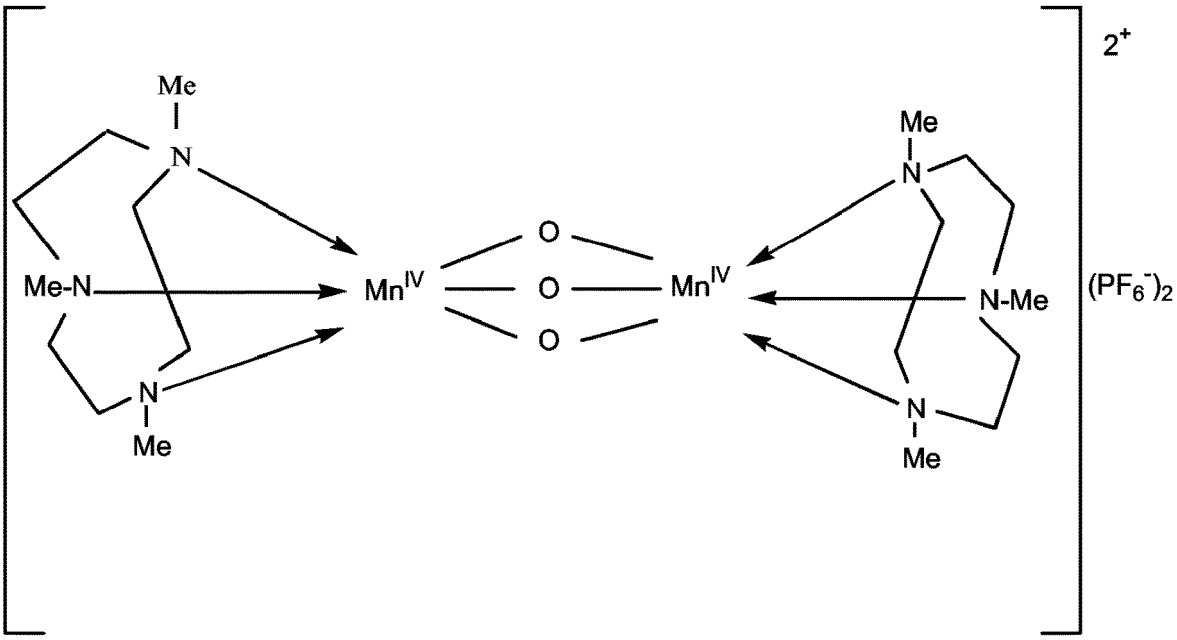
(I) $[(\text{Me-TACN})Mn^{IV}(Âμ\text{-}0)_3Mn^{IV}(\text{Me-TACN})]^{2+}(PF_6^-)_2$

(II) $[(Me\text{-}MeTACN)Mn^{IV}(Âμ\text{-}0)_3Mn^{IV}(Me\text{-}MeTACN)]^{2+}(PF_6^-)_2$
(III) $[(Me\text{-}TACN)Mn^{III}(Âμ\text{-}0)(Âμ\text{-}OAc)_2Mn^{III}(Me\text{-}TACN)]^{2+}(PF_6^-)_2$
(IV) $[(Me\text{-}MeTACN)Mn^{III}(Âμ\text{-}0)(Âμ\text{-}OAc)_2Mn^{III}(Me\text{-}MeTACN)]^{2+}(PF_6^-)_2$

which hereinafter may also be abbreviated as:

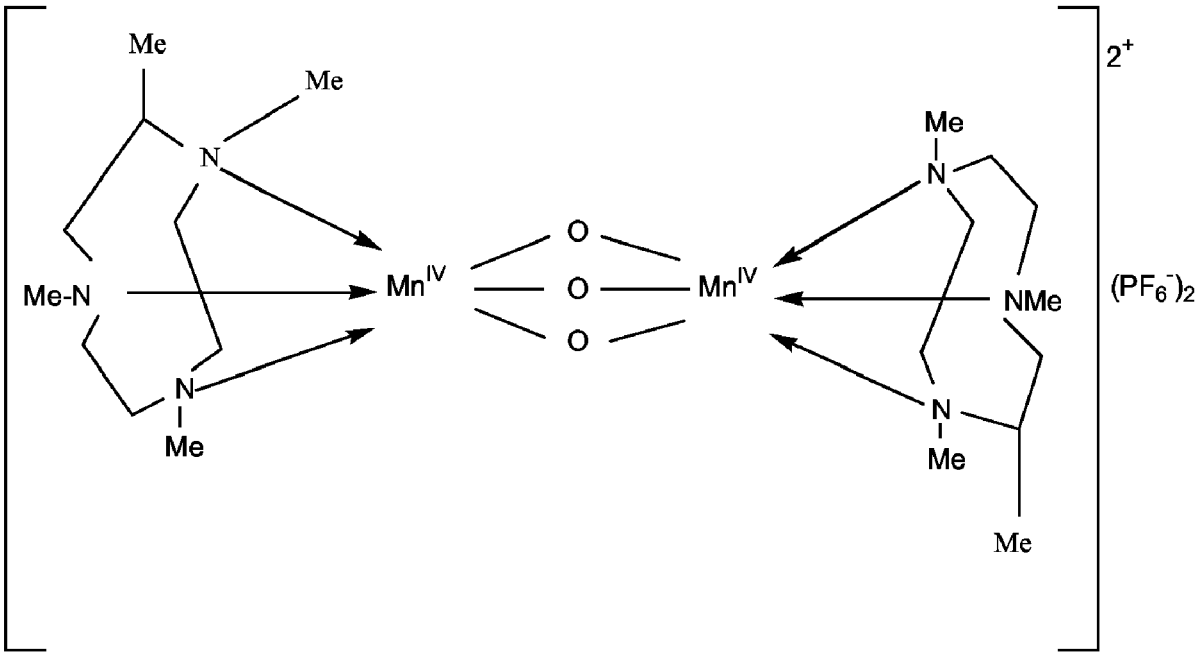
(I) $[Mn^{IV}{}_2(Âμ\text{-}0)_3(Me\text{-}TACN)_2]\ (PF_6)_2$
(II) $[Mn^{IV}{}_2(Âμ\text{-}0)_3(Me\text{-}MeTACN)_2]\ (PF_6)_2$
(III) $[Mn^{III}{}_2(Âμ\text{-}0)(Âμ\text{-}OAc)_2(Me\text{-}TACN)_2]\ (PF_6)_2$
(IV) $[Mn^{III}{}_2(Âμ\text{-}0)(Âμ\text{-}OAc)_2(Me\text{-}TACN)_2](PF_6)_2$

[0040] The structure of I is given below:



abbreviated as $[Mn^{IV}{}_2(Âμ\text{-}0)_3(Me\text{-}TACN)_2](PF_6)_2$.

[0041] The structure of II is given below:



abbreviated as $[Mn^{IV}_2(Â\mu\text{-}0)_3(Me\text{-}MeTACN)_2](PF_6)_2$.

[0042] It is of note that the manganese complexes are also disclosed in EP-A-0458397 and EP-A-0458398 as unusually effective bleach and oxidation catalysts. In the further description of this invention they will also be simply referred to as the "catalyst".

[0043] Preferably the composition of the invention comprises from 0.001 to 1, more preferably from 0.002 to 0.01 grams of bleach catalyst. Preferably the bleach catalyst is a manganese bleach catalyst.

Inorganic builder

[0044] The composition of the invention preferably comprises an inorganic builder. Suitable inorganic builders are selected from the group consisting of carbonate, silicate and mixtures thereof. Especially preferred for use herein is sodium carbonate. Preferably the composition of the invention comprises from 1 to 8, more preferably from 2 to 6 and especially from 3 to 5 grams of sodium carbonate.

Surfactant

[0045] Surfactants suitable for use herein include non-ionic surfactants, preferably the compositions are free of any other surfactants. Traditionally, non-ionic surfactants have been used in automatic dishwashing for surface modification purposes in particular for sheeting to avoid filming and spotting and to improve shine. It has been found that non-ionic surfactants can also contribute to prevent redeposition of soils.

[0046] Preferably the composition of the invention comprises a non-ionic surfactant or a non-ionic surfactant system, more preferably the non-ionic surfactant or a non-ionic surfactant system has a phase inversion temperature, as measured at a concentration of 1% in distilled water, between 40 and 70°C, preferably between 45 and 65°C. By a "non-ionic surfactant system" is meant herein a mixture of two or more non-ionic surfactants. Preferred for use herein are non-ionic surfactant systems. They seem to have improved cleaning and finishing properties and better stability in product than single non-ionic surfactants.

[0047] Phase inversion temperature is the temperature below which a surfactant, or a mixture thereof, partitions preferentially into the water phase as oil-swollen micelles and above which it partitions preferentially into the oil phase as water swollen inverted micelles. Phase inversion temperature can be determined visually by identifying at which temperature cloudiness occurs.

[0048] The phase inversion temperature of a non-ionic surfactant or system can be determined as follows: a solution containing 1% of the corresponding surfactant or mixture by weight of the solution in distilled water is prepared. The solution is stirred gently before phase inversion temperature analysis to ensure that the process occurs in chemical equilibrium. The phase inversion temperature is taken in a thermostable bath by immersing the solutions in 75 mm sealed glass test tube. To ensure the absence of leakage, the test tube is weighed before and after phase inversion temperature measurement. The temperature is gradually increased at a rate of less than 1°C per minute, until the

temperature reaches a few degrees below the pre-estimated phase inversion temperature. Phase inversion temperature is determined visually at the first sign of turbidity.

[0049] Suitable nonionic surfactants include: i) ethoxylated non-ionic surfactants prepared by the reaction of a monohydroxy alkanol or alkyphenol with 6 to 20 carbon atoms with preferably at least 12 moles particularly preferred at least 16 moles, and still more preferred at least 20 moles of ethylene oxide per mole of alcohol or alkylphenol; ii) alcohol alkoxylated surfactants having a from 6 to 20 carbon atoms and at least one ethoxy and propoxy group. Preferred for use herein are mixtures of surfactants i) and ii).

[0050] Another suitable non-ionic surfactants are epoxy-capped poly(oxyalkylated) alcohols represented by the formula:

$$R1O[CH2CH(CH3)O]x[CH2CH2O]y[CH2CH(OH)R2] \quad (I)$$

wherein R1 is a linear or branched, aliphatic hydrocarbon radical having from 4 to 18 carbon atoms; R2 is a linear or branched aliphatic hydrocarbon radical having from 2 to 26 carbon atoms; x is an integer having an average value of from 0.5 to 1.5, more preferably about 1; and y is an integer having a value of at least 15, more preferably at least 20.

[0051] Preferably, the surfactant of formula I, at least about 10 carbon atoms in the terminal epoxide unit [CH2CH(OH)R2]. Suitable surfactants of formula I, according to the present invention, are Olin Corporation's POLY-TERGENT® SLF-18B nonionic surfactants, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation.

[0052] Amine oxides surfactants are useful for use in the composition of the invention. Preferred are C10-C18 alkyl dimethylamine oxide, and C10-18 acylamido alkyl dimethylamine oxide.

[0053] Surfactants may be present in amounts from 0.1 to 10, more preferably from 0.5 to 5 and especially from 0.8 to 3 grams.

Enzymes

[0054] In describing enzyme variants herein, the following nomenclature is used for ease of reference: Original amino acid(s):position(s):substituted amino acid(s). Standard enzyme IUPAC 1-letter codes for amino acids are used.

Proteases

[0055] Suitable proteases include metalloproteases and serine proteases, including neutral or alkaline microbial serine proteases, such as subtilisins (EC 3.4.21.62) as well as chemically or genetically modified mutants thereof. Suitable proteases include subtilisins (EC 3.4.21.62), including those derived from Bacillus, such as Bacillus lentus, B. alkalophilus, B. subtilis, B. amyloliquefaciens, Bacillus pumilus and Bacillus gibsonii.

[0056] Especially preferred proteases for the detergent of the invention are polypeptides demonstrating at least 90%, preferably at least 95%, more preferably at least 98%, even more preferably at least 99% and especially 100% identity with the wild-type enzyme from Bacillus lentus, comprising mutations in one or more, preferably two or more and more preferably three or more of the following positions, using the BPN' numbering system and amino acid abbreviations as illustrated in WO00/37627, which is incorporated herein by reference:V68A, N87S, S99D, S99SD, S99A, S101G, S101M, S103A, V104N/I, G118V, G118R, S128L, P129Q, S130A, Y167A, R170S, A194P, V205I and/or M222S.

[0057] Most preferably the protease is selected from the group comprising the below mutations (BPN' numbering system) versus either the PB92 wild-type (SEQ ID NO:2 in WO 08/010925) or the subtilisin 309 wild-type (sequence as per PB92 backbone, except comprising a natural variation of N87S).

(i) G118V + S128L + P129Q + S130A
(ii) S101M + G118V + S128L + P129Q + S130A
(iii) N76D + N87R + G118R + S128L + P129Q + S130A + S188D + N248R
(iv) N76D + N87R + G118R + S128L + P129Q + S130A + S188D + V244R
(v) N76D + N87R + G118R + S128L + P129Q + S130A
(vi) V68A + N87S + S101G + V104N

[0058] Suitable commercially available protease enzymes include those sold under the trade names Savinase®, Polarzyme®, Kannase®, Ovozyme®, Everlase® and Esperase® by Novozymes A/S (Denmark), those sold under the tradename Properase®, Purafect®, Purafect Prime®, Purafect Ox®, FN3® , FN4®, Excellase®, Ultimase® and Purafect OXP® by Genencor International, those sold under the tradename Opticlean® and Optimase® by Solvay Enzymes, those available from Henkel/ Kemira, namely BLAP.

[0059] Preferred levels of protease in the product of the invention include from about 0.1 to about 10, more preferably

from about 0.5 to about 5 and especially from about 1 to about 4 mg of active protease per grams of product.

Amylases

[0060] Preferred enzyme for use herein includes alpha-amylases, including those of bacterial or fungal origin. Chemically or genetically modified mutants (variants) are included. A preferred alkaline alpha-amylase is derived from a strain of Bacillus, such as Bacillus licheniformis, Bacillus amyloliquefaciens, Bacillus stearothermophilus, Bacillus subtilis, or other Bacillus sp., such as Bacillus sp. NCIB 12289, NCIB 12512, NCIB 12513, DSM 9375 (USP 7,153,818) DSM 12368, DSMZ no. 12649, KSM AP1378 (WO 97/00324), KSM K36 or KSM K38 (EP 1,022,334). Preferred amylases include:

(a) the variants described in US 5,856,164 and WO99/23211, WO 96/23873, WO00/60060 and WO 06/002643, especially the variants with one or more substitutions in the following positions versus the AA560 enzyme listed as SEQ ID No. 12 in WO 06/002643:

9, 26, 30, 33, 82, 37, 106, 118, 128, 133, 149, 150, 160, 178, 182, 186, 193, 195, 202, 214, 231, 256, 257, 258, 269, 270, 272, 283, 295, 296, 298, 299, 303, 304, 305, 311, 314, 315, 318, 319, 320, 323, 339, 345, 361, 378, 383, 419, 421, 437, 441, 444, 445, 446, 447, 450, 458, 461, 471, 482, 484, preferably that also contain the deletions of D183* and G184*.

(b) variants exhibiting at least 95% identity with the wild-type enzyme from Bacillus sp.707 (SEQ ID NO:7 in US 6,093, 562), especially those comprising one or more of the following mutations M202, M208, S255, R172, and/or M261. Preferably said amylase comprises one of M202L or M202T mutations.

[0061] Suitable commercially available alpha-amylases include DURAMYL®, LIQUEZYME®, TERMAMYL®, TERMAMYL ULTRA®, NATALASE®, SUPRAMYL®, STAINZYME®, STAINZYME PLUS®, POWERASE®, FUNGAMYL® and BAN® (Novozymes A/S, Bagsvaerd, Denmark), KEMZYM® AT 9000 Biozym Biotech Trading GmbH Wehlistrasse 27b A-1200 Wien Austria, RAPIDASE®, PURASTAR®, ENZYSIZE®, OPTISIZE HT PLUS® and PURASTAR OXAM® (Genencor International Inc., Palo Alto, California) and KAM® (Kao, 14-10 Nihonbashi Kayabacho, 1-chome, Chuo-ku Tokyo 103-8210, Japan). Amylases especially preferred for use herein include NATALASE®, STAINZYME®, STAINZYME PLUS®, POWERASE® and mixtures thereof.

[0062] Preferably, the product of the invention comprises at least 0.01 mg of active amylase per gram of composition, preferably from about 0.05 to about 10, more preferably from about 0.1 to about 6, especially from about 0.2 to about 4 mg of amylase per gram of composition.

Additional Enzymes

[0063] Additional enzymes suitable for use in the product of the invention can comprise one or more enzymes selected from the group comprising hemicellulases, cellulases, cellobiose dehydrogenases, peroxidases, proteases, xylanases, lipases, phospholipases, esterases, cutinases, pectinases, mannanases, pectate lyases, keratinases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, ß-glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, amylases, and mixtures thereof.

Cellulases

[0064] The product of the invention preferably comprises other enzymes in addition to the protease and/or amylase. Cellulase enzymes are preferred additional enzymes, particularly microbial-derived endoglucanases exhibiting endo-beta-1,4-glucanase activity (E.C. 3.2.1.4). Preferred commercially available cellulases for use herein are Celluzyme®, Celluclean®, Whitezyme® (Novozymes A/S) and Puradax HA® and Puradax® (Genencor International).

[0065] Preferably, the protease and/or amylase of the product of the invention are in the form of granulates, the granulates comprise less than 29% of sodium sulfate by weight of the granulate or the sodium sulfate and the active enzyme (protease and/or amylase) are in a weight ratio of less than 4:1.

Crystal growth inhibitor

[0066] Crystal growth inhibitors are materials that can bind to calcium carbonate crystals and prevent further growth of species such as aragonite and calcite.

[0067] Especially preferred crystal growth inhibitor for use herein is HEDP (1-hydroxyethylidene 1,1-diphosphonic acid). Preferably, the composition of the invention comprises from 0.01 to 1, more preferably from 0.05 to 0.8 grams of

a crystal growth inhibitor, preferably HEDP.

Metal Care Agents

[0068] Metal care agents may prevent or reduce the tarnishing, corrosion or oxidation of metals, including aluminium, stainless steel and non-ferrous metals, such as silver and copper. Preferably the composition of the invention comprises from 0.001 to 0.01, more preferably from 0.002 to 0.009 grams, preferably the metal care agent is benzo triazole (BTA).

Glass Care Agents

[0069] Glass care agents protect the appearance of glass items during the dishwashing process. Preferably the composition of the invention comprises from 0.001 to 1, more preferably from 0.002 to 0.5 grams of a glass care agent, preferably the glass care agent is a zinc salt.

[0070] The dimensions and values disclosed herein are not to be understood as being strictly limited to the exact numerical values recited. Instead, unless otherwise specified, each such dimension is intended to mean both the recited value and a functionally equivalent range surrounding that value. For example, a dimension disclosed as "40 mm" is intended to mean "about 40 mm".

EXAMPLES

[0071] Two automatic dishwashing compositions (Composition land Composition 2) were made comprising the ingredients detailed herein below.

Ingredients (grams)	Composition 1	Composition 2
Powder section		
MGDA	5.00	5.00
Sulphonated Polymer	1.20	0.4
Sodium carbonate	4.00	4.00
Amylase	0.004	0.004
Protease	0.034	0.034
Sodium Percarbonate	2.00	2.00
Bleach catalyst	0.004	0.004
HEDP	0.10	0.10
Sodium sulphate, miscellaneous, etc.	Balance to 15.26	Balance to 15.26
Liquid section		
Nonionic surfactant ($R\text{-}PO_aEO_bH$)	0.84	0.84
Nonionic surfactant ($R\text{-}EO_7H$)	0.89	0.89
Miscellaneous, etc.	Balance to 2.18	Balance to 2.18
PVA film	0.64	0.64

Tea stain removal

[0072] Eight cups per test leg were stained using black tea (Assam) prepared in artificially hard water with ferric sulphate as per IKW test method (IKW working group automatic dishwasher detergents. "Methods for Ascertaining the Cleaning Performance of Dishwasher Detergents (Part B, updated 2005)". SÖFW-Journal, 132, 8 -2006 pp. 35). For each formula, two cups were placed on the top rack of a washing machine, loaded with ballast dishes, and washed using the compositions 1 and 2. The inlet water had a hardness of 360 ppm of $CaCO_3$.

[0073] As artificial ballast soil 100g of IKW soil from frozen and 36g of minced meat were added from frozen to increase the amount of soil found in consumer conditions. Artificial IKW soil was prepared according the IKW procedure and the meat soil was prepared by mixing 225g of minced meat (50% pork and 50% beef), 75g of eggs (white and yolk) and

80g of water (350 $CaCO_3$ ppm hardness), and blending it until forming a paste, then it is divided in pots containing 36g of the minced meat paste each and stored in a freezer.

[0074] The test was carried out in a Miele GSL dishwashing machine in a normal R-50°C cycle (no prewash). The detergent is added to the dishwasher when the dispenser door opens. The test was repeated three more times with the remaining cups, once all of them were washed the eight cups were graded by three independent judges, using a visual scale from 1 to 10 going from soiled to completely clean.

	Composition 1	Composition 2
Visual tea grade	6.44	2.79

[0075] From the above data it is clear that a higher level of polymer (Composition 1 vs Composition 2), resulted in an improved tea stain removal.

Claims

1. Use of a sulfonated polymer in an automatic dishwashing detergent composition for the removal of bleachable stains from dishware in automatic dishwashing.

2. Use of a sulfonated polymer according to claim 1 wherein the composition comprises at least 0.8 gram of the sulfonated polymer.

3. Use of a sulfonated polymer according to any of claims 1 or 2 for the removal of tea stains.

4. Use of a sulfonated polymer according to any of the preceding claims wherein the detergent composition is phosphate-free.

5. Use of a sulfonated polymer according to any of the preceding claims wherein the detergent composition comprises an organic complexing agent.

6. Use of a sulfonated polymer according to the preceding claim wherein the composition comprises at least 4 grams of the complexing agent and the complexing agent is preferably selected from the group consisting of methyl glycine diacetic acid, its salts and derivatives thereof, glutamic-N,N- diacetic acid, its salts and derivatives thereof, imino-disuccinic acid, its salts and derivatives thereof, carboxy methyl inulin, its salts and derivatives thereof, and mixtures thereof.

7. Use of a sulfonated polymer according to any of the preceding claims wherein the detergent composition comprises from about 1 to about 3 grams of bleach.

8. Use of a sulfonated polymer according to any of the preceding claims wherein the detergent composition comprises a bleach catalyst, preferably a manganese bleach catalyst.

9. Use of a sulfonated polymer according to any of the preceding claims wherein the detergent composition comprises a crystal growth inhibitor.

10. Use of a sulfonated polymer according to any of the preceding claims wherein the detergent composition comprises a non-ionic surfactant.

11. Use of a sulfonated polymer according to any of the preceding claims wherein the detergent composition has a pH of from about 9 to about 12 as measured in 1% weight aqueous solution at 20°C.

12. Use of a sulfonated polymer according to any of the preceding claims wherein the detergent composition has a reserve alkalinity of from about 10 to about 20 at a pH of 9.5 as measured in NaOH with 100 mL of product at 20°C.

13. Use of a sulfonated polymer according to any of the preceding claims wherein the detergent composition is in unit dose form, more preferably enveloped by a water-soluble material.

14. Use of a sulfonated polymer according to the preceding claim wherein the weight of the unit dose is from about 5 to about 25 grams.

15. Use of a sulfonated polymer according to any of the preceding claims wherein the detergent composition comprises:

i) at least 0.8 grams of the sulfonated polymer
ii) from 4 to 8 grams of a complexing agent, preferably the three sodium salt of MGDA;
ii) from 0.5 to 4 grams of bleach, preferably sodium percarbonate;
the composition having a pH of from 9 to 12 as measured in 1% weight aqueous solution at 20°C and a reserve alkalinity of from about 10 to about 20 at a pH of 9.5 as measured in NaOH with 100 mL of product at 20°C; and wherein the composition is preferably in unit dose form.

16. A method of removing bleachable stains from dishware in an automatic dishwasher, the method comprising the following steps:

a) providing soiled dishware,
b) placing the soiled dishware into an automatic dishwashing machine,
c) providing at least 0.8 grams of sulfonated polymer in an automatic dishwashing detergent composition the composition comprising:

i) from 4 to 8 grams of a complexing agent, preferably the three sodium salt of MGDA;
ii) from 0.5 to 4 grams of bleach, preferably sodium percarbonate;
the composition having a pH of from 9 to 12 as measured in 1% weight aqueous solution at 20°C and a reserve alkalinity of from about 10 to about 20 at a pH of 9.5 as measured in NaOH with 100 mL of product at 20°C;

d) running the automatic dishwashing machine, wherein the sulfonated polymer in the automatic dishwashing detergent contributes to the removal of bleachable stains.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 15 3514

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Y	WO 2007/052004 A1 (RECKITT BENCKISER NV [NL]; RECKITT BENCKISER UK LTD [GB]; GIBIS KARL-L) 10 May 2007 (2007-05-10) * formula 8a *; page 17, lines 1-5; figures; examples 2, 3; tables 2, 3	15,16	ADD. C11D17/04
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	1 October 2015	Loiselet-Taisne, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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