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(54) New use of complexing agent

(57) Use of from about 3 grams to about 6 grams of an organic complexing agent in an enzymatic automatic dishwashing detergent composition for the removal of baked-on burnt-on soils from dishware in automatic dishwashing.

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Description

TECHNICAL FIELD

[0001] The present invention is in the field of automatic dishwashing. In particular, it relates to the use of organic complexing agents, in particular methyl glycine diacetic acid for the removal of baked-on burnt-on soils.

BACKGROUND OF THE INVENTION

[0002] The automatic dishwashing detergent formulator is continuously looking for ways to improve the performance of detergents. Baked-on, burnt-on soils are among the most difficult soils to remove. In particular, baked-on, burnt-on soils containing proteins, such as egg and cheese, more in particular baked-on, burnt-on soils containing eggs are really difficult to remove. The removal of baked-on, burnt-on soils is more difficult when the detergent is phosphate free.

SUMMARY OF THE INVENTION

[0003] The present invention is based on the use of an organic complexing agent, preferably methyl glycine diacetic acid, in an automatic dishwashing detergent composition. It has been unexpectedly found that the complexing agent, preferably methyl glycine diacetic acid, improves the removal of baked-on burnt-on soils from dishware. Preferably the composition comprises about 3 grams to about 6 grams, more preferably from about 3.5 grams to about 5.5 grams of an organic complexing agent, more preferably of methyl glycine diacetic acid.

[0004] The composition for the use of the invention is sometimes herein referred to as "the composition of the invention".

[0005] This level of complexing agent favours the removal of baked-on, burnt-on soils, especially soils containing proteins such as egg and/or milk. 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.

[0006] 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 three sodium salt of MGDA.

[0007] Preferably, the composition comprises a high level of protease, from about 0.1 to about 50 mg of active protease, more preferably from about 0.1 to about 40 mg of active protease. It seems that the combination of the level of the complexing agent of the composition of the invention, in particular the tri-sodium salt of MGDA and this level of protease provides optimum removal of baked-on, burnt-on soils, in particular proteinaceous soils, such as eggs and milk based soils.

[0008] Preferably, the composition comprises more than 0.8, more preferably more than 1 and especially 1.2 or more grams of sulfonated polymer. Preferably, the sulfonated polymer comprises 2-acrylamido-2-methylpropane sulfonic acid monomers. For the purpose of this invention "dishware" encompasses tableware and cookware and anything that it is usually washed in an automatic dishwasher.

[0009] For the purpose of this invention a "sulfonated polymer" is a polymer comprising sulphur in any of its forms. The "sulfonated polymer" of the invention preferably comprises carboxyl groups.

[0010] 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.

[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] 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.

[0015] 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:

Reserve Alkalinity = % NaOH x Specific Gravity.

% NaOH = ml HCl x Normality of HClx4' / Weight of Sample Aliquot Titrated

* Equivalent weight of NaOH in the % NaOH equation,

derived from:

% NaOH = ml HCl x Normality of HCl x Equiv. Weight NaOH x 100 / 1000 x Weight of Sample Aliquot Titrated

[0016] 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, more preferably a polyvinyl alcohol film having a film of less than 100 μm tickness. The detergent composition of the invention preferably weighs from about 8 to about 25 grams, more 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.

[0017] According to a second aspect of the invention, there is provided a method of removing baked-on burnt-on soils, preferable proteinaceous based soils, from dishware in automatic dishwasher, the method comprising the following steps:

a) providing soiled dishware,
b) placing the soiled dishware into an automatic dishwashing machine,
c) providing from about 3 grams to about 6 grams of an organic complexing agent, preferably the tri-sodium salt of methyl glycine diacetic acid in an enzymatic automatic dishwashing detergent composition; and
d) running the automatic dishwashing machine, wherein the complexing agent in the automatic dishwashing detergent contributes to the removal of baked-on burnt-on soils.

[0018] The elements of the composition of the invention described herein apply *mutatis mutandis* to the use and method aspects of the invention.

SUMMARY OF THE INVENTION

[0019] The present invention relates to the use of from about 3 to about 6 grams of an organic complexing agent, in an automatic dishwashing composition to provide baked-on, burnt-on removal benefits.

Detergent composition

[0020] 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, more preferably the film has a thickness of less than 100 μm. The composition comprises an organic complexing agent and optionally but preferably a sulfonated polymer, bleach, inorganic builder (preferably carbonate and silicate), enzymes in particular protease enzymes, non-ionic surfactant, etc.

[0021] 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.

[0022] 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.

Complexing agent

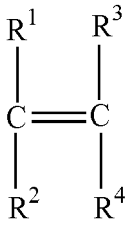
[0023] A complexing agent is a material capable of sequestering hardness ions, particularly calcium and/or magnesium. The composition of the invention comprises from about 3 to about 6 grams, more preferably from about 3.5 grams to about 5 grams of a complexing agent. The complexing agent is preferably 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, 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 tri-sodium salt of MGDA.

Sulfonated polymer

[0024] 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 at least 0.8 gram, preferably at least 1 gram, more preferably at least 1.2 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.

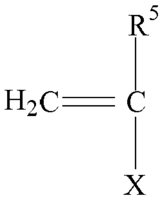
[0025] Suitable sulfonated/carboxylated polymers described herein may have a weight average molecular weight of less than or equal to about 100,000 Da, or less than or equal to about 75,000 Da, or less than or equal to about 50,000 Da, or from about 3,000 Da to about 50,000, preferably from about 5,000 Da to about 45,000 Da.

[0026] 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):



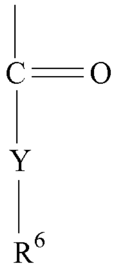
$$R^1R^2C{=}CR^3R^4 \quad \text{(I)}$$

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):



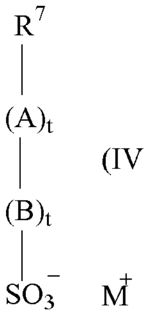
$$H_2C{=}C(R^5)X \quad \text{(II)}$$

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):



$$-C(=O)-Y-R^6 \quad \text{(III)}$$

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):



$$\begin{array}{l} R^7 \\ | \\ (A)_t \\ | \\ (B)_t \\ | \\ SO_3^- \quad M^+ \end{array} \qquad (IV)$$

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.

[0027] 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.

[0028] 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.

[0029] 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).

[0030] 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.

[0031] 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.

Bleach

[0032] 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.

[0033] 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.

[0034] 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.

[0035] 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.

[0036] 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

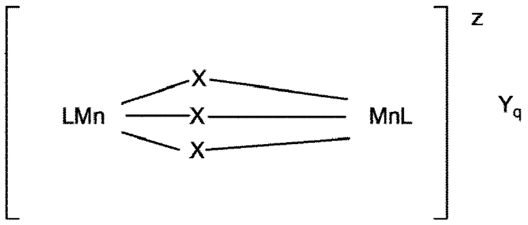
[0037] Bleach activators are typically organic peracid precursors that enhance the bleaching action in the course of cleaning at temperatures of 60° C and below. Bleach activators suitable for use herein include compounds which, under perhydrolysis conditions, give aliphatic peroxoycarboxylic acids having 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

[0038] 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.

[0039] 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].

[0040] 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).

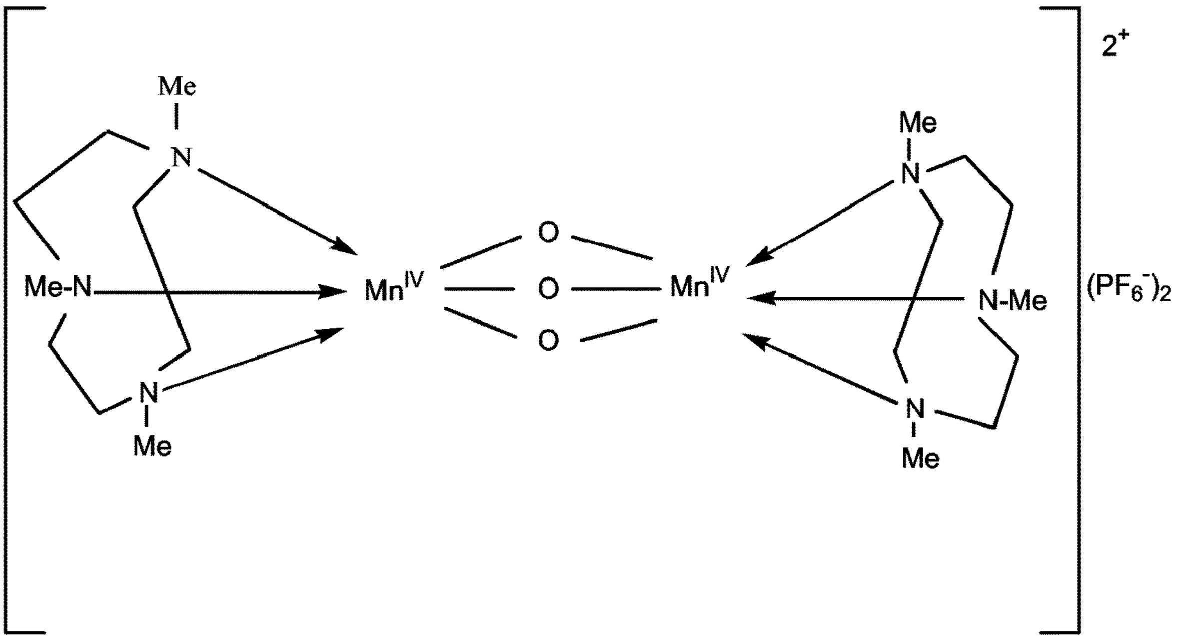
[0041] The type of counter-ion Y for charge neutrality is not critical for the activity of the complex and can be selected from, for example, any of the following counter-ions: chloride; sulphate; nitrate; methylsulphate; surfactant anions, such as the long-chain alkylsulphates, alkylsulphonates, alkylbenzenesulphonates, 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.

[0042] Consequently, the preferred manganese complexes useable in the present invention are:

(I) [(Me-TACN)Mn^{IV}(Âμ-0)$_3$Mn^{IV}(Me-TACN)]$^{2+}$(PF$_6^-$)$_2$
(II) [(Me-MeTACN)Mn^{IV}(Âμ-0)$_3$Mn^{IV}(Me-MeTACN)]$^{2+}$(PF$_6^-$)$_2$
(III) [(Me-TACN)Mn^{III}(Âμ-0)(Âμ-OAc)$_2$Mn^{III}(Me-TACN)]$^{2+}$(PF$_6^-$)$_2$
(IV) [(Me-MeTACN)Mn^{III}(Âμ-0)(Âμ-OAc)$_2$Mn^{III}(Me-MeTACN)]$^{2+}$(PF$_6^-$)$_2$ which hereinafter may also be abbreviated as:

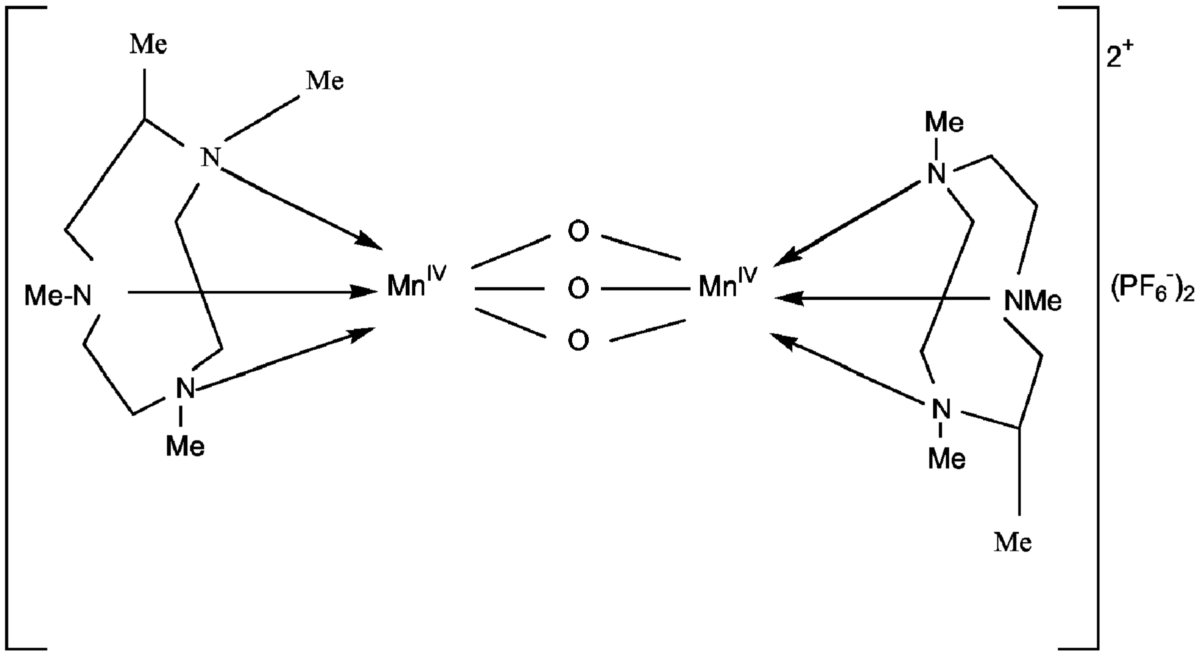
(I) [Mn$^{IV}_2$(Âμ-0)$_3$(Me-TACN)$_2$] (PF$_6$)$_2$
(II) [Mn$^{IV}_2$(Âμ-0)$_3$(Me-MeTACN)$_2$] (PF$_6$)$_2$
(III) [Mn$^{III}_2$(Âμ-0)(Âμ-OAc)$_2$(Me-TACN)$_2$] (PF$_6$)$_2$
(IV) [Mn$^{III}_2$(Âμ-0) (Âμ-OAc)$_2$(Me-TACN)$_2$](PF$_6$)$_2$

[0043] The structure of I is given below:



abbreviated as [Mn$^{IV}_2$(Âμ-0)$_3$(Me-TACN)$_2$](PF$_6$)$_2$.

[0044] The structure of II is given below:



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

[0045] 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".

[0046] 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

[0047] 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 are sodium carbonate and silicate. 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 and from 0.05 to 2 grams of silicate.

Surfactant

[0048] 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.

[0049] 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.

[0050] 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.

[0051] 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.

[0052] 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).

[0053] Another suitable non-ionic surfactants are epoxy-capped poly(oxyalkylated) alcohols represented by the formula:

R10[CH2CH(CH3)O]x[CH2CH2O]y[CH2CH(OH)R2] (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.

[0054] 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.

[0055] 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.

[0056] 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

[0057] 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

[0058] 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.

[0059] 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.

[0060] 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

[0061] 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.

[0062] Preferred levels of protease in the product of the invention include from about 0.1 to about 50, more preferably from about 1 to about 45 and especially from about 10 to about 40 mg of active protease.

Amylases

[0063] 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.

[0064] 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.

[0065] Preferably, the product of the invention comprises at least 0.01 mg, preferably from about 0.05 to about 10, more preferably from about 0.1 to about 6, especially from about 0.2 to about 5 mg of active amylase.

Additional Enzymes

[0066] 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.

[0067] 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

[0068] Crystal growth inhibitors are materials that can bind to calcium carbonate crystals and prevent further growth of species such as aragonite and calcite.

[0069] 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

[0070] 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

[0071] 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.

[0072] 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

[0073] Two dual-compartment automatic dishwashing pouches were made comprising the ingredients detailed herein below (Composition 1 and Composition 2). The pouches were made of polyvinyl alcohol (Monosol 8630 available from Kuraray) with the solid and liquid components in different compartments.

Ingredients (grams of active material)	**Composition 1**	**Composition 2**
Solid compartment		
Sodium carbonate	6.42	6.42
Sodium silicate 2R	0.14	0.14
MGDA	2.84	3.58
Sodium percarbonate	0.94	0.94
Sulfonated polymer	1.07	1.07
Protease	0.035	0.035
Amylase	0.009	0.009
Bleach catalyst	0.001	0.001
Miscellaneous	Balance to 13.84	Balance to 13.84
Liquid compartment		
Lutensol TO7	0.70	0.70
Plurafac SLF-180	1.00	1.00
Miscellaneous	Balance to 2.1300	Balance to 2.1300

MGDA	Tri-sodium salt of methyl glycine diacetic acid
Protease	Ultimase ® Supplied by Dupont
Amylase	Stainzyme Plus ® Supplied by Novozymes
Lutensol TO7	Nonionic surfactant supplied by BASF
Plurafac SLF-180	Nonionic surfactant supplied by BASF

Performance data

[0074] The cleaning power of the compositions was assessed by running a performance test containing baked-on /burnt-on soils. Two different burnt soils were tested: Burnt egg in ceramic containers and burnt Macaroni and Cheese in stainless steel pots.

[0075] To prepare 16 of ceramic bowls with burnt egg, 5 grams of butter are scooped onto the bottom of each bowl and brought to room temperature to soften the butter. On a large container 17, grade A, large eggs are then mixed and whisked, then 50 mL of the mixture are added into each bowl and mixed with butter. The egg mixture is then cooked in an 800W microwave. Four bowls at a time are then microwaved for 2 minutes at high power until the 16 egg bowls are cooked. The Egg bowls are then put aside and left to rest overnight. The following day the egg is scrapped and the bowls are baked for 15 minutes at 200°C to burn the remaining egg.

[0076] To prepare 16 stainless steel pots with macaroni and cheese, 708ml of water are boiled in a pan on a hob and 82.5g of Kraft macaroni and cheese dinner® dry pasta are added to the boiling water. The pasta is allowed to cook for 7 minutes. In a separate container 118mL of full fat milk and 10g of margarine are mixed and microwaved for 1.3min at high power to melt the margarine, once the pasta is cooked the water is drained and the pasta along with the milk and dried cheese are added into a food processor and blend for 2 minutes, ensuring the mixture is uniform. The 16 stainless steel copper based pans are then prepared by painting 10g of the mixture on the bottom of the pan. Then the pans are then baked in the oven at 180°C for 60 minutes.

[0077] Each dishwashing machine is then loaded with two egg bowls and two mac and cheese pans in the bottom basket and clean ballast dishes.

[0078] The test was executed using Maytag dishwasher in a normal light cycle setting, without prewash. The inlet water was preheated in a storage tank to 50°C and had a 127 ppm of $CaCO_3$ as hardness; additional 50g of TMD soil were added from frozen at the start of the wash. The test is repeated three more times for each composition.

[0079] To aid the visualisation of any egg residue the washed egg ceramic bowls are then stained by pouring 100mL of a talcum powder/safranin O solution (1.275g of talcum powder and 0.225g of Safranin O are dissolved in 3L of water) into the dish, swirling around until any residue is stained. The solution can be reused in the next washed egg bowl.

[0080] The items are then visually graded by three independent judges using a scale from 1 to 10, where 1 is the most soiled and 10 is the cleanest.

Results

[0081]

Treatment	Egg	MacCheese
Composition 1	5.56	2.72
Composition 2	7.84	3.78

[0082] A great improvement of the removal of baked-on, burnt-on egg and macaroni cheese takes place when the level of MGDA increases from 2.84 to 3.58 grams.

Claims

1. Use of from about 3 grams to about 6 grams of an organic complexing agent in an enzymatic automatic dishwashing detergent composition for the removal of baked-on burnt-on soils from dishware in automatic dishwashing.

2. Use according to claim 1 wherein the composition is in unit dose form.

3. Use according to any of claims 1 or 2 wherein the complexing agent is 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.

4. Use according to any of the preceding claims wherein the complexing agent is selected from the group consisting of methyl glycine diacetic acid, its salts and derivatives thereof, preferably the sodium salt of methyl glycine diacetic acid.

5. Use according to any of the preceding claims wherein the detergent composition is phosphate-free.

6. Use according to any of the preceding claims wherein the detergent composition comprises from about 0.1 to about 50 mg of active protease.

7. Use according to any of the preceding claims wherein the detergent composition comprises bleach.

8. Use according to any of the preceding claims wherein the detergent composition comprises a bleach catalyst.

9. Use according to any of the preceding claims wherein the bleach catalyst is manganese based.

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

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

12. Use according to any of the preceding claims wherein the detergent composition has a pH equal or greater than 9 to 12 as measured in 1% weight/volume aqueous solution at 20°C.

13. Use according to any of the preceding claims wherein the detergent composition has a reserve alkalinity equal or greater than about 10 to about 20 at a pH of 9.5 as measured in NaOH with 100 grams of product at 20°C.

14. Use according to any of the preceding claims wherein the detergent composition is in unit dose form, preferably in the form of a multi-compartment pack wrapped by a polyvinyl alcohol film having a thickness of less than 100 μm.

15. Use according to the preceding claim wherein the weight of the unit dose is from about 5 to about 25 grams.

16. Method of removing baked-on burnt-on soils from dishware in automatic dishwasher, the method comprising the following steps:

a) providing soiled dishware,
b) placing the soiled dishware into an automatic dishwashing machine,
c) providing from about 3 grams to about 6 grams of an organic complexing agent, preferably the three sodium salt of methyl glycine diacetic acid in an enzymatic automatic dishwashing detergent composition; and
d) running the automatic dishwashing machine, wherein the complexing agent in the automatic dishwashing detergent contributes to the removal of baked-on burnt-on soils.

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EUROPEAN SEARCH REPORT

Application Number
EP 15 15 3520

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	EP 2 166 092 A1 (PROCTER & GAMBLE [US]) 24 March 2010 (2010-03-24) * paragraphs [0014], [0016], [0020], [0027], [0086], [0091], [0095], [0097], [0102] - [0105]; claims 1, 4-9; example 1 * -----	1-9, 11-16	INV. C11D3/33 C11D3/386 C11D17/04 C11D3/39
X	WO 2007/052004 A1 (RECKITT BENCKISER NV [NL]; RECKITT BENCKISER UK LTD [GB]; GIBIS KARL-L) 10 May 2007 (2007-05-10) * formulations 8a, 8b, 8c *; figure 1/2; example 2; tables 2, 3 -----	1-5,11, 14-16	
X	WO 2011/130076 A1 (PROCTER & GAMBLE [US]; SOUTER PHILLIP FRANK [GB]; WARD GLENN STEVEN [G) 20 October 2011 (2011-10-20) *formulation 3 *; example 3 -----	1-9, 11-16	
X	WO 2007/141527 A1 (RECKITT BENCKISER NV [NL]; RECKITT BENCKISER UK LTD [GB]; HOUSMEKERIDE) 13 December 2007 (2007-12-13) * claims 1-10; example 1 * -----	1-3,5, 11-16	TECHNICAL FIELDS SEARCHED (IPC) C11D
E	WO 2015/086410 A1 (HENKEL AG & CO KGAA [DE]) 18 June 2015 (2015-06-18) * paragraphs [0003], [0010]; claims 1-3; example * -----	1-3,7,8, 10-16	

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	25 September 2015	Loiselet-Taisne, S

EPO FORM 1503 03.82 (P04C01)

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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& : member of the same patent family, corresponding document

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

EP 15 15 3520

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
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25-09-2015

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 2166092 A1	24-03-2010	NONE	
WO 2007052004 A1	10-05-2007	AT 453703 T	15-01-2010
		AU 2006310389 A1	10-05-2007
		BR PI0618263 A2	23-08-2011
		CA 2627908 A1	10-05-2007
		CN 101300337 A	05-11-2008
		EP 1948776 A1	30-07-2008
		ES 2337835 T3	29-04-2010
		JP 2009515022 A	09-04-2009
		US 2009075855 A1	19-03-2009
		WO 2007052004 A1	10-05-2007
		ZA 200803211 A	30-06-2010
WO 2011130076 A1	20-10-2011	AR 080915 A1	16-05-2012
		CA 2796436 A1	20-10-2011
		EP 2558560 A1	20-02-2013
		JP 5727588 B2	03-06-2015
		JP 2013527272 A	27-06-2013
		US 2012067373 A1	22-03-2012
		US 2015087572 A1	26-03-2015
		WO 2011130076 A1	20-10-2011
WO 2007141527 A1	13-12-2007	AT 546512 T	15-03-2012
		AU 2007255190 A1	13-12-2007
		CA 2652934 A1	13-12-2007
		EP 2024475 A1	18-02-2009
		ES 2380128 T3	08-05-2012
		PL 2024475 T3	31-07-2012
		US 2010160202 A1	24-06-2010
		WO 2007141527 A1	13-12-2007
WO 2015086410 A1	18-06-2015	DE 102013225485 A1	11-06-2015
		WO 2015086410 A1	18-06-2015

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

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US 4246612 A **[0038]**
- US 5227084 A **[0038]**
- US 5114611 A **[0038]**
- US 4810410 A **[0038]**
- WO 9906521 A **[0038]**
- EP 0458397 A **[0045]**
- EP 0458398 A **[0045]**
- WO 9422800 A **[0054]**
- WO 0037627 A **[0059]**
- WO 08010925 A **[0060]**
- US P7153818 B **[0063]**
- WO 9700324 A **[0063]**
- EP 1022334 A **[0063]**
- US 5856164 A **[0063]**
- WO 9923211 A **[0063]**
- WO 9623873 A **[0063]**
- WO 0060060 A **[0063]**
- WO 06002643 A **[0063]**
- US 6093 A **[0063]**
- US 562 A **[0063]**