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## (54) **DISHWASHING METHOD**

(57) A method of washing ware in a dishwasher wherein the dishwasher comprises a washing chamber and a door to close the washing chamber, the method comprising the steps of:

starting a dishwashing program; automatically locking the door and keeping it locked for the whole duration of the dishwashing program; and dosing at least 100 mg of active enzyme into the washing chamber.

EP 4 388 967 A1

#### Description

#### FIELD OF THE INVENTION

<sup>5</sup> **[0001]** The present invention relates to a dishwashing method, in particular a dishwashing method involving the delivery of a high level of enzymes and the locking of the dishwasher door during the entire duration of a dishwashing program.

#### BACKGROUND OF THE INVENTION

10 [0002] Dishwasher cycles are getting cooler, shorter and using less water, yet consumers expect the same high performance from their automatic dishwasher detergent. There is also a desire to make dishwasher detergent more concentrated with a reduced carbon footprint. Dishwasher users sometimes open the dishwasher door during the dishwashing process. This can affect the performance of the dishwasher. Once the door is open the dishwasher rotor can stop (requiring extra energy to star once the door is closed), the temperature of the water can decrease and steam can escape the dishwasher. The open door can also contribute to the loss of detergent, this is more important in the case of concentrated products. The open door can also contribute to the loss of the volatiles components of a perfume, and this can contribute to the change of character of a perfume.

**[0003]** It is an objective of the present invention to provide a dishwashing process which involves the use of more concentrated products with a higher level of cleaning actives and reduced amount of energy and water.

#### SUMMARY OF THE INVENTION

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**[0004]** The present invention provides a method of washing dishware/tableware in a dishwasher. The dishwasher comprises a washing chamber and a door to close the washing chamber. The method of automatic dishwashing comprises the steps of:

- i) starting a dishwashing program;
- ii) automatically locking the door when the program starts and keeping the door locked during the whole duration of the dishwashing program; and
- iii) dosing at least 100 mg of active enzyme, preferably 120 mg of active enzyme into the washing chamber.

## DETAILED DESCRIPTION OF THE INVENTION

**[0005]** All percentages, ratios and proportions used herein are by weight percent of the composition, unless otherwise specified. All average values are calculated "by weight" of the composition, unless otherwise expressly indicated. All ratios are calculated as a weight/weight level, unless otherwise specified.

[0006] All measurements are performed at 25°C unless otherwise specified.

**[0007]** As used herein, the articles including "a" and "an" are understood to mean one or more of what is claimed or described. Unless otherwise noted, all component or composition levels are in reference to the active portion of that component or composition, and are exclusive of impurities, for example, residual solvents or by-products, which may be present in commercially available sources of such components or compositions.

**[0008]** The present invention envisages a method of automatic dishwashing, in particular a method of washing ware in a dishwasher, in a domestic dishwasher. By "ware" is herein understood any cookware and tableware. The method of the invention uses a high level of enzymes and provides good soil removal and prevents the risk of losing enzymes during the wash. The method of the invention also allows for the use of more environmentally friendly programs, using less water and less energy and still providing a good level of cleaning.

**[0009]** The term "automatic dishwashing detergent composition" as used herein means a composition that contributes to cleaning and/or finishing (removing filming and providing shine) to be used in dishwashing machine.

## 50 Method of washing

**[0010]** The method of washing of the invention involves placing the ware in the dishwasher, locking the door and starting a dishwasher program. The program is run in the presence of detergent, the detergent can be delivered from the dishwasher dosing system, usually placed on the dishwasher door. Contrary to the current dishwashers, the door in the method of the invention, is locked and it cannot be open by the user during the course of the program.

**[0011]** It is not uncommon that the user opens the door of the dishwasher once a program has started, sometimes to add to the load an item that the user forgot to place in the dishwasher before the program started. When the dishwasher door is opened, wash liquor can splash contributing to the loss of detergent. The loss of detergent can be more impactful

when the product is in concentrated form and also when the wash liquor is more concentrated because less water is used. It is not only the loss of detergent that it is a problem but also the fact that the user might become in contact with the wash liquor, the wash liquor can be harsh, and the user would prefer to avoid skin contact with it.

[0012] During the course of a selected dishwashing program a domestic dishwasher generally performs one or more cycles, such as a pre-wash cycle, main wash, intermediate rinse cycle, final rinse cycle and then a drying cycle to terminate the program. During the respective cycles, wash liquor is distributed, in particular sprayed, by means of a rotating spray arm, a fixed spray nozzle, for example a top spray head, a movable spray nozzle, for example a top spinning unit, and/or some other liquid distribution apparatus, in the treatment chamber of the dishwasher cavity (herein referred to as "washing chamber"), in which wash liquor is applied to items to be washed, such as dishes and/or cutlery, to be cleaned, which are supported in and/or on at least one loading unit, for example a pull-out rack or a cutlery drawer that can preferably be removed or pulled out. To this end the dishwasher is preferably supplied with wash liquor by way of at least one supply line by an operating circulating pump, said wash liquor collecting at the bottom of the dishwasher cavity, preferably in a depression, in particular in a sump. If the wash liquor has to be heated during the respective liquid-conducting washing sub-cycle, the wash liquor is heated by means of a heating facility. This can be part of the circulating pump. At the end of the respective liquid-conducting washing sub-cycle some or all of the wash liquor present in the treatment chamber of the dishwasher cavity in each instance is pumped out by means of a drain pump.

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**[0013]** A dishwasher can usually provide a plurality of programs, such as a basic wash program, for washing normally dirty ware dried up to a certain extent; an intensive wash program, for washing very dirty ware, or in case of food rests particularly difficult to remove (very dry or burnt spots); an economy wash program, for washing lightly dirty ware or partial loads of ware; fast wash program, for a washing like the previous cycle, should a faster washing of partial ware loadings be wished. Each program comprises a plurality of sequential steps. Usually, one or two cold prewash cycles, a cleaning cycle (also known as main wash), a cold rinse cycle, a hot rinse cycle and optionally a drying cycle. During the main wash, the cleaning composition is added to the water in the dishwasher to form the wash liquor.

**[0014]** An example of an integrated storage reservoir is a receptacle built into the door of the automatic dishwasher and connected to the interior of the dishwasher by a supply line.

**[0015]** An example of an autarkic storage reservoir is a "top-down bottle" having a base outlet valve, and which can be placed, for example, in the cutlery basket of the automatic dishwasher. A removable dosing device can be for example an automated unit comprising cartridges filled with the cleaning composition and a dispensing unit capable of releasing a controlled amount of cleaning composition to the main wash and to the rinse. Different types of hardware might be part of the dosing device for controlling the dispensing of the cleaning composition, or for communicating with external devices such as data processing units, the dishwasher or a mobile device or server that a user can operate.

[0016] The storage reservoir has at least one chamber for receiving a cleaning composition. The storage reservoir can have two chambers, one to deliver the cleaning composition into the main wash and another one to deliver the cleaning composition into the rinse. The storage reservoir has very good thermal stability, especially if the reservoir is located in the interior of the dishwasher. Preferably, from 3 to 15, more preferably from 5 to 10 grams of the cleaning composition are delivered in the main wash and the rinse of each dishwashing program. The multi-dosing system can be linked to sensors that can determine, based on sensor's input, the amount of cleaning composition required. Sensors that may be used include pH, turbidity, temperature, humidity, conductivity, etc. The dishwasher may require data processing power to achieve this. It is preferred that the dishwashing will have connectivity to other devices. This may take the form of wi-fi, mobile data, blue tooth, etc. This may allow the dishwasher to be monitored and/or controlled remotely. Preferably, this also allows the machine to connect with the internet.

**[0017]** The volume of preferred storage reservoirs containing one or more chambers is from 10 to 1000 ml, preferably from 20 to 800 ml, and especially from 50 to 500 ml.

**[0018]** Preferred processes according to the invention are those wherein the cleaning composition, prior to being metered into the interior of the dishwasher, remains in the storage reservoir that is located outside (as for example WO2019/81910A1) or inside of the dishwasher for at least two, preferably at least four, particularly preferably at least eight and in particular at least twelve separate dishwashing programs.

**[0019]** The multi-dosing system can be linked to sensors that can determine, based on sensor's input, the amount of cleaning composition required.

**[0020]** In the context of the present application, "a dishwashing program" is a completed cleaning process that preferably also include a pre-rinse cycle and/or a rinse cycle in addition to the main cleaning cycle, and which can be selected and actuated by means of the program switch of the dishwasher.

**[0021]** The method of the invention is particularly suited to be used in short programs, in low temperature programs and in low water usage programs.

[0022] By "short program" is herein meant a program having a duration of less than 1 hour, preferably from 10 minutes to 40 minutes.

**[0023]** By "low temperature program" is herein meant a program having a main wash temperature of 50°C or below, preferably 45°C or below, preferably 40°C or below.

[0024] By "low water usage program" is herein meant a program that last less than an hour, preferably from 10 minutes to 40 minutes.

**[0025]** Preferably, the program for use in the method of the invention is a short, low temperature program. More preferably a low water using program. In these kind of programs (i.e., short, low temperature and low water usage) it is more important to keep the door locked during the whole duration of the program, given that the loss of time, temperature, water or cleaning actives, especially enzymes, has a greater impact on the performance of the wash. Preferably, the program for use in the method of the invention is a low energy program using less than 1 kW, preferably less than 0.5 kW and even about 0.1 kW.

**[0026]** A multi-dosing system suitable for use in the method of the invention is designed to deliver to the water of the main wash and optionally to the water of the pre-wash and to the water of the rinse, preferably the final rinse.

[0027] The composition for use in the method of the invention or part thereof can be in liquid and/or solid form. For example, some of the components of the composition can be in solid form while other can be in liquid form. The composition comprises high level of enzymes and optionally but preferably the composition can comprise a complexing agent, bleach, bleach catalyst and preferably a phosphonate, a builder, non-ionic surfactant, and glass and/or metal care agents. Preferably, the composition comprises the tri-sodium salt of MGDA, HEDP, polymer preferably a sulfonated polymer comprising 2-acrylamido-2-methylpropane sulfonic acid monomers, sodium carbonate, a bleach, preferably sodium percarbonate, a bleach activator, preferably TAED, a bleach catalyst, preferably a manganese bleach catalyst. The composition might be free of citrate. The composition can further comprise a cationic polymer that provides anti-spotting benefits. The composition is such as to provide at least 100 mg of active enzyme per wash. Preferably at least 120 mg, more preferably at least 130 mg of active enzyme per wash.

[0028] The composition for use in the method of the invention preferably has a pH as measured in 1% weight/volume aqueous solution in distilled water at 20°C of at least 10, more preferably from about 10 to less than about 11.5 and especially from about 10.5 to about 11.5. These high pH compositions can be easily used because the user cannot open the dishwasher door during the course of a program and therefore the user is not exposed to high pH washing liquors.

**[0029]** 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 mL of product at 20°C.

[0030] The composition of the invention can be provided in unit-dose form.

Automatic dishwashing cleaning composition

[0031] The automatic dishwashing cleaning composition (sometimes also referred to as "detergent composition") suitable for use in the method of the invention can be in any physical form. It can be a loose powder, a gel or presented in unit dose form. Preferably it is in unit dose form, unit dose forms include pressed tablets and water-soluble packs. The automatic dishwashing cleaning composition of the invention is preferably presented in unit-dose form and it can be in any physical form including solid, liquid and gel form. The composition for use in the method 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. Especially preferred are compositions in unit dose form wrapped in a polyvinyl alcohol film having a thickness of less than 100  $\mu$ m, preferably from 20 to 90  $\mu$ m. 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 comfortably in a dishwasher dispenser. Even though this range amounts to a low amount of detergent, the detergent comprises a high level of enzymes and it has been formulated in a way that provides all the benefits mentioned herein above.

**[0032]** The composition 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.

Cleaning actives

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[0033] The cleaning actives described herein below can be part of detergents or compositions used in the method of the invention.

Complexing agent

[0034] Complexing agents are materials capable of sequestering hardness ions, particularly calcium and/or magnesium. The composition of the invention can comprise a high level of complexing agent, however the level should not be too high otherwise enzymes, in particular proteases can be negatively affected. Too high level of complexing agent can also negatively impact on glass care.

[0035] The composition of the invention may comprise from 15% to 50%, preferably from 20% to 40%, more preferably from 20% to 35% by weight of the composition of a complexing agent selected from the group consisting of methylglycine-N,N-diacetic acid (MGDA), glutamic acid-N,N-diacetic acid (GLDA), iminodisuccinic acid (IDS), citric acid, aspartic acid -N,N-diacetic acid (ASDA) its salts and mixtures thereof. Especially preferred complexing agent for use herein is a salt of MGDA, in particular the trisodium salt of MGDA. Mixture of citrate and the trisodium salt of MGDA are also preferred for use herein. Preferably, the composition of the invention comprises from 15% to 40% by weight of the composition of the trisodium salt of MGDA.

Inorganic builder

**[0036]** 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 5 to 50%, more preferably from 10 to 40% and especially from 15 to 30% of sodium carbonate by weight of the composition.

Bleach

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**[0037]** The composition of the invention may be free of bleach or it may comprise from about 8 to about 30%, more preferably from about 9 to about 25%, even more preferably from about 9 to about 20% of bleach by weight of the composition. Preferably the composition of the invention comprises sodium percarbonate. Preferably the bleach is delivered at the same time as the bleach catalyst.

**[0038]** Inorganic and organic bleaches are suitable for use herein. Inorganic bleaches include perhydrate salts such as perborate, percarbonate, 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.

**[0039]** 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.

[0040] Potassium peroxymonopersulfate is another inorganic perhydrate salt of utility herein.

**[0041]** Typical organic bleaches are organic peroxyacids, especially dodecanediperoxoic acid, tetradecanediperoxoic acid, and hexadecanediperoxoic acid. Mono- and diperazelaic acid, monoand 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.

**[0042]** 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- $\alpha$ -naphthoic acid and magnesium monoperphthalate, (b) the aliphatic or substituted aliphatic peroxy acids, such as peroxylauric acid, peroxystearic acid,  $\epsilon$ -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).

Bleach Catalyst

**[0043]** If the composition comprises bleach then it may also comprise 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.

**[0044]** Bleach catalysts preferred for use herein include manganese triazacyclononane and related complexes; Co, Cu, Mn and Fe bispyridylamine and related complexes; and pentamine acetate cobalt(III) and related complexes.

**[0045]** The composition of the invention may comprise from 0.001 to 0.5, more preferably from 0.002 to 0.05% of bleach catalyst by weight of the composition. Preferably the bleach catalyst is a manganese bleach catalyst, more preferably manganese 1,4,7-trimethyl-1,4,7-triazocyclononane.

Bleach Activators

**[0046]** 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 phenol sulfonates, in particular n-nonanoylor 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 0.01 to 5, preferably from 0.2 to 2% by weight of the composition of bleach activator, preferably TAED. Preferably the bleach activator is delivered at the same time as the bleach.

#### Phosphonate

**[0047]** The composition of the invention may comprise a high level of phosphonate, preferably HEDP. It comprises preferably from 1% to 7%, more preferably 1% to 6% by weight of the composition of HEDP.

#### Polymer

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**[0048]** The polymer, if present, 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 15% by weight of the second composition. Sulfonated/carboxylated polymers are particularly suitable for the second composition.

**[0049]** 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.

[0050] Preferred sulfonated monomers include one or more of the following: 1-acrylamido-1-propanesulfonic acid, 2-acrylamido-2-propanesulfonic acid, 2-methyl-1-propanesulfonic acid, 2-methacrylamido-2-methyl-1-propanesulfonic acid, 3-methacrylamido-2-hydroxy-propanesulfonic acid, allylsulfonic acid, methallylsulfonic acid, allyloxy-benzenesulfonic acid, methallyloxybenzenesulfonic acid, 2-hydroxy-3- (2-propenyloxy) propanesulfonic acid, 2-methyl-2-propen-1-sulfonic acid, styrenesulfonic acid, vinylsulfonic acid, 3-sulfopropyl, 3-sulfopropyl methacrylate, sulfomethacrylamide, sulfomethylmethacrylamide and mixtures of said acids or their water-soluble salts.

**[0051]** 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 nonionic 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.

**[0052]** 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. The carboxylic acid is preferably (meth)acrylic acid. The sulfonic acid monomer is preferably 2-acrylamido-2-propanesulfonic acid (AMPS).

**[0053]** 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.

**[0054]** Suitable polymers include anionic carboxylic polymer of low molecular weight. They can be homopolymers or copolymers with a weight average molecular weight of less than or equal to about 200,000 g/mol, or less than or equal to about 50,000 g/mol, or from about 3,000 to about 50,000 g/mol, preferably from about 5,000 to about 45,000 g/mol. The polymer may be a low molecular weight homopolymer of polyacrylate, with an average molecular weight of from 1,000 to 20,000, particularly from 2,000 to 10,000, and particularly preferably from 3,000 to 5,000.

**[0055]** The polymer may be a copolymer of acrylic with methacrylic acid, acrylic and/or methacrylic with maleic acid, and acrylic and/or methacrylic with fumaric acid, with a molecular weight of less than 70,000. Their molecular weight ranges from 2,000 to 80,000 and more preferably from 20,000 to 50,000 and in particular 30,000 to 40,000 g/mol. and a ratio of (meth)acrylate to maleate or fumarate segments of from 30:1 to 1:2.

**[0056]** The polymer may be a copolymer of acrylamide and acrylate having a molecular weight of from 3,000 to 100,000, alternatively from 4,000 to 20,000, and an acrylamide content of less than 50%, alternatively less than 20%, by weight of the polymer can also be used. Alternatively, such polymer may have a molecular weight of from 4,000 to 20,000 and

an acrylamide content of from 0% to 15%, by weight of the polymer.

[0057] Polymers suitable herein also include itaconic acid homopolymers and copolymers.

**[0058]** Alternatively, the polymer can be selected from the group consisting of alkoxylated polyalkyleneimines, alkoxylated polycarboxylates, polyethylene glycols, styrene co-polymers, cellulose sulfate esters, carboxylated polysaccharides, amphiphilic graft copolymers and mixtures thereof.

Ethylene oxide - propylene oxide block copolymer

**[0059]** A composition suitable for use in the method of the invention preferably comprises an ethylene oxide - propylene oxide block copolymer. The ethylene oxide - propylene oxide block copolymer preferably has a cloud point of 20°C or greater than 20°C, preferably 21°C or greater than 21°C, or preferably 22°C or greater than 22°C.

**[0060]** Preferably, the ethylene oxide - propylene oxide triblock has a cloud point lower than 50°C, preferably lower than 40°C.

**[0061]** Preferably, the ethylene oxide - propylene oxide block copolymer is a triblock copolymer. Preferably the ethylene oxide - propylene oxide block copolymer is a triblock copolymer having one of the following structures:

(I)

EOx1 POy1 EOx2

POy2 EOx3 POy3 (II)

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wherein each of x1, x2 and x3 is independently in the range of from 1 to 50, and each of y1, y2 and y3 is independently in the range of from 10 to 70.

**[0062]** The ethylene oxide-propylene oxide-ethylene oxide triblock copolymer of Formula I preferably has an average propylene oxide chain length of between 10 and 70, preferably between 20 and 60, more preferably between 25 and 55 propylene oxide units.

**[0063]** The ethylene oxide-propylene oxide-ethylene oxide triblock copolymer of Formula II preferably has an average ethylene oxide chain length of between 1 and 50, preferably between 2 and 40, more preferably between 3 and 30 ethylene oxide units.

**[0064]** Preferably, the ethylene oxide-propylene oxide triblock copolymer has a weight average molecular weight of between about 1000 and about 10,000 Daltons, preferably between about 1200 and about 8000 Daltons, more preferably between about 1500 and about 7000 Daltons, even more preferably between about 1750 and about 5000 Daltons, most preferably between about 2000 and about 4000 Daltons.

**[0065]** Suitable ethylene oxide-propylene oxide triblock copolymers are commercially available under the Pluronic PE and Pluronic RPE series from the BASF company, or under the Tergitol L series from the Dow Chemical Company. Particularly suitable materials are Pluronic PE 9200, Tergitol L81, Tergitol L62, Tergitol L61, Pluronic RPE 3110 and Pluronic RPE 2520.

[0066] The composition preferably comprises surfactants in addition to the block co-polymer.

Method of measuring the cloud point

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[0067] The cloud point temperature can be determined as follows: a solution containing 1% of the corresponding material (e.g. the block co-polymer) by weight of the solution is prepared in distilled water. The solution is stirred gently before analysis to ensure that the process occurs in chemical equilibrium. The cloud point temperature is taken in a thermostatic bath by immersing the solution in a 75 mm sealed glass test tube. To ensure the absence of leakage, the test tube is weighed before and after the cloud point 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 cloud point. The cloud point temperature is determined visually at the first sign of turbidity.

Surfactant

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**[0068]** 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.

**[0069]** 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.

**[0070]** 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.

[0071] 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.

[0072] 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).

[0073] Other 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)

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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. **[0074]** 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 POLYTERGENT® SLF-18B nonionic surfactants, as described, for example, in WO 94/22800, published October 13, 1994 by Olin Corporation.

**[0075]** A ternary mixture of non-ionic surfactant can be included in compositions suitable for use in the method of the invention. Compositions comprising this mixture have been found to exhibit good grease suspension, even at low temperatures, and drying properties especially on items treated in a dishwashing operation.

**[0076]** The compositions may comprise a ternary surfactant mixture comprising; a) a non-ionic surfactant having a cloud point of 50°C or above (herein referred to as "high cloud point non-ionic surfactant"), and b) a non-ionic surfactant having a cloud point below 50°C (herein referred to as "low cloud point non-ionic surfactant"), wherein the weight ratio of a) to b) is preferably in the range of from 2:1 to 1:2. The ternary surfactant mixture may further comprises an ethylene oxide-propylene oxide triblock copolymer having a cloud point below 50°C, preferably below 40°C.

**[0077]** Preferably, the high cloud point nonionic surfactant has a cloud point in the range of from 60°C to 80°C and the low cloud point nonionic surfactant has a cloud point in the range of from 8°C to 35°C. Particularly good results can be achieved by compositions comprising a non-ionic surfactant mixture, wherein the high cloud point non-ionic surfactant is an alkoxylkated non-ionic surfactant having a single alkoxylate type, and the low cloud point non-ionic surfactant is an alkoxylkated non-ionic surfactant having at least two alkoxylate types.

[0078] The alkoxylated non-ionic surfactants of high cloud point may be prepared by the reaction of a monohydroxy alkanol or alkylphenol with 6 to 22 carbon atoms, preferably 8 to 20 carbon atoms, most preferably 10 to 18 carbon atoms. It is preferred that the type of alkoxylate surfactant is ethoxylate, butoxylate or propoxylate with ethoxylate being especially preferred. Preferably the high cloud point surfactants have 3 to 20 moles, particularly preferred 4 to 10 moles, and still more preferred 5 to 8 moles of alkylene oxide, particularly ethylene oxide, per mole of alcohol or alkylphenol. A particularly preferred high cloud point non-ionic surfactant is C10-C15 with 5-10 EO, more preferably C13 with 7EO. The high cloud point non-ionic surfactants may be prepared from either branched or linear chain fatty alcohols of the above types.

[0079] Preferred examples of high cloud point non-ionic surfactants are Lutensol TO7 (BASF), Marlipal O13/70 (Sasol), Imbentin-T/070 (Kolb), Emuldac AS-11 (Sasol) and Emuldac AS-20 (Sasol).

**[0080]** The alkoxylated non-ionic surfactants of low cloud point may be prepared by the reaction of a monohydroxy alkanol or alkylphenol with 4 to 25 carbon atoms, preferably 6 to 20 carbon atoms, most preferably 8 to 14 carbon atoms. It is preferred that the low cloud point surfactant has 2 to 45 moles in total of alkylene oxide per mole of surfactant. It is preferred that the type of alkoxylates in low cloud point surfactant is a mixture of at least two of ethoxylate, butoxylate and/or propoxylate, with a mixture of ethoxylate and propoxylate being especially preferred. Preferably the low cloud

point surfactants have 2 to 25 moles, especially 5 to 20 moles of ethylene oxide per mole of alcohol or alkylphenol and 2 to 40 moles, more preferably 5 to 30 moles of propylene oxide per mole of alcohol or alkylphenol. A mixture of butylene oxide or propylene oxide is also possible. A particularly preferred low cloud point surfactant is C10-C12 with 10-20 EO and 10-20 PO. The low cloud point non-ionic surfactants may be prepared from either branched or linear chain fatty alcohols of the above types.

**[0081]** Low cloud point surfactants may also include surfactants which are ethoxylated and butoxylated mono-hydroxy alkanols or alkylphenols, which additionally comprises polyoxyethylene-polyoxypropylene block copolymer units. The alcohol or alkylphenol portion of such surfactants constitutes more than 30%, preferably more than 50%, more preferably more than 70% by weight of the overall molecular weight of the non-ionic surfactant.

[0082] Preferred examples of low cloud point non-ionic surfactants are Plurafac SLF-180 (BASF) and Ecosurf LFE-1410 (Dow).

**[0083]** The low cloud point surfactant is typically more hydrophobic than the high cloud point surfactant and the amounts and types of the two surfactants in the claimed mixture are preferably selected such that the foaming characteristics of the composition are controlled to within the desired range. For automatic dishwashing applications it is usual to desire low-foaming characteristics

[0084] It is especially preferred that the high cloud point non-ionic surfactant is an ethoxylated non-ionic surfactant and the low cloud point non-ionic surfactant is a mixed propoxylated-ethoxylated-propoxylated non-ionic surfactant.

[0085] The weight ratio of high cloud point to low cloud point non-ionic surfactant is preferably in the range 2:1 to 1:2, more preferably 1.5:1 to 1:1.5.

### Inorganic builder

**[0086]** 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 5 to 60%, more preferably from 10 to 50% and especially from 15 to 45% of sodium carbonate by weight of the composition. The composition of the present invention might comprise from 2% to 8%, preferably from 3% to 6% by weight of the composition of a crystalline sodium silicate. The crystalline sodium silicate, is preferably a layered silicate and preferably has the composition NaMSi<sub>x</sub>  $O_{2x+1.y}$  H<sub>2</sub>O, in which M denotes sodium or hydrogen, x is 1.9 to 4 and y is 0 to 20. The especially preferred silicate for use herein has the formula:  $Na_2Si_2O_5$ .

#### Enzymes

[0087] 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 ILTPAC 1-letter codes for amino acids are used. The method of the invention involves the delivery of at least 100 mg of active enzyme per wash, preferably at least 120 mg of active enzyme per wash. Enzymes suitable for use in the method of the invention include amylases, proteases, lipases, xylases, hemicellulases, cellulases, etc

#### 40 Proteases

[0088] The composition of the invention preferably comprises a protease. A mixture of two or more proteases can also contribute to an enhanced cleaning across a broader temperature, cycle duration, and/or substrate range, and provide superior shine benefits, especially when used in conjunction with an anti-redeposition agent and/or a sulfonated polymer. [0089] Suitable proteases include metalloproteases and serine proteases, including neutral or alkaline microbial serine proteases, such as subtilisins (EC 3.4.21.62). Suitable proteases include those of animal, vegetable or microbial origin. In one aspect, such suitable protease may be of microbial origin. The suitable proteases include chemically or genetically modified mutants of the aforementioned suitable proteases. In one aspect, the suitable protease may be a serine protease, such as an alkaline microbial protease or/and a trypsin-type protease. Examples of suitable neutral or alkaline proteases include: (a) subtilisins (EC 3.4.21.62), especially those derived from Bacillus, such as Bacillus sp., B. lentus, B. alkalophilus, B. subtilis, B. amyloliquefaciens, B. pumilus, B. gibsonii, and B. akibaii described in WO2004067737, WO2015091999, WO2015024739, WO2015143360, US 6,312,936, US 5,679,630, US 4,760,025, DE102006022216A1, DE 102006022224A1, WO2015089447, WO2015089441, WO2016066756, WO2016066757, WO2016069557, WO2016069563, WO2016069569.

(b) trypsin-type or chymotrypsin-type proteases, such as trypsin (e.g., of porcine or bovine origin), including the Fusarium protease described in WO 89/06270 and the chymotrypsin proteases derived from Cellumonas described in WO 05/052161 and WO 05/052146.

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- (c) metalloproteases, especially those derived from *Bacillus amyloliquefaciens* described in WO07/044993A2; from *Bacillus, Brevibacillus, Thermoactinomyces, Geobacillus, Paenibacillus, Lysinibacillus* or *Streptomyces spp.* described in WO2014194032, WO2014194054 and WO2014194117; from *Kribella alluminosa* described in WO2015193488; and from Streptomyces and *Lysobacter* described in WO2016075078.
- (d) protease having at least 90% identity to the subtilase from Bacillus sp. TY 145, NCIMB 40339, described in WO92/17577 (Novozymes A/S), including the variants of this Bacillus sp TY145 subtilase described in WO2015024739, and WO2016066757.
- (e) protease having at least 90%, preferably at least 92% identity with the amino acid sequence of SEQ ID NO:85 from WO2016/205755 comprising at least one amino acid substitution (using the SEQ ID NO:85 numbering) selected from the group consisting of 1, 4, 9, 21, 24, 27, 36, 37, 39, 42, 43, 44, 47, 54, 55, 56, 74, 80, 85, 87, 99, 102, 114, 117, 119, 121, 126, 127, 128, 131, 143, 144, 158, 159, 160, 169, 182, 188, 190, 197, 198, 212, 224, 231, 232, 237, 242, 245, 246, 254, 255, 256, and 257, including the variants found in WO2016/205755 and WO2018/118950.
- (f) protease having at least 90%, preferably at least 92%, more preferably at least 98% identity with the amino acid sequence of SEQ ID NO:1 from US 10,655,090 B2. A preferred protease has 100% identity with SEQ ID NO:1 from US 10,655,090 B2. Another preferred protease has 1 to 4 modifications with respect to SEQ ID NO:1 from US 10,655,090 B2.

[0090] Especially preferred proteases for the detergent of the invention are:

- (a) 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, N76D, N87S, S99D, S99AD, S99A, S101G, S101M, S103A, V104N/I, G118V, G118R, S128L, P129Q, S130A, Y167A, R170S, A194P, V205I, Q206L/D/E, Y209W and/or M222S. and/or
  - (b) protease having at least 95%, more preferably at least 98%, even more preferably at least 99% and especially 100% identity with the amino acid sequence of SEQ ID NO:85 from WO2016/205755 comprising at least one amino acid substitution (using the SEQ ID NO:85 numbering) selected from the group comprising:

P54E/G/I/L/Q/S/T/V; S99A/E/H/I/K/M/N/Q/R/T/V;S126A/D/E/F/G/H/I/L/M/N/Q/R/T/V/;
D127A/E/F/G/H/I/L/M/N/P/Q/S/T/V/W/Y; F 128A/C/D/E/G/H/I/K/L/M/N/P/Q/R/S/T/W, A37T, S39E, A47V, T56Y, I80V, N85S, E87D, T114Q, and N242D;

**[0091]** Most preferably the additional protease is either selected from the group of proteases 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
- (vii) S99AD

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- or selected from the group of proteases comprising one or more, preferably two or more, preferably three or more, preferably four or more of the below mutations versus SEQ ID NO:1 from WO2018/118950:
  - P54T, S99M, S126A/G, D127E, F128C/D/E/G, A37T, S39E, A47V, T56Y, I80V, N85S, E87D, T114Q, and N242D.
  - **[0092]** Most preferred for use herein are proteases wherein the protease is a variant having at least 60% identity with the amino acid sequence of SEQ ID NO:1 of WO2019/125894 A1 and comprising at least one amino acid substitution (using the SEQ ID NO: 1 numbering) selected from the group consisting of: X54T; X126A, D, G, V, E, K, I; X127E, S, T, A, P, G, C; and X128E, C, T, D, P, G, L, Y, N and X211L. Preferably, a variant having at least 90% identity with the amino acid sequence of SEQ ID NO:1 and said variant comprising at least one amino acid substitution (using the SEQ ID NO:1 numbering) selected from the group consisting of P54T, S126A, D127E, F128G and M211L
- Other preferred protease for use herein include a protease wherein the protease is a variant having at least 90% identity with the amino acid sequence of SEQ ID NO:1 of WO2019/245839 A1 and the variant comprises one or more amino acid substitutions at one or more positions corresponding to SEQ ID NO: 1 positions selected from:

1C/D/E/M/N, 21L, 37A, 54A, 73V, 76D/H/N/T, 83G, 84D/E/F, 85I/M, 86I/S/T/V, 87T, 88M/V, 89F/W, 91I, 95A/N/S,

96M/Q, 97E, 98M, 99A/F/H/I/K/L/Q/T/W/Y, 102L, 104E, 105L, 106I/V, 108A, 109I, 112C, 114M/N, 115A/E/H/Q, 116A/E/G/H/Q, 118A/D/N, 122C, 124E/Q, 126I/Q/V, 128H/I/L/M/N/Q/S/T/V/Y, 129D/H, 130N, 131D/E/N/P/Q, 135A/D/H/K/L/M/N/Q/T/V/W/Y, 138D/E, 139E/L, 141A/E/F/H/Y, 142A/D/E, 143E/H/K/M/S/V, 156E, and 157C/D/E wherein the amino acid positions of the variant are numbered by correspondence with the amino acid sequence of SEQ ID NO: 1.

[0093] Suitable commercially available additional protease enzymes include those sold under the trade names Alcalase®, Savinase®, Primase®, Durazym®, Polarzyme®, Kannase®, Liquanase®, Liquanase Ultra®, Savinase Ultra®, Savinase Evity®, Ovozyme®, Neutrase®, Everlase®, Coronase®, Blaze®, Blaze Ultra®, Blaze Evity® and Esperase® by Novozymes A/S (Denmark); those sold under the tradename Maxatase®, Maxacal®, Maxapem®, Properase®, Purafect®, Purafect Prime®, Purafect Ox®, FN3®, FN4®, Excellase®, Ultimase®, Extremase® and Purafect OxP® by Dupont; those sold under the tradename Opticlean® and Optimase® by Solvay Enzymes; and those available from Henkel/Kemira, namely BLAP (sequence shown in Figure29 of US 5,352,604 with the following mutations S99D + S101 R + S103A + V104I + G159S, hereinafter referred to as BLAP), BLAP R (BLAP with S3T + V4I + V199M + V205I + L217D), BLAP X (BLAP with S3T + V4I + V205I) and BLAP F49 (BLAP with S3T + V4I + A194P + V199M + V205I + L217D); and KAP (Bacillus alkalophilus subtilisin with mutations A230V + S256G + S259N) from Kao.

**[0094]** Especially preferred for use herein are commercial proteases selected from the group consisting of Properase<sup>®</sup>, Blaze Evity<sup>®</sup>, Savinase Evity<sup>®</sup>, Extremase<sup>®</sup>, Ultimase<sup>®</sup>, Everlase<sup>®</sup>, Savinase<sup>®</sup>, Excellase<sup>®</sup>, Blaze Ultra<sup>®</sup>, BLAP and BLAP variants.

Preferably the method of the invention involves the delivery of at least 90 mg of active protease per wash.

**[0095]** Preferred levels of protease in a detergent for use in the method of the invention include from about 0.5 to about 15 and especially from about 2 to about 12 mg of active protease/g of composition.

#### **Amylases**

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**[0096]** Preferably the composition of the invention may comprise an amylase. Suitable alpha-amylases include 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. NCBI 12289, NCBI 12512, NCBI 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) variants described in WO 96/23873, WO00/60060, WO06/002643 and WO2017/192657, especially the variants with one or more substitutions in the following positions versus SEQ ID NO. 12 of WO06/002643:
- 26, 30, 33, 82, 37, 106, 118, 128, 133, 149, 150, 160, 178, 182, 186, 193, 202, 214, 231, 246, 256, 257, 258, 269, 270, 272, 283, 295, 296, 298, 299, 303, 304, 305, 311, 314, 315, 318, 319, 339, 345, 361, 378, 383, 419, 421, 437, 441, 444, 445, 446, 447, 450, 461, 471, 482, 484, preferably that also contain the deletions of D 183\* and G184\*. (b) variants exhibiting at least 90% identity with SEQ ID No. 4 in WO06/002643, the wild-type enzyme from Bacillus SP722, especially variants with deletions in the 183 and 184 positions and variants described in WO 00/60060, WO2011/100410 and WO2013/003659 which are incorporated herein by reference.
- (c) 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 mutations in the following positions M202, M208, S255, R172, and/or M261. Preferably said amylase comprises one or more of M202L, M202V, M202S, M202T, M202I, M202Q, M202W, S255N and/or R172Q. Particularly preferred are those comprising the M202L or M202T mutations. (d) variants described in WO 09/149130, preferably those exhibiting at least 90% identity with SEQ ID NO: 1 or SEQ ID NO:2 in WO 09/149130, the wild-type enzyme from Geobacillus Stearophermophilus or a truncated version thereof
- (e) variants exhibiting at least 89% identity with SEQ ID NO:1 in WO2016091688, especially those comprising deletions at positions H183+G184 and additionally one or more mutations at positions 405, 421, 422 and/or 428.
- (f) variants exhibiting at least 60% amino acid sequence identity with the "PcuAmyl a-amylase" from Paenibacillus curdlanolyticus YK9 (SEQ ID NO:3 in WO2014099523).
  - (g) variants exhibiting at least 60% amino acid sequence identity with the "CspAmy2 amylase" from Cytophaga sp. (SEQ ID NO:1 in WO2014164777).
  - (h) variants exhibiting at least 85% identity with AmyE from Bacillus subtilis (SEQ ID NO:1 in WO2009149271).
- (i) variants exhibiting at least 90% identity with the wild-type amylase from Bacillus sp. KSM- K38 with accession number AB051102.
- (j) variants exhibiting at least 80% identity with the mature amino acid sequence of AAI10 from Bacillus sp (SEQ ID NO:7 in WO2016180748), preferably comprising a mutation in one or more of the following positions modification

in one or more positions 1, 54, 56, 72, 109, 113, 116, 134, 140, 159, 167, 169, 172, 173, 174, 181, 182, 183, 184, 189, 194, 195, 206, 255, 260, 262, 265, 284, 289, 304, 305, 347, 391, 395, 439, 469, 444, 473, 476, or 477 (k) variants exhibiting at least 80% identity with the mature amino acid sequence of the fusion peptide (SEQ ID NO:14 in US 2019/0169546), preferably comprising one or more of the mutations H1\*, N54S + V56T, A60V, G109A, R116Q/H + W167F, L173V, A174S, Q172N, G182\*, D183\*,N195F, V206L/Y, V208L, K391A, K393A, I405L, A421H, A422P, A428T, G476K and/or G478K. Preferred amylases contain both the deletions G182\* and G183\* and optionally one or more of the following sets of mutations:

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1. HI* + G109A+ N195F + V206Y + K391A;

2. H1* + N54S + V56T + G109A + A1745 + N195F + V206L + K391A + G476K)

3. H1* + N54S + V56T + A60V + G109A + R116Q + W167F + Q172N + L173V + A1745 + N195F + V206L + I405L + A421H + A422P + A428T

4. H1* + N545 + V56T + G109A + R116Q + A1745 + N195F + V206L + I405L + A421H + A422P + A428T;

5. H1* + N545 + V56T + G109A + R116H + A1745 + N195F + V208L + K393A + G478K;
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(I) variants exhibiting at least 80% identity with the mature amino acid sequence of Alicyclobacillus sp. amylase (SEQ ID NO:8 in WO2016180748).

[0097] The amylase can be an engineered enzyme, wherein one or more of the amino acids prone to bleach oxidation have been substituted by an amino acid less prone to oxidation. In particular it is preferred that methionine residues are substituted with any other amino acid. In particular it is preferred that the methionine most prone to oxidation is substituted. Preferably the methionine in a position equivalent to 202 in SEQ ID NO:2 is substituted. Preferably, the methionine at this position is substituted with threonine or leucine, preferably leucine.

[0098] Suitable commercially available alpha-amylases include DURAMYL®, LIQUEZYME®, TERMAMYL®, TERMAMYL ULTRA®, NATALASE®, SUPRAMYL®, STAINZYME®, STAINZYME PLUS®, FUNGAMYL®, ATLANTIC®, INTENSA® 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®, POWERASE®, PREFERENZ S® series (including PREFERENZ S1000® and PREFERENZ S2000® and PURASTAR OXAM® (DuPont., Palo Alto, California) and KAM® (Kao, 14-10 Nihonbashi Kayabacho, 1-chome, Chuo-ku Tokyo 103-8210, Japan). In one aspect, suitable amylases include ATLANTIC®, STAINZYME®, POWERASE®, INTENSA® and STAINZYME PLUS®, ACHIEVE ALPHA® and mixtures thereof.

**[0099]** 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/g of composition. **[0100]** Preferably, the protease and/or amylase of the composition of the invention are in the form of granulates, the granulates comprise more than 29% of sodium sulfate by weight of the granulate and/or the sodium sulfate and the active enzyme (protease and/or amylase) are in a weight ratio of between 3:1 and 100: 1 or preferably between 4:1 and 30: 1 or more preferably between 5:1 and 20:1.

## Perfume

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**[0101]** Compositions useful for use in the method of the invention can comprise a perfume. Preferably the composition comprises from 0.05 to 2% by weight of the composition of perfume. The perfume preferably comprises at least 10% by weight of the perfume of blooming perfume ingredients selected from the group consisting of: ingredients having a boiling point of less than 260°C and a logarithm of octanol/water partition coefficient (ClogP) determined by the fragment approach of Hansch and Leo of at least 3.

**[0102]** A blooming perfume ingredient is characterized by its boiling point (B.P.) and its octanol/water partition coefficient (P). The octanol/water partition coefficient of a perfume ingredient is the ratio between its equilibrium concentrations in octanol and in water. The preferred perfume ingredients of this invention have a B.P., determined at the normal, standard pressure of 760 mm Hg, of 260°C or lower, preferably less than 255°C; and more preferably less than 250°C, and an octanol/water partition coefficient P of 1,000 or higher. Since the partition coefficients of the preferred perfume ingredients of this invention have high values, they are more conveniently given in the form of their logarithm to the base 10, logP. Thus the preferred perfume ingredients of this invention have logP of 3 or higher, preferably more than 3.1, and even more preferably more than 3.2.

**[0103]** The boiling points of many perfume ingredients are given in, e.g., "Perfume and Flavor Chemicals (Aroma Chemicals)," Steffen Arctander, published by the author, 1969.

**[0104]** The logP of many perfume ingredients has been reported; for example, the Pomona92 database, available from Daylight Chemical Information Systems, Inc. (Daylight CIS), Irvine, California, contains many, along with citations to the original literature. However, the logP values are most conveniently calculated by the "CLOGP" program, also

available from Daylight CIS. This program also lists experimental logP values when they are available in the Pomona92 database. The "calculated logP" (ClogP) is determined by the fragment approach of Hansch and Leo (cf., A. Leo, in Comprehensive Medicinal Chemistry, Vol. 4, C. Hansch, P. G. Sammens, J. B. Taylor and C. A. Rarnsden, Eds., p. 295, Pergamon Press, 1990, ). The fragment approach is based on the chemical structure of each perfume ingredient, and takes into account the numbers and types of atoms, the atom connectivity, and chemical bonding. The ClogP values, which are the most reliable and widely used estimates for this physicochemical property, are preferably used instead of the experimental logP values in the selection of perfume ingredients which are useful in the present invention.

**[0105]** Thus, when a perfume composition which is composed of ingredients having a B.P. of 260°C or lower and a ClogP, of 3 or higher, is used in an automatic dishwashing detergent composition, the perfume is very effusive and very noticeable when the product is used. Examples of blooming perfume ingredients can be found in Tables 1 and 2 of EP 0 888 441 B 1.

#### Metal Care Agents

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[0106] 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 0.1 to 5%, more preferably from 0.2 to 4% and especially from 0.3 to 3% by weight of the product of a metal care agent, preferably the metal care agent is benzo triazole (BTA).

## 20 Glass Care Agents

**[0107]** Glass care agents protect the appearance of glass items during the dishwashing process. Preferably the composition of the invention comprises from 0.1 to 5%, more preferably from 0.2 to 4% and specially from 0.3 to 3% by weight of the composition of a metal care agent, preferably the glass care agent is a zinc containing material, specially hydrozincite.

#### Cationic polymer

**[0108]** The composition preferably comprises from 0.5 to 5%, preferably from 0.5 to 2% by weight of the composition of cationic polymer. The cationic polymer provides filming benefits. The cationic polymer comprises in copolymerized form from:

i. 60% to 99% by weight of the cationic polymer of at least one monoethylenically unsaturated polyalkylene oxide monomer of the formula I (monomer (A))

$$H_{2}C = C X - Y + R_{2} - O \xrightarrow{n} R_{3}$$

in which the variables have the following meanings:

- X is -CH2- or -CO-, if Y is -O-; X is -CO-, if Y is -NH-;
- Y is -O- or -NH-;
- R1 is hydrogen or methyl;
- R2 are identical or different C2-C6-alkylene radicals;
- R3 is H or C1-C4 alkyl;
- n is an integer from 3 to 100, preferably from 15 to 60,
- ii. from 1 to 40% by weight of the cationic polymer of at least one quaternized nitrogen-containing monomer, selected from the group consisting of at least one of the monomers of the formula IIa to IId (monomer (B))

in which the variables have the following meanings:

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R is C1-C4 alkyl or benzyl;

R' is hydrogen or methyl;

Y is -O- or -NH-;

A is C1-C6 alkylene;

X- is halide, C1-C4-alkyl sulfate, C1-C4-alkylsulfonate and C1-C4-alkyl carbonate.

iii. from 0 to 15% by weight of the cationic polymer of at least one anionic monoethylenically unsaturated monomer (monomer (C)), and

iv. from 0 to 30% by weight of the cationic polymer of at least one other nonionic monoethylenically unsaturated monomer (monomer (D)),

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and the cationic polymer has a weight average molecular weight (Mw) from 2,000 to 500,000, preferably from 25,000 g/mol to 200,000 g/mol.

[0109] In preferred cationic polymers the variables of monomer (A) have the following meanings:

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X is -CO-;

Y is -O-;

R<sub>1</sub> is hydrogen or methyl;

R<sub>2</sub> is ethylene, linear or branched propylene or mixtures thereof;

40 R<sub>3</sub> is methyl;

n is an integer from 15 to 60.

**[0110]** Preferably, the cationic polymer comprises from 60 to 98% by weight of monomer (A) and from 1 to 39% by weight of monomer (B) and from 0.5 to 6% by weight of monomer (C).

**[0111]** In preferred cationic polymers monomer (A) is methylpolyethylene glycol (meth)acrylate and wherein monomer (B) is a salt of 3-methyl-1-vinylimidazolium.

[0112] Preferably, the cationic polymer comprises from 69 to 89% of monomer (A) and from 9 to 29% of monomer (B).

**[0113]** In preferred cationic polymers, the weight ratio of monomer (A) to monomer (B) is  $\geq$  2:1 and for the case where the copolymer comprises a monomer (C), the weight ratio of monomer (B) to monomer (C) is also  $\geq$  2:1, more preferably is  $\geq$  2.5:1 and preferably monomer (A) comprises methylpolyethylene glycol (meth)acrylate and monomer (B) comprises a salt of 3-methyl-1-vinylimidazolium.

**[0114]** A preferred composition for use in the method of the invention comprises:

- a) from 20% to 40% by weight of the composition of MGDA, preferably the trisodium salt of methylglycine-N,N-diacetic acid:
- b) from 10% to 30% by weight of the composition of carbonate;
- c) from 0.5 % to 6% by weight of the composition of HEDP;
- d) from 2% to 6% by weight of the composition of a polymer, preferably a sulfonate polymer;

- e) non-ionic surfactant;
- f) amylase;
- g) protease; and optionally
- h) glass and/or metal care agent.

Auto-dosing detergent system

**[0115]** An auto-dosing detergent system can be suitable for use herein. The auto-dosing detergent system can be operable to selectively dispense portions of a composition from a reservoir into the washing chamber. A reservoir cartridge may contain a stock of a composition in an amount sufficient for two or more doses, preferably for three or more and more preferably for five or more doses of dishwashing product. A cartridge may be disposable or be designed to be refillable. A combination of cartridges can provide segregated stocks of components in amounts sufficient to provide multiple doses of dishwashing products. Directions may be provided to guide the user to make certain selections in dependence upon factors such as level of soil on the dishwashing.

**[0116]** 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."

Claims

- 1. A method of washing ware in a dishwasher wherein the dishwasher comprises a washing chamber and a door to close the washing chamber, the method comprising the steps of:
  - i) starting a dishwashing program;
  - ii) automatically locking the door and keeping it locked for the whole duration of the dishwashing program; and
  - iii) dosing at least 100 mg of active enzyme into the washing chamber.
- A method according to claim 1 comprising the step of dosing at least 120 mg of active enzyme into the washing chamber.
  - **3.** A method according to any of claims 1 or 2 wherein the dishwashing program is a short program having a duration of less than 1 hour, preferably from 10 minutes to 40 minutes.
  - **4.** A method according to any of the preceding claims wherein the dishwashing program comprises a main-wash and optionally a pre-wash and/or a rinse and the temperature of the washing liqueur of the main-wash is less than 50°C, preferably 45°C or less.
- **5.** A method according to any of the preceding claims wherein the dishwashing program has a duration of from 10 to 40 minutes and the temperature of washing liqueur of the main wash is 45°C or less.
  - **6.** A method according to any of the preceding claims wherein the dishwashing program comprises a main-wash and optionally a pre-wash and/or a rinse and the main-wash uses 5 liters of water or less, preferably 4 liters or less.
  - **7.** A method according to any of the preceding claims wherein the dishwasher program uses less than 1kW, preferably less than 0.5 kW.
  - 8. A method according to any of the preceding claims wherein the active enzyme is delivered into the main wash.
  - **9.** A method according to any of the preceding claims wherein the active enzyme is delivered as part of a detergent composition.
  - 10. A method according to the preceding claim wherein the detergent composition is in powder, liquid, gel or unit-dose form.
    - **11.** A method according to the preceding claim wherein the detergent composition is in unit-dose form and the weight of the unit-dose is 15 grams or less, preferably 10 grams or less.

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12. A method according to any of claims 9 to 11 wherein the detergent composition comprises a perfume wherein the

perfume comprises at least 10% by weight of the perfume of blooming perfume ingredients selected from the group consisting of: ingredients having a boiling point of less than 260°C and a logarithm of octanol/water partition coefficient (ClogP) determined by the fragment approach of Hansch and Leo of at least 3. 5 13. A method according to any of claims 9 to 12 wherein the detergent composition has a pH of at least 10 as measured in a 1% weight/volume aqueous solution in distilled water at 20°C. 14. A method according to any of claims 9 to 13 wherein the detergent composition comprises bleach. 10 15. A method according to any of claims 9 to 14 wherein the enzyme is selected from the group consisting of amylase, protease and a mixture thereof. 15 20 25 30 35 40 45 50 55



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