



(51) International Patent Classification:

C11D 17/00 (2006.01) *C11D* 3/33 (2006.01)
C11D 3/37 (2006.01) *C11D* 17/04 (2006.01)
C11D 3/39 (2006.01)

(21) International Application Number:

PCT/US2016/015876

(22) International Filing Date:

1 February 2016 (01.02.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15153514.3 2 February 2015 (02.02.2015) EP

(71) Applicant: **THE PROCTER & GAMBLE COMPANY**
[US/US]; One Procter & Gamble Plaza, Cincinnati, Ohio
45202 (US).

(72) Inventors: **URQUHART, Claire**; Procter & Gamble
Technical Centre Ltd., Newcastle Innovation Centre, Whit-
ley Road, Longbenton, P.O. Box: Forest Hall No. 2, New-
castle-upon-Tyne NE12 9TS (GB). **RANDHAWA, Ash-**
mita; Procter & Gamble Technical Centre Ltd., Newcastle
Innovation Centre, Whitley Road, Longbenton, P.O. Box:
Forest Hall No. 2, Newcastle-upon-Tyne NE12 9TS (GB).

(74) Agent: **KREBS, Jay A.**; c/o THE PROCTER & GAMBLE
COMPANY, Global Patent Services, One Procter &
Gamble Plaza, C8-229, Cincinnati, Ohio 45202 (US).

(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: NEW USE OF SULFONATED POLYMERS

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



NEW USE OF SULFONATED POLYMERS

TECHNICAL FIELD

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

BACKGROUND OF THE INVENTION

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
10 different kinds of stains. Tea and coffee stains are particularly difficult to remove. The problem
is more acute when the detergent is phosphate free.

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

15

SUMMARY OF THE INVENTION

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
20 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.

For the purpose of this invention a “sulfonated polymer” is a polymer comprising sulphur in any
of its forms.

25

The composition for the use of the invention is sometimes herein referred to as “the composition
of the invention”.

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.

- 5 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,
10 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.
- 15 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
20 salts thereof, especially preferred for use herein is the sodium salt of MGDA.

- 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
25 preferred are compositions comprising a crystal growth inhibitor, in particular HEDP and preferably a non-ionic surfactant.

- 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
30 invention is free of citrate, thus preferred for use herein are citrate free compositions.

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.

5

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
10 alkali in reserve to deal with any added acid –coming from the water and/or the soils on the dishware- while maintaining the pH.

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
15 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
20 detergent has been formulated in a way that provides all the benefits mentioned herein above.

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.

A pH meter (for example An Orion Model 720A) with a Ag/AgCl electrode (for example an
25 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 HCl x 4' / Weight of Sample Aliquot Titrated

* Equivalent weight of NaOH in the % NaOH equation,

derived from:

- 5 % NaOH = ml HCl x Normality of HCl x Equiv. Weight NaOH x 100 / 1000 x Weight of Sample Aliquot Titrated

DETAILED DESCRIPTION OF THE INVENTION

- 10 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

- 15 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
- 20 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.

- 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
- 25 about 10 to less than about 11.5 and especially from about 10.5 to about 11.5.

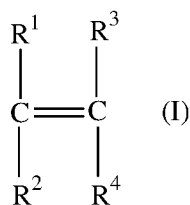
The composition of the invention preferably has a reserve alkalinity of from about 10 to about 20, more preferably from about 12 to about 18 at a pH of 9.5 as measured in NaOH with 100 grams of product at 20°C.

5 Sulfonated polymer

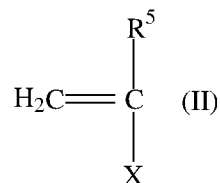
The polymer is used in any suitable amount from about 0.1% to about 30%, preferably from 0.5% to about 20%, more preferably from 1% to 10% by weight of the composition. The composition of the invention comprises preferably at least 1 gram, more preferably at least 1.5
 10 grams of sulfonated polymer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

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
 15 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.

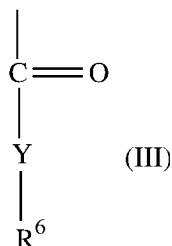
As noted herein, the sulfonated/carboxylated polymers may comprise (a) at least one structural unit derived from at least one carboxylic acid monomer having the general formula (I):



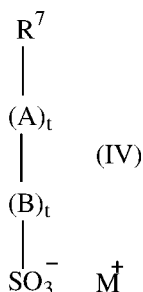
20 wherein R^1 to R^4 are independently hydrogen, methyl, carboxylic acid group or CH_2COOH and wherein the carboxylic acid groups can be neutralized; (b) optionally, one or more structural units derived from at least one nonionic monomer having the general formula (II):



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):



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
 5 O or N; and at least one structural unit derived from at least one sulfonic acid monomer having the general formula (IV):



10 wherein R^7 is a group comprising at least one sp^2 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, R^7 is a C_2 to C_6 alkene. In another aspect, R^7 is ethene, butene or propene.

15 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
 20 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.

Preferably, the polymer comprises the following levels of monomers: from about 40 to about
 25 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.

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, allylsulfonic acid, methallylsulfonic acid, allyloxybenzenesulfonic acid, methallyloxybenzenesulfonic 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).

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.

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

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 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.

5

Bleach

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.

Inorganic and organic bleaches are suitable for use herein. Inorganic bleaches include
10 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
15 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.

20

Typical organic bleaches are organic peroxyacids, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid, and diperoxyhexadecanedioic 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
25 in the context of this invention.

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 -
30 naphthoic acid and magnesium monoperphthalate, (b) the aliphatic or substituted aliphatic peroxy acids, such as peroxyauric acid, peroxysearic acid, ϵ -phthalimidoperoxyacaproic

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-
5 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.

10 Bleach Activators

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
15 peroxydicarboxylic 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 tetraacetylenediamine (TAED), acylated triazine derivatives, in particular 1,5-diacetyl-2,4-
20 dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils, in particular tetraacetyl glycoluril (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-
25 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

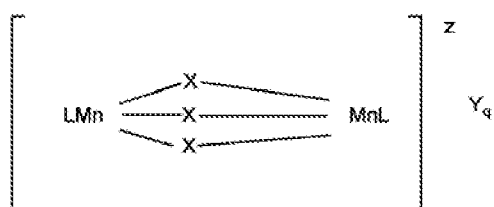
30

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.

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, O₂²⁻, O₂⁻, 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].

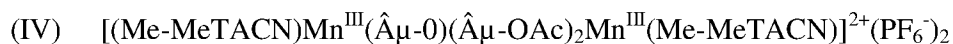
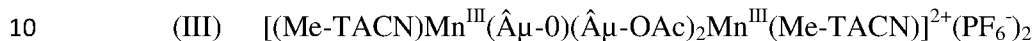
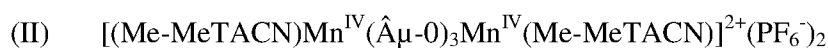
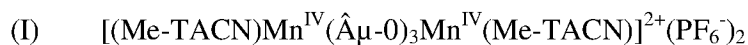
Preferred manganese-complexes are those wherein x is either CH₃COO⁻ or O²⁻ or mixtures thereof, most preferably wherein the manganese is in the IV oxidation state and x is O²⁻. Preferred ligands are those which coordinate via three nitrogen atoms to one of the manganese centres, preferably being of a 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).

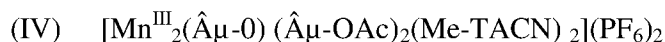
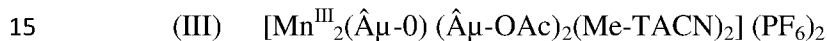
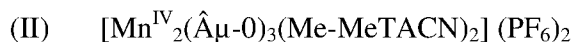
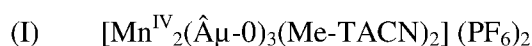
The type of counter-ion Y for charge neutrality is not critical for the activity of the complex and

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.

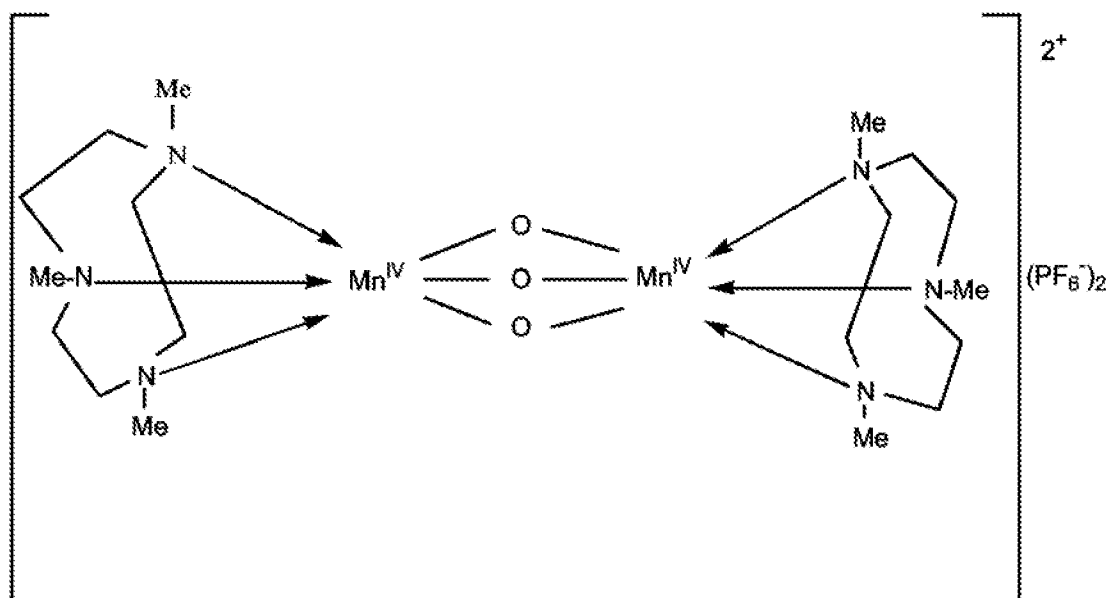
Consequently, the preferred manganese complexes useable in the present invention are:



which hereinafter may also be abbreviated as:

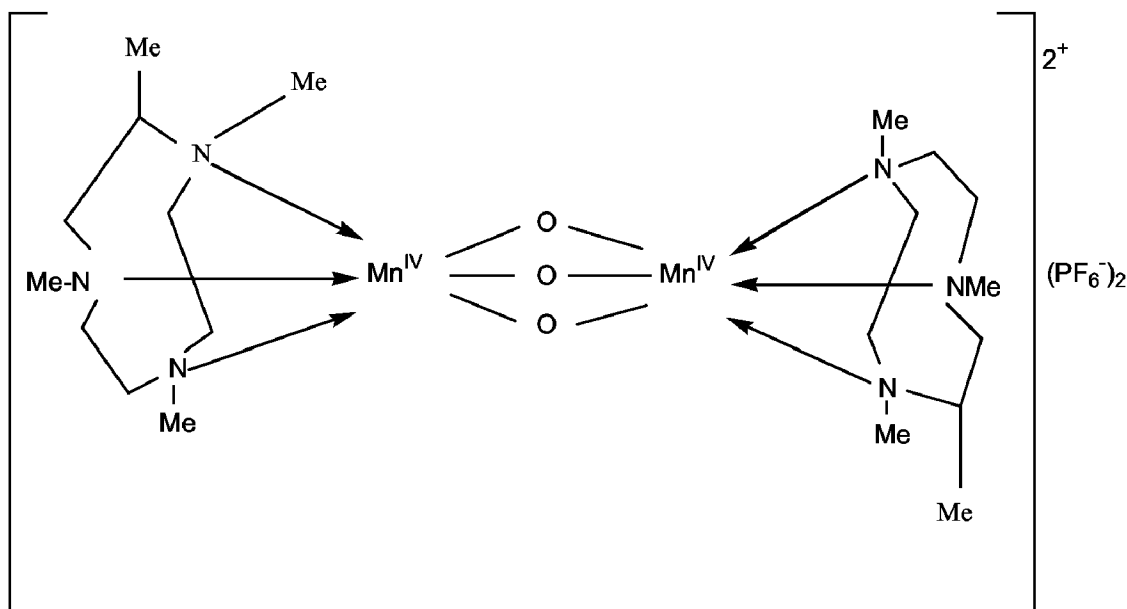


The structure of I is given below:



20 abbreviated as $[\text{Mn}^{\text{IV}}_2(\hat{\text{A}}\mu\text{-O})_3(\text{Me-TACN})_2](\text{PF}_6)_2$.

The structure of II is given below:



abbreviated as $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_3(\text{Me-MeTACN})_2] (\text{PF}_6)_2$.

- 5 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".

10 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

- 15 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

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.

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.

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.

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.

Suitable nonionic surfactants include: i) ethoxylated non-ionic surfactants prepared by the reaction of a monohydroxy alkanol or alkylphenol 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
 5 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).

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



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
 15 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.

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
 20 Olin Corporation's POLY-TERGENT® SLF-18B nonionic surfactants, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation.

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.

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

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

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*.

- 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.

- 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

- 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.

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

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.

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 Wehlstrasse 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.

5

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.

10 Additional Enzymes

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, 15 pectinases, mannanases, pectate lyases, keratinases, reductases, oxidases, phenoloxidases, lipoxxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase, amylases, and mixtures thereof.

Cellulases

20

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® 25 (Novozymes A/S) and Puradax HA® and Puradax® (Genencor International).

30

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

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

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

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

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.

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

Two automatic dishwashing compositions (Composition 1 and Composition 2) were made comprising the ingredients detailed herein below.

Ingredients (grams)	Composition 1	Composition 2
<i>Powder section</i>		
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
<i>Liquid section</i>		
Nonionic surfactant (R-PO _a EO _b H)	0.84	0.84
Nonionic surfactant (R-EO ₇ H)	0.89	0.89
Miscellaneous, etc.	Balance to 2.18	Balance to 2.18
PVA film	0.64	0.64

Tea stain removal

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
5 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 CaCO₃.

As artificial ballast soil 100g of IKW soil from frozen and 36g of minced meat were added from
10 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 CaCO₃ 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.

The test was carried out in a Miele GSL dishwashing machine in a normal R-50°C cycle (no pre-wash). 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

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

What is claimed is:

1. Use of a sulfonated polymer in an automatic dishwashing detergent composition for the removal of bleachable stains from dishware in automatic dishwashing.
- 5 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
10 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
15 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, iminodisuccinic 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
20 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
25 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
30 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.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/015876

A. CLASSIFICATION OF SUBJECT MATTER

INV. C11D17/00 C11D3/37 C11D3/39 C11D3/33
ADD. C11D17/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 2 662 436 A1 (PROCTER & GAMBLE [US]) 13 November 2013 (2013-11-13)	1-16
Y	paragraphs [0018], [0020], [0021], [0137], [0138]; claims 5-14; examples -----	15,16
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
X	US 2010/222247 A1 (ZIPFEL JOHANNES [DE] ET AL) 2 September 2010 (2010-09-02) paragraphs [0039] - [0048], [0051] - [0058], [0209] - [0211]; claims 1-8 -----	1-3, 10-12



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

26 April 2016

Date of mailing of the international search report

06/05/2016

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Loiselet-Taisne, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/015876

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 2662436	A1	13-11-2013	EP 2662436 A1	13-11-2013
			US 2013303424 A1	14-11-2013

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

US 2010222247	A1	02-09-2010	AT 514768 T	15-07-2011
			DE 102007042907 A1	12-03-2009
			EP 2185677 A1	19-05-2010
			ES 2367089 T3	28-10-2011
			KR 20100061669 A	08-06-2010
			US 2010222247 A1	02-09-2010
			WO 2009033973 A1	19-03-2009
