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(54) Title: MODIFIED HYPERBRANCHED ALKOXYLATED POLYALKYLENE IMINES

(57) Abstract: This invention deals with polyalkylene imines and their derivatives bearing side chains originating from polycondensation or polyaddition reactions using alkylene oxides, and lactones and/or hydroxy carbon acids, their manufacture, intermediates and uses, for example in laundry or dishwashing.

WO 2024/175409 A1

Modified hyperbranched alkoxyated polyalkylene imines

This invention deals with modified hyperbranched alkoxyated polyalkylene imine polymers (in this present invention abbreviated as “inventive polymer” or “polymer of the invention” whenever the inventive polymers are meant), their manufacture, their uses, particularly for use in cleaning compositions such as laundry detergent compositions, and specifically for improved clay removal and/or oily/fatty soil removal in laundry care.

Detergent formulators are continuously faced with the task of developing improved products to remove a broad spectrum of soils and stains from fabrics and hard surfaces. Chemically and physico-chemically, the varieties of soils and stains spectrum range from polar soils, such as proteinaceous, clay, and inorganic soils, to non-polar soils, such as soot, carbon-black, by-products of incomplete hydrocarbon combustion, and organic soils like sebum. The removal of greasy (i.e., oily/fatty) stains has been a particularly challenging problem. This challenge has been accentuated by the recent high interest and motivation to reduce the level of surfactants in cleaning detergents for environmental, sustainability and cost reasons. A reduction of the amount of surfactants added, especially a reduction of anionic surfactants, such as linear alkyl benzene sulfonate, LAS, has typically been found to lead to an erosion of oily/fatty stain removal. Additionally, the global trend of using washing conditions at lower temperature further diminishes grease cleaning capabilities of typical detergents, since the class of oily and fatty stains shows the greatest performance drop when the temperature is decreased. On the other hand, clay soil stains, although in some instances contacting the fabric fibers with less force, nevertheless provide a specific type of soil removal problem due to the high degree of charge associated with the clay itself. This high surface charge density may act to repel some laundry ingredients, thus surfactants alone cannot remove or carry away the clay into the laundry liquor.

Another global trend is the compaction of laundry detergents, in order to improve the sustainability in terms of water usage and/or transportation costs, as well as to improve the convenience for the end consumer (e.g., single mono dose products, tabs, pouches and the like), which leads to a high market demand for new raw materials that have a higher weight-efficiency and a significantly broader performance profile.

A further strongly emerging trend is the desire to improve the “footprint” of any product, be it in terms of its origin like being from natural or renewable resources, or compared to previous products, its production in terms of production efficiency and thus reduced usage of energy, its efficiency in usage such as reduced amounts for the same performance or higher performance at the same amount levels used, its persistence in the natural environment after its usage, especially its biodegradation, since recycling is technically very challenging and therewith economically not attractive.

Hence, due to the climate change, one of the most important targets of the detergent and cleaner (D&C) industry today is to significantly lower the CO₂ emission per wash, by improving cold water conditions, improving the cleaning efficiency at low temperatures of 30 °C and below, and to lower

the amounts of chemicals employed per wash, and increasing the weight-efficiency of the cleaning technologies. Another important target of the D&C industry is the need for biodegradable polymers, to improve the sustainability of the detergent formulations and to avoid the potential accumulation of the polymers or their degradation products, resulting from incomplete biodegradation of the polymers in the ecosystem, thus lowering the persistence in nature after usage of the materials.

As a result of these trends, there is a strong need for new biodegradable cleaning polymers that provide both excellent primary (i.e., soil removal) and secondary (i.e., whiteness maintenance) cleaning benefits for both hydrophobic and hydrophilic stains, and an improved biodegradability. The materials should exhibit good soil removal for oily/fatty and particulate stains and should also lead to improved whiteness maintenance, minimizing the amount of suspended and emulsified oily/fatty and particulate soil from redepositing on the surfaces of the textiles or hard surfaces. Preferably, the new ingredients would also display a synergy with other cleaning technologies, such as other cleaning polymers, surfactants and/or enzymes, known for improving solely the oily/fatty or particulate stain removal and/or whiteness of fabrics and hard surfaces, leading to further improved detergent compositions.

Alkoxylated polyalkylene imine polymers, especially the class of alkoxylated hyperbranched polyethylene imine (PEI) and alkoxylated linear polypropylene imine homo- and copolymers, are known in the literature to be able to contribute to particulate or to oily/fatty soil removal, especially at low surfactant levels and at cold water conditions (30 °C and below). However, their performance is not sufficient, both from a perspective of oily/fatty soil removal capability and also from a perspective of a broader performance profile. Moreover, their biodegradation performance generally is poor, and thus not acceptable for current and future requirements. Ideally, the polymers are readily biodegradable, i.e., show equal to or more than 60% oxygen consumption after 28 days in the OECD 301 F test or at least show equal to or more than 60% after 56 days in the OECD 301 F test. Alternatively, the polymers are inherently biodegradable in the OECD 302B test, i.e., show equal to or more than 70% dissolved organic carbon (DOC) levels. Hence, there was a need to find improved polymer architectures with a superior performance profile, a feasible preparation process and an improved biodegradation behavior.

In the following, a summary of the most relevant publications in the field of the present invention is given.

Alkoxylated polyalkylene imines are well known as additives for laundry detergents (e.g., EP3301154, EP3167034, EP112593 and WO2020/030469) or hard surface cleaners.

EP2209837B1 describes amphiphilic water-soluble alkoxylated polyalkylene imines, for improved oily/fatty stain removal in detergents. In general, various polyalkylene imines may be used as core materials which are based on different radicals A1 interconnecting the nitrogen atoms. The radicals A1 might be identical or different, linear or branched C2-C6-alkylene radicals, such as 1,2-alkylenes. Preferably, 1,2-ethylene, 1,2-propylene and 1,6-hexamethylene are being used. EP2209837B1 solely discloses homopolymers with good wash performance, but no favorable combination of wash performance and biodegradability is shown. In focus of this patent are linear (homo-)oligoamines such

as 1,6-hexamethylene diamine as well as branched (homo-)polyethylene imines, as disclosed in the examples. The polymers contain PEO/PPO block modification with 24 to 50 EO units and 30 to 50 PO units, thus the alkoxylate chains are longer than those described in WO2006108856A2. Due to the longer PEO/PPO chains, their performance in terms of oily/fatty soil removal is improved. Biodegradability of the polyamines themselves and of the alkoxylated derivatives are not mentioned at all.

More specifically, polypropylene imines and alkoxylated polypropylene imines for cleaning applications are described in EP2961819 B1, which discloses such polymers with number average molecular weight M_n of the backbone being in the range from 300 to 4,000 g/mol, preferably from 400 to 2,000 g/mol, determined by size exclusion chromatography. Biodegradation behavior of these polymers is not mentioned.

Even more specifically, polyethylene/-propylene imine copolymers are described in the patent application WO2021254828 A1. However, this application solely discloses co-polymers of 1,3-propylene diamine (PDA) which results in linear polypropylene imines that are different from the hyperbranched polymers of the present invention. In addition, WO2021254828 A1 is completely silent with respect to biodegradability of the polymers.

WO 2021/165468 and unpublished patent applications EP 21176904.7, EP 21176906.2, EP 21192170.5 and EP 21192169.7 describe modified (homo-)polyalkylene imines and -amines which show better biodegradation than the previously known compounds. The alkylene oxide chains in these alkoxylated polymers are modified with lactones/hydroxy carbon acids, leading to ester and/or amide functionalities in those chains. However, the core of the modified polyalkylene imines, i.e., the polyalkylene imine itself, is still not biodegradable. WO 2021/165468 discloses that the molecular weight (M_w) of the polyalkylene imine backbone or of the polyamine backbone lies in the range of 50 to 10 000 g/mol, preferably in the range of 500 to 5000 g/mol, more preferably in the range of 600 to 2 000 g/mol. The only polymers mentioned in the experimental section, besides one based on a low molecular weight oligoamine (N4-Amine with MW 174 g/mol), are based on hyperbranched polyethylene imines which as such are not biodegradable: hyperbranched poly(ethylene imine) has a biodegradation of < 10% after 28 days in the OECD 301 F test.

WO 2009/114854 describes the cross-linking of hyperbranched polyethylene imines with short chain linkers having a biodegradable bond, such as an ester, an amide, a disulfide, or a phosphate bond. The cross-linked polyethylene imines are subsequently condensed with DNA/RNA sequences and used in pharmaceutical compositions, more specifically in gene therapy. In contrast to the present invention, the polyethylene imine itself remains non-biodegradable, since the modification takes place post-polymerisation and not, as is the case of the present invention, during polymerization. In addition, no biodegradation values are documented in WO2009/114854.

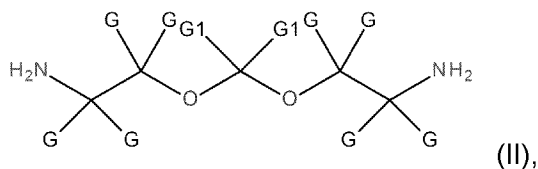
Shim and coworkers (Biomacromolecules 2008, 9, p. 444-455) describe the controlled delivery of plasmid DNA and siRNA to intracellular targets using ketalized polyethylene imine. The authors have used a ketal group containing diamine (Formula II with G = H and G1 = methyl) to cross-link hyperbranched polyethylene imine. They have done so, as with WO 2009/114854, in a post-

polymerization fashion, leaving the polyethylene imine unmodified and thus non-biodegradable. The authors have described the pH sensitivity of the ketal group towards acid conditions to result in a chemical degradation of the cross-linked polyethylene imine complexes into the individual polyethylene imines. Also here, no biodegradation values are disclosed. Since all aqueous biodegradation test methods are carried out at pH 7,4, where the ketal group is stable, no contribution from the ketal group during the biodegradation test method would be expected. In addition, the authors did not modify the polyethylene imine during polymerization.

Although there have been already many different polyalkylene imines and alkoxyated polyalkylene imines described in the cited publications above, including their preparation process and their use in detergents, there is still a need for polymers that exhibit further improved performance, such as an improved oily/fatty stain and clay removal in laundry, while at the same time showing an improved biodegradation behavior. This polymer profile would enable among others the design of highly concentrated and sustainable multi-benefit detergent formulations.

More specifically, there is still a strong need for new cleaning polymers that provide both excellent primary (i.e., soil removal) and secondary (i.e., whiteness maintenance) cleaning benefits, ideally for both hydrophobic and hydrophilic stains. Furthermore, a simplified manufacturing process for the polyalkylene imine backbone and the corresponding modified hyperbranched alkoxyated polyalkylene imine is needed as well.

The present inventors surprisingly found that the reaction of alkylene imines with certain amines can be used for the synthesis of modified hyperbranched alkoxyated polyalkylene imines bearing a core that significantly enhances wash performance and biodegradability of the inventive polymers. The state-of-the-art describes hyperbranched polyalkylene imines as being prepared via a cationic polymerization mechanism, wherein the alkylene imine is being polymerized at elevated temperature in an aqueous solution containing a weak acid, such as CO₂, and an amine comprising the same amount of carbon atoms as the imine, which is incorporated in the backbone of the hyperbranched polyalkylene imine. These commercially produced polyalkylene imines are not biodegradable (<10% oxygen consumption after 28 days in the OECD 301 F test method). Here, it was found that replacing the before mentioned amine by an amine comprising at least one carbon atom more than the imine resulted in a novel polyalkylene imine with improved biodegradability, the so-called backbone-modified polyalkylene imine. The degree of the improved biodegradability is dependent on the nature of the amine. Preferably, the amine is selected from the group consisting of propylenediamine (PDA), tetramethylenediamine (TMDA), pentamethylenediamine (PMDA), hexamethylenediamine (HMDA), heptamethylenediamine, octamethylenediamine (OMDA), dipropylene-triamine (DPTA), tripropylene-tetramine (TPTA), 4,7,10-Trioxa-tridecane-1,13-diamine (TTD), 4,9-Dioxado-decane-1,12-diamine (DODA), Poly-(propylenglykol)-bis-(2-aminopropylether), oligo or poly(alkylene glycol) di- and triamines and a compound as defined according to formula (II)



wherein G represents identical or different alkyl groups or H, preferably H, a methyl or ethyl group, more preferably all G are H and G1 represents identical or different alkyl groups or H, preferably both G1 are methyl groups.

- 5 Additionally, it was found that modifications of the present backbone-modified polyalkylene imines, such as the alkoxylation with alkylene oxides and optionally also the incorporation of lactones/hydroxy carbon acids either in between the alkylene oxide chains and the polyalkylene imine backbone or within the alkylene oxide chains, lead to modified hyperbranched alkoxyated poly-alkylene imines demonstrating excellent wash performance. Thus, the present polymers combine
- 10 the advantage of a biodegradable polyalkylene imine backbone (the core) and a biodegradable shell together with superior behavior as a cleaning formulation ingredient.
- Moreover, the hyperbranched structure of the present polymers provides significant advantages over a linear structure, such as an easier synthesis (one-step synthesis vs. two-step synthesis of hyper-branched vs linear PEI) and a more cost-effective production.
- 15 Thus, the object of the present invention is to provide novel modified hyperbranched alkoxyated polyalkylene imine obtainable by a process comprising the following steps:

- a) reaction of (i) at least one amine (A) with (ii) at least one alkylene imine to obtain a first intermediate (I1), wherein the amine (A) comprises at least one carbon atom more than the imine,
- 20 b) optionally reaction of the first intermediate (I1) with at least one first alkylene oxide (AO1), wherein at least 0.5 mol of first alkylene oxide (AO1) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain second intermediate (I2),
- c) optionally reaction of the first intermediate (I1) or the second intermediate (I2) with at least one first lactone (LA1) and/or at least one first hydroxy carbon acid (HA1), wherein 0.25 to 10 mol
- 25 of first lactone (LA1) and/or first hydroxy carbon acid (HA1) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain third intermediate (I3)
- d) reaction of the first (I1), second (I2) or third intermediate (I3) (i) with at least one second alkylene oxide (AO2) or (ii) with a mixture of 1) at least one second alkylene oxide (AO2) with 2) at least one second lactone (LA2) and/or at least one second hydroxy carbon acid (HA2),
- 30 wherein at least 5.0 mol of second alkylene oxide (AO2) and for the mixture additionally at least 1.0 mol of second lactone (LA2) and/or second hydroxy carbon acid (HA2) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain a fourth intermediate (I4),
- e) optionally reaction of the fourth intermediate (I4) (i) with at least one third alkylene oxide (AO3)
- 35 or (ii) with a mixture of 1) at least one third alkylene oxide (AO3) with 2) at least one third lactone (LA3) and/or at least one third hydroxy carbon acid (HA3), wherein at least 5.0 mol of

third alkylene oxide (AO3) and for the mixture additionally at least 1.0 mol of third lactone (LA3) and/or third hydroxy carbon acid (HA3) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain a fifth intermediate (I5),

- f) optionally reaction of the fourth intermediate (I4) or fifth intermediate (I5) with at least one fourth lactone (LA4) and/or at least one fourth hydroxy carbon acid (HA4), wherein at least 1.0 mol of fourth lactone (LA4) and/or fourth hydroxy carbon acid (HA4) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain a sixth intermediate (I6),
- g) optionally reaction of the fourth intermediate (I4), fifth intermediate (I5) or sixth intermediate (I6) with at least one C1-C18 alkylation or esterification reagent, in order to obtain the modified hyperbranched alkoxylated polyalkylene imine.

As described above, the polymer of the invention may be further modified by reactions with alkylene oxides and lactones and/or hydroxy acids to yield modified hyperbranched alkoxylated polyalkylene imines which bear at least one side chain attached to an amino group of the core, i.e. the first intermediate (I1), such side chain comprising at least one alkylene oxide (AO) and, optionally, at least one lactone and/or hydroxy acid per side chain, and/or may be quaternized to introduce non-permanent or permanent quaternization of the amino groups of the core of the inventive polymer. In the following, any alkylene oxide is generically referred to as "AO", ethylene oxide is sometimes referred to as "EO", propylene oxide as "PO", butylene oxide as "BuO". "PEO" is used sometimes herein to describe polyethylene oxide homopolymers or PEO-blocks within a larger polymer structure; likewise, "PPO" describes the poly propylene oxide homopolymers or polymer-blocks within a larger polymer structure.

A polyalkylene imine with such side chains is sometimes also called a "modified polyalkylene imine" within this disclosure to specifically distinguish from an "unmodified polyalkylene imine" bearing no such side chains and from the "backbone-modified polyalkylene imines", whereas the term "polyalkylene imine" generally herein includes any such polyalkylene imine either bearing side chains and/or being quaternized or neither bearing side chains nor being quaternized.

A process to produce the inventive polymers is also part of this invention.

The use of such polymers of this invention for all kinds of applications for which the previously known polyethylene imines, polypropylene imines, and their alkoxylated derivatives have been used is encompassed by this present invention as well.

Compositions comprising such polyalkylene imines of this invention like those compositions in which the previously known polyethylene imines, polypropylene imines, and their alkoxylated derivatives have been employed – either the inventive polyalkylene imine instead of such known compounds or in combinations with such known compounds – forms part of this invention as well.

The term "polymer", "polymer of the invention" or "inventive polymer", as used herein, refers to polyalkylene imines prepared as described below and/or in the appended claims. The before terms should be understood broadly, meaning that they encompass the non-alkoxylated (unmodified) but

backbone-modified polyalkylene imines, such as the intermediate described in Embodiment 20, as well as the modified hyperbranched alkoxyated polyalkylene imines.

Thus, subjects of the present invention are the following Embodiments 1 to 33 as defined and further explained with further embodiments hereinafter and further exemplified in the experimental section:

5

Embodiment 1

A modified hyperbranched alkoxyated polyalkylene imine obtainable by a process comprising the following steps:

- 10 a) reaction of (i) at least one amine (A) with (ii) at least one alkylene imine to obtain a first intermediate (I1), wherein the amine (A) comprises at least one carbon atom more than the imine,
- b) optionally reaction of the first intermediate (I1) with at least one first alkylene oxide (AO1), wherein at least 0.5 mol of first alkylene oxide (AO1) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain second intermediate (I2),
- 15 c) optionally reaction of the first intermediate (I1) or the second intermediate (I2) with at least one first lactone (LA1) and/or at least one first hydroxy carbon acid (HA1), wherein 0.25 to 10 mol of first lactone (LA1) and/or first hydroxy carbon acid (HA1) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain third intermediate (I3)
- d) reaction of the first (I1), second (I2) or third intermediate (I3) (i) with at least one second alkylene oxide (AO2) or (ii) with a mixture of 1) at least one second alkylene oxide (AO2) with 2) at least one second lactone (LA2) and/or at least one second hydroxy carbon acid (HA2), wherein at least 5.0 mol of second alkylene oxide (AO2) and for the mixture additionally at least 1.0 mol of second lactone (LA2) and/or second hydroxy carbon acid (HA2) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain a fourth intermediate (I4),
- 20 e) optionally reaction of the fourth intermediate (I4) (i) with at least one third alkylene oxide (AO3) or (ii) with a mixture of 1) at least one third alkylene oxide (AO3) with 2) at least one third lactone (LA3) and/or at least one third hydroxy carbon acid (HA3), wherein at least 5.0 mol of third alkylene oxide (AO3) and for the mixture additionally at least 1.0 mol of third lactone (LA3) and/or third hydroxy carbon acid (HA3) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain a fifth intermediate (I5),
- 30 f) optionally reaction of the fourth intermediate (I4) or fifth intermediate (I5) with at least one fourth lactone (LA4) and/or at least one fourth hydroxy carbon acid (HA4), wherein at least 1.0 mol of fourth lactone (LA4) and/or fourth hydroxy carbon acid (HA4) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain a sixth intermediate (I6),
- 35 g) optionally reaction of the fourth intermediate (I4), fifth intermediate (I5) or sixth intermediate (I6) with at least one C1-C18 alkylation or esterification reagent in order to obtain the modified hyperbranched alkoxyated polyalkylene imine.

Polyalkylene imines are linear or (hyper)branched polymers comprising primary, secondary and/or tertiary amino groups formed by polymerization of alkylene imine monomers in the presence of an amine which serves as a starter for the polymer formation. The polyalkylene imines of the present invention are hyperbranched and formed by a ring opening process of the alkylene imine monomers.

5 In contrast, for example, polyethylene imines that are synthesized by hydrolysis of polyoxazolines results in solely linear polyethylene imines, which is different from the present polymers in terms of chemistry and properties. In addition, polypropylene imines prepared by (co-)polycondensation of 1,3-propylene diamine also lead to linear polyalkylene imines (WO2021254929 A1).

The term “hyperbranched”, as used herein, in relation to modified hyperbranched alkoxyated poly-
10 alkylene imines refers to its definition as known to those of skill in the art. A hyperbranched polymer comprises generally polydisperse branched macromolecules which are preferably prepared in a single synthetic polymerization step that forms imperfect branches, generally in a non-deterministic way. However, there are many preferable synthetic strategies known in the art to prepare hyper-
15 branched polymers with lower polydispersity. They are typically characterized by their degree of branching (DB). The imine-based hyperbranched polymer of the invention comprises tertiary, secondary, and primary amines before being alkoxyated, in which case the primary amines might as an example be converted to secondary and/or tertiary amines and secondary amines might, for example, be converted to tertiary amines, leading to the same imperfect branched structure. The term
20 degree of branching (DB) has a meaning known in the field of branched macromolecules, and use herein is consistent with that meaning. A preferable definition is provided, for example, in C. J. Hawker, R. Lee, and J. M. J. Fréchet (1991), “The One-Step Synthesis of Hyperbranched Dendritic Polyesters,” J. Am. Chem. Soc., 113: 4583, which is incorporated herein by reference in its entirety. For the purpose of the present invention, the expression/term “modified” relates to the presence of
25 (predominately) hydrophobic oligo- or polyester blocks based on lactones or hydroxyl carbon acids, such as caprolactone and/or lactic acid, or a combination of such lactones or hydroxyl carbon acids with alkylene oxides, such as ethylene oxide and/or propylene oxide attached to the inventive poly-
alkylene imines to result in the modified compound. The presence of alkylene oxides within or next to the (predominately) hydrophobic polyester blocks lead to an amphiphilic nature and thus to excellent cleaning properties of the inventive polymers in detergent applications. Inventive polymers bearing
30 such modification are also called being “alkoxyated” and/or “modified and alkoxyated”.

Within the context of the present invention, the term “NH-functionality” is defined as follows: A primary amino group (-NH₂) has two NH-functionalities, a secondary amino group only one NH-functionality, and a tertiary amino group, by consequence, has no reactive NH-functionality.

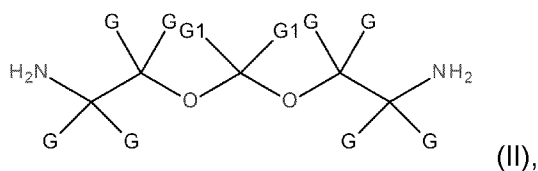
In preferred Embodiments the term “the amine (A) comprises at least one carbon atom more than
35 the imine”, as used herein, indicates that the amine comprises 1, 2, 3, 4, 5, 6 or more carbon atoms more than the monomeric imine used to form the backbone-modified polyalkylene imine of the invention. Thus, in case ethylene imine is used as imine the amine (A) comprises at least 3, 4, 5, 6 or more carbon atoms. In case, propylene imine is used to synthesize the backbone-modified poly-
alkylene imine of the invention the amine (A) comprises at least 4, 5, 6 or more carbon atoms.

In step (g), the initially obtained terminal hydroxy groups of the fourth intermediate (**I4**), fifth intermediate (**I5**) or sixth intermediate (**I6**) are further reacted with at least one C1-C18 alkylation or esterification reagent. Typical alkylation reagents such as alkyl halides and/or carbon acids and/or carbon acid derivatives such as carbon acid anhydrides, carbon acid esters or carbon acid halides are employed, to obtain terminal end-groups selected from unsubstituted or at least monosubstituted C₁-C₁₈-alkyl, C₇-C₁₈-aralkyl, -(CO)-C₁-C₁₈-alkyl, -(CO)-C₂-C₁₈-alkenyl and/or -(CO)-C₇-C₁₈-aralkyl, wherein the substituents are selected from -COOH or a salt thereof. Preference is given to carbon acid anhydrides, specifically to alkyl-chain-substituted succinic anhydrides, examples being C₆ to C₁₈-substituted succinic anhydrides. Examples of products commercially available include Pentasize 8 or Pentasize 68 (C₁₈ alkenyl succinic anhydride or C₁₆/C₁₈ alkenyl succinic anhydride, respectively, from Trigon Chemie GmbH).

Embodiment 2

The modified hyperbranched alkoxyated polyalkylene imine according to Embodiment 1, wherein the at least one amine (A)

- (i) has 1, 2, 3 or 4 amino groups, preferably 2, 3 or 4 amino groups;
- (ii) has at least three carbon atoms, preferably 3 to 12 carbon atoms, more preferably 3 to 9 carbon atoms;
- (iii) comprises at least one primary and/or at least one secondary amino group, preferably at least two primary amino groups; and/or
- (iv) is selected from the group consisting of propylenediamine (PDA), tetramethylenediamine (TMDA), pentamethylenediamine (PMDA), hexamethylenediamine (HMDA), heptamethylenediamine, octamethylenediamine (OMDA), dipropylene-triamine (DPTA), tripropylene-tetramine (TPTA), 4,7,10-Trioxa-tridecane-1,13-diamine (TTD), 4,9-Dioxado-decane-1,12-diamine (DODA), Poly-(propylenglykol)-bis-(2-aminopropylether), oligo or poly(alkylene glycol) di- and triamines and a compound as defined according to formula (II)



wherein G represents identical or different alkyl groups or H, preferably H, a methyl or ethyl group, more preferably all G are H and G1 represents identical or different alkyl groups or H, preferably both G1 are methyl groups.

Embodiment 3

The modified hyperbranched alkoxyated polyalkylene imine according to Embodiment 1 or 2, wherein the at least one alkylene imine is ethylene imine or propylene imine, preferably ethylene imine.

Embodiment 4

The modified hyperbranched alkoxyated polyalkylene imine according to any of Embodiments 1 to 3, wherein the alkylene oxides AO1 to AO3 are independently of each other selected from the group consisting of C₂-C₁₂-alkylene oxides, preferably ethylene oxide, propylene oxide and butylene oxide.

- 5 In preferred Embodiments, two types of alkylene oxides (AO1, AO2 and AO3) employed consecutively for the synthesis of the modified hyperbranched alkoxyated polyalkylene imine are different from each other.

For clarifications of this Embodiment, this means that AO1, AO2 and AO3 may be identical or different from each other

- 10 AO1 is preferably propylene oxide and/or butylene oxide or a mixture of predominantly propylene oxide or butylene oxide with ethylene oxide.

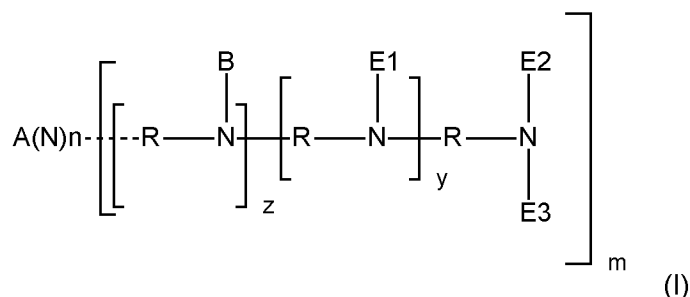
AO2 is preferably ethylene oxide or a mixture of predominantly ethylene oxide and propylene oxide and/or butylene oxide.

- 15 AO3 is preferably propylene oxide or a mixture of predominantly propylene oxide and ethylene oxide and/or butylene oxide.

Embodiment 5

The modified hyperbranched alkoxyated polyalkylene imine according to any of Embodiments 1 to 4, wherein said modified hyperbranched alkoxyated polyalkylene imine is defined according to general formula (I)

20



wherein the variables are defined as follows:

- 25 R represents identical or different, linear or branched C₂-C₁₂-alkylene radicals, preferably C₂- or C₃-alkylene radicals;

y is an integer having a value in the range of 0 to 150, preferably of 0 to 10;

z is an integer having a value in the range of 0 to 150, preferably of 0 to 10;

- 30 A is the amine comprising n NH-functionalities, wherein n is an integer between 1 to 8, preferably 3 to 8, wherein the dotted line indicates the bond between the NH-functionalities and the structure in brackets of Formula (I) and wherein m indicates the total number of polyalkylene imine side chains attached to the amine, with the proviso that $m \leq n$;

B represents a continuation of the polyalkylene imine by branching;

E1-3 represent independent of each other

- 5 i) $-(R1-O)_p-H$, wherein p is an integer having a value of 1 to 150, preferably 15 to 90; or
 ii) any mixture of $-(R1-O)-$ and $-(C(O)-R2-O)-$, wherein total number of $-(R1-O)-$ is an integer having a value of 1 to 150 and of $-(C(O)-R2-O)-$ is an integer having a value of 1 to 10, arranged in any order and having a terminal -H,

10 wherein R1 represents identical or different, linear or branched C_2 - C_{12} -alkylene radicals, preferably C_2 - or C_3 -alkylene radicals and

R2 represents identical or different, linear or branched C_2 - C_{10} -alkylene radicals, preferably linear or branched C_2 - C_5 -alkylene radicals.

Typical abbreviations such as "C2-C12 alkylene oxides" and the like have their ordinary meaning as used in this field of organic chemistry and which well-known to the person skilled in the art.

15

Embodiment 6

The modified hyperbranched alkoxyated polyalkylene imine according to Embodiment 5, wherein

- i) the total number of $-(R1-O)-$ is an integer having a value of 5 to 120, preferably 20 to 90; and/or
20 ii) the total number of $-(C(O)-R2-O)-$ is an integer having a value of 2, 3, 4, 5, 6, 7 or 8.

Embodiment 7

The modified hyperbranched alkoxyated polyalkylene imine according to any of Embodiments 1 to 6, wherein

- 25 i) step b) for AO1 between 0,5 and 1,2 per mol NH-functionality in I1, is carried out as a one-step reaction, optionally in the presence of water and/or a catalyst, and/or
 ii) step b) for AO1 larger than 1,2 per mol NH-functionality in I1 is carried out as a two-step reaction, wherein the first step is carried out optionally in the presence of water and the second step is carried out without any water, but in the presence of a catalyst, and/or
30 iii) the weight average molecular weight (Mw) of the first intermediate (I1) lies in the range of 50 to 10 000 g/mol, preferably in the range of 150 to 5 000 g/mol, more preferably in the range of 200 to 2500 g/mol.

35 Molecular weights of the modified hyperbranched alkoxyated polyalkylene imines can be determined by gel permeation chromatography (GPC) and/or light scattering (LS). The GPC measurements can be carried out on a column combination of three following columns: HFIP-LG Guard, PL HFIPGEL and PL HFIPGel. Further details are disclosed in the experimental section.

"Mw" is the weight average molecular weight and "Mn" is number average molecular weight. The respective values of Mw and/or Mn can be determined as described within the experimental section below.

The molar mass distribution Mw/Mn obtained by GPC is equal to the polydispersity index (PDI), the PDI being without unit [g/mol / g/mol].

Embodiment 8

The modified hyperbranched alkoxyated polyalkylene imine according to any of Embodiments 1 to 7 containing at least two, preferably at least four tertiary amino groups.

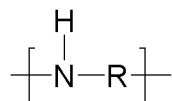
In principle, polyalkylene imine polymers generally may be linear or branched. The polymers of the present invention are hyperbranched with the branching forming a tertiary amino group, wherein branches may be relatively short alkylene amino groups as such (e.g., -(CH₂)₃-NH₂ groups) up to very long side chains which may contain further amino-groups being similarly branched etc, thus leading to highly branched structures such as the typical highly branched polyethylene imine (PEI).

By consequence, the inventive polymers have a basic skeleton (backbone, i.e., Intermediate I1), which comprises primary, secondary and tertiary nitrogen atoms which are joined by i) alkylene or ii) any substituted or non-substituted linear or branched alkyl or aryl (derived from amine A) radicals (depicted as R):

- primary amino moieties terminate the main and also the side chains of the basic skeleton and whose hydrogen atoms may be subsequently replaced by side chains when modified with alkylene oxides and/or lactones/hydroxy acids:



- secondary amino moieties whose hydrogen atom may be subsequently replaced by side chains when modified with alkylene oxides and/or lactones/hydroxy acids:



- tertiary amino moieties which branch the main chain and the side chains:



For the sake of completeness, it is indicated that the variable B indicating the branching of the polyalkylene imine backbone of compounds according to general formula (I) contains at least one fragment with at least one further amino moiety including a two times, three times or even higher degree of branching. The degree of branching may be determined, for example, by NMR-spectroscopy such as ¹H-NMR or preferably ¹³C-NMR spectroscopy.

In preferred Embodiments, the backbone-modified polyalkylene imines comprise a plurality of primary, secondary and tertiary amino groups, whereas the backbone of the modified hyperbranched alkoxylated polyalkylene imines comprises only tertiary amino groups, optionally accompanied by amide groups (in case of amide formation when using lactones and/or hydroxy carbon acids in at least one of the steps (c) to (f)).

In further preferred Embodiments, more than 50%, preferably at least 75% and even more preferably at least 80% of the primary and secondary amino groups in the modified hyperbranched alkoxylated polyalkylene imine are reacted with the first lactone (LA1) and/or the first hydroxy carbon acid (HA1) to form an amide bond.

The amine number for primary, secondary, and tertiary amines is determined in accordance with the standard DIN EN ISO 9702.

Embodiment 9

The modified hyperbranched alkoxylated polyalkylene imine according to any of Embodiments 1 to 8, wherein said modified hyperbranched alkoxylated polyalkylene imine demonstrates at least 20%, preferably at least 40% or more preferably at least 60% biodegradability according to standard OECD 301F within 56 days, preferably within 28 days.

For the purposes of this invention, aerobic biodegradation in wastewater according to OECD 301 F is expressed as a percentage of the theoretical oxygen demand (ThOD, which is measured by the elemental analysis of the compound of interest), which is needed to completely biodegrade the polymer sample. Thus, the amount of oxygen taken up by the microbial population during biodegradation of the test substance (corrected for uptake by blank inoculum, run in parallel) is expressed as a percentage of ThOD. The obtained values are preferably measured in triplicate using the OECD 301F manometric respirometry method. The consumption of oxygen is determined by measuring the change in pressure in the apparatus using an OxiTop® C (Xylem 35 Analytics Germany Sales GmbH & Co KG). Details for the tests performed are given in the experimental section below.

A main advantage of the present invention in terms of biodegradation is that not only the "shell" (i.e., the side chains in the modified polymer which are attached to the (unmodified) hyperbranched polyalkylene imine) but also the "core" (i.e., the unmodified hyperbranched polyalkylene imines according to this invention) exhibits a beneficial degree of biodegradation. Currently known polyalkylene imines of the art and their alkoxylated derivatives (including those comprising also lactones and the like besides solely AO, i.e., the modified hyperbranched alkoxylated polyalkylene imines) are not per se entirely biodegradable as the core (i.e., the polyalkylene imines of the art, e.g., solely containing ethylene imine, propylene imine or mixtures thereof) is not biodegradable to any significant extent.

Hence, as the present invention provides backbone-modified hyperbranched polyalkylene imines, which by themselves already show a significant rate of biodegradation, and the modification of those polymers (as a core) with side chains which in turn also show a significant rate of biodegradation, the combined core-shell-product (i.e., the modified hyperbranched alkoxylated polyalkylene imine) inherits this significant rate of biodegradation and that will, after enzymatic degradation in aqueous

environment, exhibit only such fragments that should not be persistent in nature. Moreover, these inventive polymers demonstrate also wash performance comparable to currently used products.

Embodiment 10

- 5 The modified hyperbranched alkoxyated polyalkylene imine according to any of Embodiments 1 to 9, wherein the amine (A) is the compound of formula (II), wherein all G are H and both G1 are methyl groups and the alkylene imine is ethylene imine.

Embodiment 11

- 10 The modified hyperbranched alkoxyated polyalkylene imine according to any of Embodiments 1 to 10, wherein
- i) in steps b), d) and/or e) the alkylene oxide (AO1, AO2 and AO3) is independent of each other at least one C₂-C₁₂-epoxide, preferably ethylene oxide and/or propylene oxide and/or butylene oxide, and/or
 - 15 ii) in steps c), d), e) and/or f) the lactone (LA1, LA2, LA3 and/or LA4) is independent of each other caprolactone, γ - or δ -valerolactone, or lactide, and/or
 - iii) in steps c), d), e) and/or f) the hydroxy carbon acid (HA1, HA2, HA3 and/or HA4) is independent of each other lactic acid or glycolic acid.
- 20 The modified hyperbranched alkoxyated polyalkylene imines of the invention may comprise side chains which are attached to nitrogen atoms of said polymer. The side chains are made up from C₂-C₁₂-alkylene oxides, lactones and/or hydroxy carbon acids. Typically, a side chain comprises at least one alkylene oxide (AO) and at least one lactone (LA) and/or at least one hydroxy acid (HA). The reaction to prepare a side chain comprising AO, LA and HA is – by way of example for the
- 25 preparation of the side chains in general - typically done by reacting the hyperbranched polyalkylene imine with the at least one AO and the at least one LA and/or HA in a stepwise manner, according to steps (b) to (f) of the inventive process, thereby creating block structures.
- However, it is also possible as described in steps (d) and (e) of the inventive process, to use mixtures of the AO and LA and/or HA. By adding mixtures of all ingredients at the very same time or by
- 30 adding the different ingredients at least shortly after each other with a preferably as short as possible time-lag, before the conversion of all monomers has been completed, random copolymer side chains are being formed that are attached to the nitrogen atoms of the backbone.
- If a combination of stepwise addition and addition of mixtures is applied, random copolymer chains with inherent block sequences are being formed.
- 35 Preferably, a side chain comprises more than 5 more preferably more than 10, even more preferably more than 15 units per NH-functionality of the inventive polymer stemming from AO, and at least 1 unit per NH-functionality stemming from LA and/or HA. All such numbers are numbers “on average” meaning that such numbers refer to the average number for such unit per NH-functionality calculated based on all NH-functionalities of a polyalkylene imine.

Additionally, it has to be noted within the context of the process according to the present invention that those primary amino moieties of the respective backbone, which are reacted first with at least one lactone and/or at least one hydroxy carbon acid are transferred into an amido moiety wherein one of the originally two hydrogen atoms of the respective primary amino moiety is replaced by a
5 fragment originating from the respective lactone or hydroxy carbon acid, whereas the second hydrogen atom of the primary amino moiety of the backbone does not get substituted by this reaction. Beyond that, such a second hydrogen atom of the primary amino moiety of the backbone does also not become substituted within the further reaction steps, e.g., further reactions with AO, LA and/or HA.

10 It is to be emphasized that the reactions leading to the inventive polymers are statistical reactions, meaning there is never just one chemically exactly defined compound present, but an inventive polymer always is a mixture of slightly deviating structures, all stemming from the same reaction within one reaction space; the difference of those structures clearly stemming from the facts that no reaction proceeds in exactly the same way and the same speed on all functional units, especially as the
15 chemical reactivities of the functional units – here mainly those of the NH-functionalities, differs according to their environment, meaning that a primary amino group reacts differently than a secondary amine (specifically in terms of reaction with a lactone and/or a hydroxy carbon acid, as described above), and also the chemical environment of the groups may be different in the monomers employed; this leads in an overall view to slightly deviating structures being present, and thus any polymer of this invention being defined as in the various embodiments including the numbered Embodiments 1 to 33, and exemplified in the examples never is just one chemical compound, but always a mixture of slightly deviating compounds, having a statistical distribution. As the reactivities of those groups are not differing by a large extent, the deviation is relatively small. Hence, defining a polymer of the invention by their monomers is a viable way of defining the structures. Also, defining the composition of the side chains by average numbers (including those variables defined in the present and
25 following Embodiments based on the numbers of NH-functionalities being present in the polyalkylene imine – such number of functionalities being themselves an average number due to this factual mixture – is a useful way of defining the overall composition of any mixture herein defined as “an modified hyperbranched alkoxylated polyalkylene imine of the invention”).
30 Therefore, unless otherwise indicated, the values, ranges and ratios given in the specification for n, the number of NH-functionalities, and the molecular weight (Mn) relate to the number average values of the mixture obtained as the inventive polymers containing individual, slightly from each other deviating chemical structures of several polymer-compounds, with “the hyperbranched polyalkylene imine” defining this mixture being the result from the preparation method. As known in polymer science, the weight-average molecular weight (Mw) is then a measure for the (in)homogeneity within
35 the mixture of different species in “the hyperbranched polyalkylene imine”.

Suitable lactones and/or hydroxy carbon acids can be aliphatic, cycloaliphatic or aromatic.

Particularly suitable aromatic hydroxy carbon acids are hydroxy-substituted benzoic acids and naphthalene carboxylic acids, such as p-hydroxyethyl benzoic acid and 2-hydroxynaphthalene-6-carboxylic acid. Preference is given to aliphatic hydroxy carbon acids, especially to those with hydroxyl groups in the ω position, and their lactones. In general, the aliphatic hydroxy carbon acids have from 1 to 22 alkylene radicals, preferably from 2 to 10 alkylene radicals, more preferably from 2 to 5 alkylene radicals. The alkylene radicals may be linear or branched. Examples which may be mentioned are glycolic acid, lactic acid and its lactide, gamma-hydroxybutyric acid and gamma-butyrolactone, delta-hydroxyvaleric acid and gamma- and delta-valerolactone, epsilon-hydroxycaproic acid and epsilon-caprolactone, 12-hydroxystearic acid and ricinoleic acid, and also mixtures, especially including naturally occurring acids. Preferably, glycolic acid, lactic acid, epsilon-caprolactone or lactide, or mixtures thereof, are employed, even more preferably epsilon-caprolactone.

In preferred Embodiments, two types of lactones (LA1, LA2 and LA3) employed consecutively for the synthesis of the modified hyperbranched alkoxyated polyalkylene imine are different from each other.

For clarifications of this Embodiment, LA1, LA2, LA3 and LA4 may be identical or different from each other.

In preferred Embodiments, two types of hydroxy carbon acids (HA1, HA2 and HA3) employed consecutively for the synthesis of the modified hyperbranched alkoxyated polyalkylene imine are different from each other.

For clarifications of this Embodiment, HA1, HA2, HA3 and HA4 may be identical or different from each other.

Embodiment 12

The modified hyperbranched alkoxyated polyalkylene imine according to any of Embodiments 1 to 11, wherein

- i) in steps b), d) and/or e) in total 5 to 100 mol, preferably 10 to 80 mol, more preferably 12 to 60 mol, most preferably 15 to 40 mol of alkylene oxide (AO1, AO2 and/or AO3) is employed per mol of NH-functionality of first intermediate (I1), wherein more than 70 mol%, preferably more than 90 mol% of the alkylene oxide is based on ethylene oxide, and/or
- ii) in steps c), d), e) and/or f) in total 1 to 10 mol, preferably 1 to 6 mol, more preferably 2 to 5 mol of lactone (LA1, LA2, LA3 and/or LA4) and/or 1 to 20 mol, preferably 2 to 15 mol, more preferably 3 to 10 mol of hydroxy carbon acid (HA1, HA2 and/or HA3) is employed per mol of NH-functionality of first intermediate (I1).

It is noted that the alkylene oxide used to prepare the inventive polymer may be derived from a fossil or non-fossil carbon source or even a mixture of the before mentioned. Preferably, the amount of non-fossil carbon atoms in the alkoxy side chains is at least 10%, at least 20%, at least 40%, at least 70%, at least 95% or it solely comprises non-fossil derived carbon atoms. The skilled person is well-

aware of commercial alkylene oxide products made of non-fossil carbon sources (these products are often sold as being sustainable, renewable or bio-based). For example, Croda International, Snaith, UK, sells ethylene oxide and related products based on bio-ethanol as ECO Range. Additionally, methods to prepare bio-based propylene oxide are also known (see Abraham, D. S., "Production of propylene oxide from propylene glycol" Master's Thesis University of Missouri-Columbia (2007) (75 pages)).

Embodiment 13

The modified hyperbranched alkoxyated polyalkylene imine according to any of Embodiments 1 to 12, wherein

- i) in steps b), d) and/or e) in total 25 to 120 mol, preferably 30 to 110 mol, more preferably 35 to 100 mol, most preferably 40 to 90 mol of alkylene oxide (AO1, AO2 and/or AO3) is employed per mol of NH-functionality of first intermediate (I1), whereas less than 70 mol%, preferably less than 60 mol% of the alkylene oxide is based on ethylene oxide, and/or
- ii) in steps c), d), e) and/or f) in total 1 to 10 mol, preferably 2 to 8 mol, more preferably 3 to 7 mol of lactone (LA1, LA2, LA3 and/or LA4) and/or 1 to 20 mol, preferably 2 to 15 mol, more preferably 3 to 10 mol of hydroxy carbon acid (HA1, HA2, HA3 and/or HA4) is employed per mol of NH-functionality of first intermediate (I1).

Embodiment 14

The modified hyperbranched alkoxyated polyalkylene imine according to any of Embodiments 1 to 13, wherein

- i) in steps b), d) and/or e) the alkylene oxide (AO1, AO2 and/or AO3) is ethylene oxide and/or propylene oxide and/or butylene oxide and/or
- ii) in steps c), d), e) and/or f) the lactone (LA1, LA2, LA3 and/or LA4) is in at least one step caprolactone.

Embodiment 15

The modified hyperbranched alkoxyated polyalkylene imine according to any of Embodiments 1 to 14, wherein

- (1) in step a) the amine (A) is TPTA and the alkylene imine is ethylene imine reacted in a 1:4 molar ratio; and
in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- (2) in step a) the amine (A) is TPTA and the alkylene imine is ethylene imine reacted in a 1:3 molar ratio; and
in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or

- (3) in step a) the amine (A) is TPTA and the alkylene imine is ethylene imine reacted in a 1:2 molar ratio; and
in d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- 5 (4) in step a) the amine (A) is TPTA and the alkylene imine is ethylene imine reacted in a 1:4 molar ratio;
in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- 10 (5) in step a) the amine (A) is PDA and the alkylene imine is ethylene imine reacted in a 1:4.5 molar ratio;
in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- 15 (6) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:10 molar ratio;
in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- 20 (7) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:5 molar ratio;
in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- 25 (8) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:5 molar ratio;
in step c) at least 3 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- 30 (9) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:4 molar ratio;
in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
- 35

in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or

(10) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:3 molar ratio;

5 in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and

in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or

10 (11) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:10 molar ratio;

in step b) at least 1.1 mol of butylene oxide is employed per mol of NH-functionality of first intermediate (I1); and

in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and

15 in step d) at least 15 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); and

in step e) at least 15 mol of propylene oxide is employed per mol of NH-functionality of first intermediate (I1); or

20 (12) in step a) the amine (A) is the compound of formula (II), wherein all G are H and both G1 are methyl groups and the alkylene imine is ethylene imine reacted in a 1:4 molar ratio; and

in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or

(13) in step a) the amine (A) is the compound of formula (II), wherein all G are H and both G1 are methyl groups and the alkylene imine is ethylene imine reacted in a 1:4 molar ratio; and

25 in step b) at least 0.9 mol of propylene oxide is employed per mol of NH-functionality of first intermediate (I1);

in step d) a mixture of at least 10 mol of ethylene oxide and at least 1 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1).

30 Embodiment 16

The modified hyperbranched alkoxylated polyalkylene imine according to any of Embodiments 11 to 15, wherein at least 50 %, preferably at least 60% and most preferably at least 80%, even more preferably at least 90, and most preferably at least 95% of all side chains attached to the NH-functionalities of one specific modified hyperbranched alkoxylated polyalkylene imine have the same structural order, in that sense that the structural order is defined by the order of the given alkylene oxides, lactones and/or hydroxy carbonic acids employed during the stepwise synthesis of the polymer of the invention.

Without wishing being bound by the following explanation, a rationale exists to explain the resulting structures of the hyperbranched polyalkylene imines and the modified hyperbranched alkoxyated polyalkylene imines: Due to the fact that the reactions in questions necessarily employed to prepare those structural orders of the side chains, and thus to prepare the specific inventive polymers, are reactions of quite reactive species which can lead under suitable conditions to almost complete and even “essentially complete” conversions of almost 100 % if not even 100%, for each step of the inventive process, the statistical deviation of the composition of the mixture of “the hyperbranched polyalkylene imines” in question is not that high, which in turn means that the structural order of the side chains do not show much deviation. Thus, it is a reliable assumption which can in principle be proven by sophisticated and thus time-consuming and expensive analytical means – such as multi-dimensional NMR-analyses – that it is generally accepted that such deviation exists; hence, no “specific modified hyperbranched alkoxyated polyalkylene imine” will be “just one chemical compound of a clearly defined chemical structure”, but clearly will consist of a a) mixture of slightly differing compounds, such differences lying in b) slight deviations already in the structure of compound making up “the (backbone-modified) hyperbranched polyalkylene imine” being employed for the further modification steps, and c) the slight deviations in the structural orders of the side chains attached by way of d) multi-step reactions due to e) variations in the chemical reactivities of the NH- and subsequently formed OH-functionalities, f) slight differences in the reactivities of employed AO, LA and HA due to their structure and g) due to their reactivities towards the slightly differing reactivities NH- and subsequently formed OH-functionalities, and h) due to slight inhomogeneities occurring in a commercial scale process. All of those factors a) to h) – to just mention a few important ones – lead to a “specific modified hyperbranched alkoxyated polyalkylene imine” which is not one specific chemical compound but in fact a mixture of slightly differing compounds having an overall very similar chemical structure; thus, such structure is best described by average numbers for the variables and percentages for the amounts of the dominating structural order.

Furthermore, experimental evidence created by the inventors, but not included in the Example part of this description suggests that a trans-esterification reaction of the lactone and/or hydroxy carbon acid derived part may occur within the alkoxy side chain. This reaction was solely observed for lactones and/or hydroxy carbon acids that reacted with each other and/or with AO to form ester bonds, but not for those that were directly attached to the NH-functionality of the polyalkylene imine to form amide bonds. The trans-esterification reaction was observed in cases where a prior reaction of lactones and/or hydroxy carbon acids with each other and/or with AO to form ester bonds was followed by a later reaction with alkylene oxides, such as ethylene oxide and/or propylene oxide. Such observation appears consistent with the fact that the reaction with the alkylene oxides is carried out under high pressure, high temperature and furthermore strong alkaline conditions. Such trans-esterification will be, in addition to the previous parameters, another factor that provides uncertainty to the final structure of the inventive polymers.

Embodiment 17

The modified hyperbranched alkoxyated polyalkylene imine according to any of Embodiments 1 to 16, which is further modified by quaternization using standard means, including protonation by pH-adjustment or permanent quaternization by standard means such as alkylation using standard reagents, preferably by alkylation, to a degree of from 5 to 100, preferably of from 5 to 95, more preferably of from 50 to 95, even more preferably of from 75 to 95 percent of all nitrogen-atoms within the inventive polymer.

It is well-known to a person of skill in the art that hyperbranched alkoxyated polyalkylene imine structures in general and such modified hyperbranched alkoxyated polyalkylene imine structures can be quaternized using standard means, due to their in principle chemical similarity with already known structures of this general type, and the known ability to modify those known structures by quaternization.

Clearly, also the present structures described herein as hyperbranched polyalkylene imines and modified hyperbranched alkoxyated polyalkylene imines can be quaternized as well.

A suitable degree of quaternization is up to 100%, in particular from 5 to 95%. The quaternization is conducted preferably by introducing C1-C22-alkyl groups, C1-C4-alkyl groups and/or C7-C22-aralkyl groups and may be undertaken in a customary manner by reaction with corresponding alkyl halides and dialkyl sulfates.

The quaternization may be advantageous in order to adjust the inventive polymer to the particular composition such as laundry compositions in which they are to be used, and to achieve better compatibility and/or phase stability of the formulation.

The quaternization of the inventive polymer is achieved preferably by introducing C1-C22 alkyl, C1-C4-alkyl groups and/or C7-C22 aralkyl, aryl or alkylaryl groups and may be undertaken in a customary manner by reaction with corresponding alkyl-, aralkyl - halides and dialkylsulfates, as described for example in WO 09/060059.

Quaternization can be accomplished, for example, by reacting an inventive polymer with an alkylation agent such as a C1-C4-alkyl halide, for example with methyl bromide, methyl chloride, ethyl chloride, methyl iodide, n-butyl bromide, isopropyl bromide, or with an aralkyl halide, for example with benzyl chloride, benzyl bromide or with a di-C1-C22-alkyl sulfate in the presence of a base, especially with dimethyl sulfate or with diethyl sulfate. Suitable bases are, for example, sodium hydroxide and potassium hydroxide.

The amount of alkylating agent determines the amount of quaternization of the amino groups in the polymer, i.e., the amount of quaternized moieties.

The amount of the quaternized moieties can be calculated from the difference of the amine number in the non-quaternized amine and the quaternized amine. The amine number can be determined according to the method described in DIN 16945.

The quaternization can be carried out without any solvent. However, a solvent or diluent like water, acetonitrile, dimethylsulfoxide, N-methylpyrrolidone, etc. may be used. The reaction temperature is usually in the range from 10°C to 150°C and is preferably from 50°C to 100°C.

5 The quaternization may be advantageous in order to adjust the modified hyperbranched alkoxyated polyalkylene imine to the particular composition such as laundry compositions in which they are to be used, and to achieve better compatibility and/or phase stability of the formulation.

Embodiment 18

10 A process to prepare a modified hyperbranched alkoxyated polyalkylene imine according to any one of Embodiments 1 to 17 comprising carrying out the process steps according to any one of Embodiments 1 to 17.

In particular, the process comprises the following steps:

- a) reaction of (i) at least one amine (A) with (ii) at least one alkylene imine to obtain a first intermediate (I1), wherein the amine (A) comprises at least one carbon atom more than the imine,
- 15 b) optionally reaction of the first intermediate (I1) with at least one first alkylene oxide (AO1), wherein at least 0.5 mol of first alkylene oxide (AO1) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain second intermediate (I2),
- c) optionally reaction of the first intermediate (I1) or the second intermediate (I2) with at least one first lactone (LA1) and/or at least one first hydroxy carbon acid (HA1), wherein 0.25 to 10 mol
20 of first lactone (LA1) and/or first hydroxy carbon acid (HA1) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain third intermediate (I3)
- d) reaction of the first (I1), second (I2) or third intermediate (I3) (i) with at least one second alkylene oxide (AO2) or (ii) with a mixture of 1) at least one second alkylene oxide (AO2) with 2) at least one second lactone (LA2) and/or at least one second hydroxy carbon acid (HA2),
25 wherein at least 5.0 mol of second alkylene oxide (AO2) and for the mixture additionally at least 1.0 mol of second lactone (LA2) and/or second hydroxy carbon acid (HA2) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain a fourth intermediate (I4),
- e) optionally reaction of the fourth intermediate (I4) (i) with at least one third alkylene oxide (AO3) or (ii) with a mixture of 1) at least one third alkylene oxide (AO3) with 2) at least one third lactone (LA3) and/or at least one third hydroxy carbon acid (HA3), wherein at least 5.0 mol of
30 third alkylene oxide (AO3) and for the mixture additionally at least 1.0 mol of third lactone (LA3) and/or third hydroxy carbon acid (HA3) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain a fifth intermediate (I5),
- 35 f) optionally reaction of the fifth intermediate (I5) or fourth intermediate (I4) with at least one fourth lactone (LA4) and/or at least one fourth hydroxy carbon acid (HA4), wherein at least 1.0 mol of fourth lactone (LA4) and/or fourth hydroxy carbon acid (HA4) is employed per mol of first intermediate (I1), in order to obtain a sixth intermediate (I6),

- g) optionally reaction of the fourth intermediate (**I4**), fifth intermediate (**I5**) or sixth intermediate (**I6**) with at least one C1-C18 alkylation or esterification reagent,

in order to obtain the modified hyperbranched alkoxyated polyalkylene imine.

- 5 All of the terms within Embodiment 18 have already been defined and explained in detail herein before within the description of the Embodiments 1 to 17, such terms and definitions of course apply to this Embodiment 18.

The conversion rate of each reaction step may be monitored: Only when the previous reaction has proceeded to a conversion rate of at least 90%, preferably at least 95%, more preferably at least 99%, and even more preferably at least 99,5 % or even more has been achieved, the next reactant may be added which in turn is also monitored for its conversion rate to detect when this next reaction has proceeded to a conversion rate of at least 90%, preferably at least 95%, more preferably at least 99%, and even more preferably at least 99,5 % or even more has been achieved, then the even next reaction is to be added – and so on until all reactants have been reacted and the reaction of the last reactant added has proceeded to a conversion rate of at least 90%, preferably at least 95%, more preferably at least 99%, and even more preferably at least 99,5 % or even more has been achieved. All other structural orders of the side chains as defined above but also the undefined structures resulting from non-controllable parameters are performed in this defined manner, leading – on statistical average – to a defined structural order directly derived from the way such a stepwise reaction is performed.

The conversion rate of each of the respective steps can be determined according to methods known to the skilled person, such as NMR-spectroscopy, such as ¹³C-NMR-spectroscopy and/or ¹H-NMR-spectroscopy.

- For the reaction conditions such as catalysts, temperatures, duration, purification etc. of the reactions to produce the units of the side chains of the inventive modified hyperbranched alkoxyated polyalkylene imines, the respective information within the disclosures WO 2021/165468 and unpublished patent applications EP 21176904.7, EP 21176906.2, EP 21192170.5 and EP 21192169.7 is fully encompassed into this recent disclosure by way of reference.

- For the ring-opening polymerization of the alkylene imine with the amine to generate intermediate **I1**, any acidic catalyst can be used, preferably any weak acid catalyst, in particular carbon dioxide in water.

- The reaction of intermediate **I1** or intermediate **I2** with LA or HA and the reaction of any of the intermediates with AO can be carried out without any catalyst or in the presence of any catalyst which aids deprotonation of the amino group or the hydroxy group, such as potassium hydroxide, potassium methoxide or potassium tert.butylhydroxide to name only very few. Preferred catalysts for reacting the intermediate **I1** or intermediate **I2** with LA or HA are selected from Sn octanoate or alkali metal hydroxides or alkali metal alkoxides, such as KOH, NaOH, KOMe, K^tBu or NaOMe.

Within this preferred embodiment, the alkoxylation is carried out in the presence of at least one catalyst and/or in the absence of water. Within this single step reaction of the alkoxylation step, the catalyst is preferably a basic catalyst. Examples of suitable catalysts are alkali metal and alkaline earth metal hydroxides such as sodium hydroxide, potassium hydroxide and calcium hydroxide, alkali metal alkoxides, in particular sodium and potassium C1-C4-alkoxides, such as sodium methoxide, sodium ethoxide and potassium tert-butoxide, alkali metal and alkaline earth metal hydrides such as sodium hydride and calcium hydride, and alkali metal carbonates such as sodium carbonate and potassium carbonate. Preference is given to the alkali metal hydroxides and the alkali metal alkoxides, a particular preference being given to potassium hydroxide and sodium hydroxide. Typical use amounts for the base are from 0.05 to 10% by weight, in particular from 0.5 to 2% by weight, based on the total amount of polyalkylene imine and alkylene oxide.

Embodiment 19

Process according to Embodiment 18, wherein the modified hyperbranched alkoxyated polyalkylene imine is further submitted to the following process steps of

- a) quaternization using standard means, including protonation by pH-adjustment or permanent quaternization by standard means such as alkylation using standard reactants, preferably by alkylation, to a degree of from 5 to 100, preferably of from 5 to 95, more preferably of from 50 to 95, even more preferably of from 75 to 95 percent of all nitrogen-atoms within the polyalkylene imine; and/or
- b) purification using standard means such as steam distillation, thermal distillation, vacuum evaporation, including removal of all solvent, dialysis and/or
- c) drying using standard drying means such as spray-, drum, paddle-, vacuum-drying means including agglomeration methods such as fluidized-bed-drying,

to obtain a purified (quaternized) polymer solution, a purified liquid (quaternized) polymer, a solid, e.g., granulated or co-granulated (quaternized) polymer or a purified solid (quaternized) polymer, respectively.

In case that after the reaction leading to the inventive polymer residual monomers are present to a non-desirable extent, the resulting product mixture containing the polyalkylene imine may be further purified by standard means to reduce the content of residual monomers, but also to reduce the amount of possible by-products, reduce the amount(s) of the solvent(s) employed (i.e., to concentrate) or replace solvent(s) with other solvents. Such processes are known to a person of skill in this field.

Preferably, undesirable amounts of residual non-reacted monomers are removed, preferably by means of distillative processes, more preferably by thermal distillative processes, which may additionally comprise the application of reduced pressure to increase the speed and/or the effectiveness of the removal.

In a preferred embodiment only the additional process step b) is employed.

Embodiment 20

A compound that is the first intermediate (I1) according to Embodiment 1, step a).

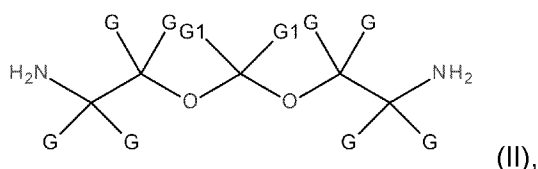
5 In detail, said compound is obtainable by a process comprising or consisting of the step:

- reaction of (i) at least one amine (A) with (ii) at least one alkylene imine to obtain a first intermediate (I1), wherein the amine (A) comprises at least one carbon atom more than the imine.

10 In preferred embodiments, the amine comprises at least 2, 3, 4 or 5 carbon atoms more than the imine.

Moreover, the at least one amine (A)

- (i) has 1, 2, 3 or 4 amino groups, preferably 2, 3 or 4 amino groups;
- (ii) has at least three carbon atoms, preferably 3 to 12 carbon atoms, more preferably 3 to 9 carbon atoms;
- 15 (iii) comprises at least one primary and/or at least one secondary amino group, preferably at least two primary amino groups; and/or
- (iv) is selected from the group consisting of propylenediamine (PDA), tetramethylenediamine (TMDA), pentamethylenediamine (PMDA), hexamethylenediamine (HMDA), heptamethylenediamine, octamethylenediamine (OMDA), dipropylene-triamine (DPTA), tripropylene-tetramine (TPTA), 4,7,10-Trioxa-tridecane-1,13-diamine (TTD), 4,9-Dioxado-decane-1,12-diamine (DODA), Poly-(propylenglykol)-bis-(2-aminopropylether), oligo or poly(alkylene glycol) di- and triamines and a compound as defined according to formula (II)



25 wherein G represents identical or different alkyl groups or H, preferably H, a methyl or ethyl group, more preferably all G are H and G1 represents identical or different alkyl groups or H, preferably both G1 are methyl groups.

In various embodiments of this aspect, the at least one alkylene imine is ethylene imine and/or propylene imine, more preferably the at least one alkylene imine is ethylene imine.

30 In one embodiment of the present invention, the at least one amine (A) is reacted with the at least one alkylene imine in a molar ratio of from 1:1 to 1:150 to obtain a first intermediate (I1). In a preferred embodiment of the present invention, the at least one amine (A) is reacted with the at least one alkylene imine in a molar ratio of from 1:1 to 1:50, more preferably in a molar ratio of from 1:1 to 1:20, to obtain a first intermediate (I1).

35

Use of and compositions comprising the inventive modified hyperbranched alkoxyated polyalkylene imines

Part of this invention is also the use of the inventive modified hyperbranched alkoxyated polyalkylene imines for various fields of applications, where they can replace currently known similar

5 structures, but bring in their enhanced rate of biodegradation compared to those previously known structures.

Embodiment 21

10 Use of at least one modified hyperbranched alkoxyated polyalkylene imine according to any one of Embodiments 1 to 17 or producible or produced by a process according to any of Embodiments 18 to 19 in

- a) cleaning compositions, preferably as additive for liquid, solid or semi-solid detergent formulations, particularly for liquid detergent formulations, preferably concentrated liquid detergent formulations or single mono doses laundry detergent formulations, or liquid hand dish washing
15 detergent formulations or solid automatic dish washing formulations;
- b) in fabric and home care products,
- c) in formulations for electro plating;
- d) in cementitious compositions;
- e) in agrochemical formulations, preferably as dispersant;
- 20 f) as adhesion promoters, for example for printing inks for laminate films;
- g) as an assistant (adhesion), for example for production of multilayer composite films, with compatibilization not just of different polymer layers but also of metal foils;
- h) as adhesion promoters for adhesives, for example in conjunction with polyvinyl alcohol, butyrate and acetate and styrene copolymers, or as a cohesion promoter for label adhesives;
- 25 i) as a primer in coatings applications for improvement of adhesion on substrates such as glass, wood, plastic and metal;
- j) for improvement of wet adhesion, for example in standard emulsion paints, and for improvement of instantaneous rain resistance of paints, for example for road markings;
- k) as complexing agents, especially with high binding capacity for heavy metals such as Hg, Pb,
30 Cu, Ni;
- l) as a flocculant, for example in water treatment/water processing;
- m) as a penetration aid, for example for active metal salt formulations in wood protection;
- n) as corrosion inhibitors, for example for iron and nonferrous metals, and in the sectors of petroleum production and of secondary oil production;
- 35 o) for immobilization of proteins and enzymes; microorganisms or as immobilizing supports of enzymes and microorganisms;
- p) for blocking and sealing, for example mineral oil and natural gas industry;
- q) as fixatives, for example in the textile industry, especially as formaldehyde-free cofixers;

- r) as an additive in the cosmetic formulations, for example for hair-setting compositions and hair rinses;
- s) as an assistant in the papermaking industry, for example for acceleration of dewatering, elimination of contraries, neutralization of charge and paper coating as a multipurpose assistant;
- 5 t) for separation of oil and water, for example in the metalworking industry;
- u) as an additive for landfill seals;
- v) as a flocculant;
- w) as a swimming pool algicide;
- x) for production of bitumen chemicals by reaction with fatty acids;
- 10 y) as an anti-swelling agent in order that clay absorbs water in a retarded manner;
- z) as an emulsifier or emulsion breaker;
 - aa) as a surfactant in the industrial cleaning (IC) sector;
 - bb) as a wood protector;
 - cc) for preparation of complexing agents (polycarboxylates);
 - 15 dd) for production of assistants for ore mining and mineral processing;
 - ee) as a dispersant for pigments, ceramic, carbon black, carbon, carbon fibers, metal powders, such as emulsifier or dispersant for inks for e.g. ink jet printing;
 - ff) for gas scrubbing as an absorbent of CO₂, NO_x, SO_x, Cl₂ and aldehydes, and for neutralization of acidic constituents;
 - 20 gg) for water softening;
 - hh) as a crystallization inhibitor in e.g. agrochemical formulations, oil-field uses;
 - ii) as a rheology modifier (thickener);
 - jj) as an assistant or as a component for assistants for the extraction and processing of oil, coal and natural gas;
 - 25 kk) for production of synthetic rubber and rubber chemicals;
 - ll) as an additive in coolants, lubricants and cooling lubricants;
 - mm) as assistants in the construction chemicals sector;
 - nn) as a constituent of galvanizing baths; or
 - oo) for production of nonviral gene vectors.

30

A subject matter of the present invention is the use of the above-mentioned modified hyperbranched alkoxylated polyalkylene imine in fabric and home care products, in cosmetic formulations, as crude oil emulsion breaker, in pigment dispersions for ink jet inks, in formulations for electro plating, in cementitious compositions and/or as dispersant for agrochemical formulations, preferably in cleaning compositions and/or in fabric and home care products, in particular cleaning compositions for improved clay removal or oily and fatty stain removal, wherein the cleaning composition is preferably a laundry detergent formulation and/or a manual dish wash detergent formulation, more preferably a liquid laundry detergent formulation and/or a liquid manual dish wash detergent formulation.

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The modified hyperbranched alkoxyated polyalkylene imine can be added to cosmetic formulations, as crude oil emulsion breaker, in pigment dispersions for ink jet inks, formulations for electro plating, in cementitious compositions. However, the inventive compounds can also be added to (used in) washing or cleaning compositions.

- 5 Another subject-matter of the present invention is, therefore, a cleaning composition, fabric and home care product, industrial and institutional cleaning product, cosmetic formulation, crude oil emulsion breaker, pigment dispersion for ink jet inks, formulation for electro plating, cementitious composition and/or dispersant for agrochemical formulations, comprising at least one modified hyperbranched alkoxyated polyalkylene imine, as defined above.
- 10 Preferably, it is a cleaning composition and/or fabric and home care product, comprising at least one modified hyperbranched alkoxyated polyalkylene imine, as defined above, preferably for improved clay removal or oily and fatty stain removal, preferably a laundry detergent formulation and/or a manual dish wash detergent formulation, more preferably a liquid laundry detergent formulation and/or a liquid manual dish wash detergent formulation.
- 15 In another preferred embodiment of the present invention, the cleaning composition may be used for soil removal of particulate stains and/or oily and fatty stains, and additionally for whiteness maintenance, preferably in laundry care.
- In another embodiment, the cleaning composition of the present invention is a hard surface cleaning composition that may be used for cleaning various surfaces such as hard wood, tile, ceramic, plastic,
- 20 leather, metal, glass.
- In another embodiment, the cleaning composition of the present invention is a liquid or solid automatic dish wash detergent composition, preferably a solid automatic dish wash detergent composition, that may be used for cleaning dish ware, e.g., dish ware such as glasses, wherein the inventive modified hyperbranched alkoxyated polyalkylene imine is improving the removal of stubborn soils.
- 25 In another embodiment, the cleaning composition is designed to be used in personal care and pet care compositions such as shampoo compositions, body wash formulations, liquid or solid soaps.
- In this invention, a preferred area of application for the use of the modified hyperbranched alkoxyated polyalkylene imine is the field of fabric and home care products and cleaning compositions, preferably cleaning compositions for industrial and institutional use and the use by consumers in their
- 30 household.

Embodiment 22

The use according to Embodiment 21 in cleaning compositions and/or in fabric and home care products, preferably in liquid and solid detergent compositions, such detergent compositions preferably being

- 35 a) manual and automatic dish wash detergent compositions, comprising the at least one modified hyperbranched alkoxyated polyalkylene imine, and the at least one chelating agent and/or the at least one surfactant or - more preferably - a chelating agent in case of a liquid or solid au-

automatic dish wash composition and a surfactant system in case of a liquid manual dish wash detergent composition, respectively; and/or

- b) laundry detergent compositions comprising the at least one modified hyperbranched alkoxylated polyalkylene imine, and at least one surfactant or - preferably - a surfactant system.

5

Within such preferred application areas of use, typical tasks have to be fulfilled, all of which are commonly encompassed by the term “cleaning”, but in fact comprise different tasks such as clay removal or removing oily and fatty residues, solid residues, amphiphilic residues and hydrophilic residues. Other tasks are the protection of the goods to be cleaned from deterioration, such as protecting glass from corroding, silverware from oxidation, colors from fading etc. Other tasks are improving the overall appearance of the to be cleaned goods, such as increasing or restoring the color, the whiteness, imparting or increasing a shine. For many such applications additional ingredients are typically added, for cleaning applications important ones are for example enzymes, which help biologically to degrade residues.

15

Embodiment 23

The use according to any of Embodiments 21 to 22 for

- i) clay removal, and/or
- ii) improved removal of oily/fatty stains, and/or
- 20 iii) soil removal of particulate stains, and/or
- iv) dispersion and/or emulsification of soils, and/or
- v) modification of treated surface to improve removal upon later re-soiling, and/or
- vi) whiteness improvement, and/or
- vii) – when at least one enzyme selected from the list consisting of lipases, hydrolases, amylases, proteases, cellulases, hemicellulases, phospholipases, esterases, DNases, mannanases, xy-
- 25 lanases, dispersins, oxidoreductases, cutinases, pectate lyases, pectinases, lactases and peroxidases, and combinations of at least two of the foregoing types, more preferably at least one enzyme being selected from proteases, is present – additionally for improvement of removal of oily/fatty stains, food stain removal and/or removal of complex stains,

30

most preferably in cleaning compositions for

- i) clay removal and/or ii) removal of oily/fatty stains, each of the before mentioned options i) to vii) preferably for use in a laundry detergent formulation and/or a manual dish wash detergent formulation and/or in a formulation suitable for (pre)-treatment of textiles and/or soap bars, more preferably in a liquid laundry detergent formulation and/or a liquid manual dish wash detergent formulation.

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Embodiment 24

The use according to any of Embodiments 21 to 23 in cleaning compositions and/or in fabric and home care products, preferably in cleaning compositions for in fabric and home care, the cleaning

composition preferably being a laundry detergent formulation or a dish wash detergent formulation, even more preferably being a liquid laundry detergent formulation or a liquid dish wash detergent formulation.

- Such ingredients are typically formulated with other ingredients in formulations and compositions, which may be also called "products" (as they are provided from a supplier as a formulation to another customer who uses such formulation directly for cleaning purposes etc. or for producing another formulation, which in turn could be sold to consumers as a "product" to be used by the consumer).

Embodiment 25

- A composition that is a fabric and home care product, cleaning composition, industrial and institutional cleaning product, cosmetic or personal care product, oil field-formulation such as crude oil emulsion breaker, pigment dispersion for inks such as ink-jet inks, electro plating product, cementitious composition, lacquer, paint, agrochemical formulation, preferably a laundry detergent, a dish wash composition, a cleaning composition and/or a fabric and home care product, each comprising at least one modified hyperbranched alkoxyated polyalkylene imine according to any of the Embodiments 1 to 17 or obtained by or obtainable by a process according to any of Embodiments 18-19.

Embodiment 26

- A composition according to Embodiment 25 being a solid or liquid laundry detergent composition or a solid or liquid manual dish wash detergent composition, preferably a liquid laundry detergent or liquid manual dish wash detergent composition, more preferably a liquid laundry detergent composition, comprising the least one modified hyperbranched alkoxyated polyalkylene imine, preferably the at least one modified hyperbranched alkoxyated polyalkylene imine according to any one of Embodiments 1 to 17 or obtained by or obtainable by a process according to any of Embodiments 18-19; optionally further comprising at least one enzyme, preferably selected from one or more lipases, hydrolases, amylases, proteases, cellulases, hemicellulases, phospholipases, esterases, DNases, mannanases, xylanases, dispersins, oxidoreductases, cutinases, pectate lyases, pectinases, lactases, pectate lyases, mannanases and peroxidases, and combinations of at least two of the foregoing types, preferably at least one enzyme being selected from proteases, optionally containing at least one antimicrobial agent, wherein the at least one modified hyperbranched alkoxyated polyalkylene imine is present in an amount ranging from about 0.01% to about 20%, preferably from about 0.05% to 15%, more preferably from about 0.1% to about 10%, and most preferably from about 0.5% to about 5%, in relation to the total weight of such composition or product, and such product or composition further comprising from about 1% to about 70% by weight of at least one surfactant, preferably an anionic surfactant, or even more preferably of a surfactant system comprising at least one anionic surfactant.

Embodiment 27

A composition being a solid or liquid automatic dish wash detergent composition, preferably a solid automatic dish wash detergent composition, comprising the at least one backbone-modified polyalkylene imine according to Embodiment 20 (the compound that is the first intermediate (I1) according to Embodiment 1, step a)),

optionally further comprising at least one enzyme, preferably selected from one or more lipases, hydrolases, amylases, proteases, cellulases, hemicellulases, phospholipases, esterases, DNases, mannanases, xylanases, dispersins, oxidoreductases, cutinases, pectate lyases, pectinases, lactases, pectate lyases, mannanases and peroxidases, and combinations of at least two of the foregoing

types, preferably at least one enzyme being selected from proteases and amylases,

optionally containing at least one antimicrobial agent,

optionally containing at least one compound selected from alkali metal percarbonate, alkali metal perborate and alkali metal persulfate,

optionally containing at least one zinc salt,

optionally at least one chelating agent selected from methylglycinediaceticacid (MGDA), glutamic acid diacetate (GLDA), citric acid and salts thereof,

wherein the at least one backbone-modified polyalkylene imine is being present in a total amount ranging from about 0.001% to about 10%, preferably from about 0.005% to 5%, more preferably from about 0.01% to about 3%, and most preferably from about 0.1% to about 2%, and such product or composition further comprising at least one chelating agent being present in a total amount from about 1% to about 70%, preferably from 10% to about 60% and even more preferably from 30% to about 50%, and

optionally further comprising at least one surfactant or more preferably a surfactant system in a total amount of from about 1% to about 70% by weight,

all weight percent in relation to the total weight of such composition.

Embodiment 27a

A composition according to Embodiment 27, being a solid automatic dish wash detergent composition, comprising the at least one backbone-modified polyalkylene imine according to Embodiment 20 (the compound that is the first intermediate (I1) according to Embodiment 1, step a)),

additionally comprising at least one chelating agent selected from methylglycinediaceticacid (MGDA), glutamic acid diacetate (GLDA), citric acid and salts thereof,

at least one enzyme selected from proteases and/or amylases,

at least one bleaching agent selected from alkali metal percarbonate, alkali metal perborate and

alkali metal persulfate, preferably alkali metal percarbonate,

at least one non-ionic surfactant,

optionally at least one disintegrant, preferably a super-disintegrant, more preferably PVPP, and

optionally containing at least one zinc salt.

Super-disintegrants are known by a person of skill in the art, e.g. from EP1004661, EP1263814 and EP1036839, and are discussed also in Pharmaceutical Technology, Volume 2006 Supplement, Issue 5, "A Comparative Study of Current Superdisintegrants", October 1, 2006.

5 Embodiment 28

Composition according to Embodiment 27 and 27a being a detergent composition, wherein the backbone-modified polyalkylene imine according to Embodiment 20 (the compound that is the first intermediate (I1) according to Embodiment 1, step a)), is employed for preventing or reducing glass corrosion.

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Embodiment 29

Composition according to any of Embodiments 25 and 26 being a detergent composition, comprising as surfactant at least one anionic surfactant.

15 Embodiment 29a

Composition according to any of Embodiments 25, 26 and 29 being a liquid detergent composition, comprising as surfactant at least one non-ionic surfactant, and further comprising water.

Embodiment 29b

20 Composition according to any of Embodiments 25, 26, 29 and 29a, being a liquid detergent composition, comprising as surfactant at least one non-ionic surfactant, further comprising water and additionally comprising at least one enzyme selected from the list consisting of lipases, hydrolases, amylases, DNases, proteases, cellulases, hemicellulases, phospholipases, esterases, mannanases, xylanases, dispersins, oxidoreductases, cutinases, pectate lyases, pectinases, lactases and peroxidases, and combinations of at least two of the foregoing types, preferably selected from one or more lipases, hydrolases, amylases, proteases, cellulases, and combinations of at least two of the foregoing types, more preferably at least one enzyme being selected from proteases.

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Embodiment 30

30 Composition according to any of Embodiments 25, 26, 29, 29a and 29b being a detergent composition, comprising at least one further polymer selected from multifunctional alkoxyated polyethylene imines, multifunctional alkoxyated diamines, or terephthalic acid-based soil release polyesters, or mixtures thereof.

35 Embodiment 31

Composition according to any of Embodiments 25, 26, 29, 29a, 29b and 30 being a liquid detergent composition, comprising as surfactant at least one 2-propylheptyl ethoxylated non-ionic surfactant having an average degree of ethoxylation of from 3 to 8.

Embodiment 32

Composition according to any one of Embodiments 25 to 31 further comprising an antimicrobial agent selected from the group consisting of 2-phenoxyethanol and 4,4'-dichloro 2-hydroxydiphenylether; preferably comprising 2-phenoxyethanol in an amount ranging from 2ppm to 5% by weight of the composition; more preferably comprising 0.1 to 2% of phenoxyethanol or preferably comprising 4,4'-dichloro 2-hydroxydiphenylether in a concentration from 0.001 to 3%, more preferably 0.002 to 1%, even more preferably 0.01 to 0.6%, each by weight of the composition.

Embodiment 33

Method of preserving an aqueous composition according to any one of Embodiments 25 to 32 against microbial contamination or growth, which method comprises addition of an antimicrobial agent selected from the group consisting of 2-phenoxyethanol and 4,4'-dichloro 2-hydroxydiphenylether.

It is also preferred in the present invention that the cleaning composition comprises (besides at least one modified hyperbranched alkoxylated polyalkylene imine as described above) additionally at least one enzyme, preferably selected from one or more lipases, hydrolases, amylases, proteases, cellulases, hemicellulases, phospholipases, esterases, DNases, mannanases, xylanases, dispersins, oxidoreductases, cutinases, pectate lyases, pectinases, lactases and peroxidases, preferably selected from one or more lipases, hydrolases, amylases, proteases, cellulases and combinations of at least two of the foregoing types, more preferably at least one enzyme being selected from proteases.

Preferably, the such inventive cleaning composition is a fabric and home care product or an industrial and institutional (I&I) cleaning product, preferably a fabric and home care product, more preferably a laundry detergent or manual dish washing detergent, comprising at least one inventive modified hyperbranched alkoxylated polyalkylene imine, and optionally further comprising at least one surfactant or a surfactant system, providing improved removal, dispersion and/or emulsification of soils and / or modification of treated surfaces and / or whiteness maintenance of treated surfaces.

At least one inventive modified hyperbranched alkoxylated polyalkylene imine as described herein (such modified hyperbranched alkoxylated polyalkylene imine as defined before and especially in the Embodiments 1 to 17 are in this following section also termed "inventive polymer") is present in said inventive cleaning compositions at a concentration of from about 0.01% to about 20%, preferably from about 0.05% to 15%, more preferably from about 0.1% to about 10%, and most preferably from about 0.5% to about 5%, in relation to the total weight of such composition or product; such cleaning composition may – and preferably does – further comprise a from about 1% to about 70% by weight of a surfactant system.

Even more preferably, the cleaning compositions of the present invention comprising at least one inventive polymer, and optionally further comprising at least one surfactant or a surfactant system, are those for primary cleaning (i.e., removal of stains) within laundry and manual dish wash applica-

tions, even more specifically, for removal of clay or oily and fatty stains such as those on fabrics and dishware, and may additionally comprise at least one enzyme selected from the list consisting of lipases, hydrolases, amylases, proteases, cellulases, hemicellulases, phospholipases, esterases, DNases, mannanases, xylanases, dispersins, oxidoreductases, cutinases, pectate lyases, pecti-
5 nases, lactases and peroxidases, and combinations of at least two of the foregoing types of enzymes, more preferably at least one enzyme being selected from proteases.

In one preferred embodiment, the cleaning composition of the present invention is a liquid or solid laundry detergent composition.

10 In another preferred embodiment, the cleaning composition of the present invention is a liquid or solid (e.g., powder or tab/unit dose) detergent composition for manual or automatic dish wash, preferably either a liquid manual dish wash detergent composition or a solid automatic dish wash composition.

In one embodiment, the inventive polymers of the present invention may be utilized in cleaning compositions comprising a surfactant system comprising C10-C15 alkyl benzene sulfonates (LAS) as the
15 primary surfactant and one or more additional surfactants selected from non-ionic, cationic, amphoteric, zwitterionic or other anionic surfactants, or mixtures thereof.

In a further embodiment, the inventive polymers may be utilized in cleaning compositions, such as laundry detergents of any kind, and the like, comprising C8-C18 linear or branched alkyl ether sul-
20 fates with 1-5 ethoxy-units as the primary surfactant and one or more additional surfactants selected from non-ionic, cationic, amphoteric, zwitterionic or other anionic surfactants, or mixtures thereof.

In a further embodiment the inventive polymers may be utilized in cleaning compositions, such as laundry detergents of any kind, and the like, comprising C12-C18 alkyl ethoxylate surfactants with 5-
10 ethoxy-units as the primary surfactant and one or more additional surfactants selected from anionic, cationic, amphoteric, zwitterionic or other non-ionic surfactants, or mixtures thereof.

25 In a further embodiment the inventive polymers may be utilized in cleaning compositions, such as laundry detergents of any kind, and the like, comprising bio-based surfactants like rhamnolipids and/or sophorolipids as the primary surfactant.

In one embodiment of the present invention, the inventive polymer is a component of a cleaning composition, such as preferably a laundry or a dish wash formulation, more preferably a liquid laun-
30 dry or manual dish wash formulation, that each additionally comprise at least one surfactant, preferably at least one anionic surfactant.

The selection of the additional surfactants in these embodiments may be dependent upon the application and the desired benefit.

As used herein, the articles "a" and "an" when used in a claim or an embodiment, are understood to
35 mean one or more of what is claimed or described. As used herein, the terms "include(s)" and "including" are meant to be non-limiting, and thus encompass more than the specific item mentioned after those words.

The compositions of the present disclosure can “comprise” (i.e., contain other ingredients), “consist essentially of” (comprise mainly or almost only the mentioned ingredients and other ingredients in only very minor amounts, mainly only as impurities), or “consist of” (i.e., contain only the mentioned ingredients and in addition may contain only impurities not avoidable in a technical environment, preferably only the ingredients) the components of the present disclosure.

The term “at least one”, as used herein, includes but is not limited to 1, 2, 3, 4, 5, 6, 7, 8, 9 and more.

Similarly, the terms “substantially free of ...” or “substantially free from ...” or “(containing/comprising) essentially no ...” may be used herein; this means that the indicated material is at the very minimum not deliberately added to the composition to form part of it, or, preferably, is not present at analytically detectable levels. It is meant to include compositions whereby the indicated material is present only as an impurity in one of the other materials deliberately included. The indicated material may be present, if at all, at a level of less than 1%, or even less than 0.1%, or even more less than 0.01%, or even 0%, by weight of the composition.

The term “about”, as used herein, encompasses the exact number “X” mentioned as e.g., “about X%” etc., and small variations of X, including from minus 5 to plus 5 % deviation from X (with X for this calculation set to 100%), preferably from minus 2 to plus 2 %, more preferably from minus 1 to plus 1 %, even more preferably from minus 0,5 to plus 0,5 % and smaller variations. Of course, if the value X given itself is already “100%” (such as for purity etc.) then the term “about” clearly can and thus does only mean deviations thereof which are smaller than “100”.

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.

All temperatures herein are in degrees Celsius (°C) unless otherwise indicated. Unless otherwise specified, all measurements herein are conducted at 20°C and under atmospheric pressure. In all embodiments of the present disclosure, all percentages are by weight of the total composition, unless specifically stated otherwise. All ratios are weight ratios, unless specifically stated otherwise.

Description of cleaning compositions, formulations and their ingredients

The phrase “cleaning composition” as used herein includes compositions and formulations designed for cleaning soiled material. Such compositions and formulations include those designed for cleaning soiled material or surfaces of any kind.

Compositions for “industrial and institutional cleaning” includes such cleaning compositions being designed for use in industrial and institutional cleaning, such as those for use of cleaning soiled material or surfaces of any kind, such as hard surface cleaners for surfaces of any kind, including tiles, carpets, PVC-surfaces, wooden surfaces, metal surfaces, lacquered surfaces.

“Compositions for Fabric and Home Care” include cleaning compositions and formulations including but not limited to laundry cleaning compositions and detergents, fabric softening compositions, fabric enhancing compositions, fabric freshening compositions, laundry prewash, laundry pretreat, laundry additives, spray products, dry cleaning agent or composition, laundry rinse additive, wash additive, post-rinse fabric treatment, ironing aid, dish washing compositions, hard surface cleaning compositions, unit dose formulation, delayed delivery formulation, detergent contained on or in a porous substrate or nonwoven sheet, and other suitable forms that may be apparent to one skilled in the art in view of the teachings herein and detailed herein below when describing the compositions. Such compositions may be used as a pre-laundering treatment, a post-laundering treatment, or may be added during the rinse or wash cycle of the laundering operation, preferably during the wash cycle of the laundering or dish washing operation, and as further detailed herein below when describing the use and application of the inventive polymers and compositions comprising such polymers.

The cleaning compositions of the invention may be in any form, namely, in the form of a liquid; a solid such as a powder, granules, agglomerate, paste, tablet, pouches, bar, gel; an emulsion; types delivered in dual- or multi-compartment containers; single-phase or multi-phase unit dose; a spray or foam detergent; premoistened wipes (i.e., the cleaning composition in combination with a nonwoven material such as that discussed in US 6,121,165, Mackey, et al.); dry wipes (i.e., the cleaning composition in combination with a nonwoven materials, such as that discussed in US 5,980,931, Fowler, et al.) activated with water by a user or consumer; and other homogeneous, non-homogeneous or single-phase or multiphase cleaning product forms.

The liquid cleaning compositions of the present invention preferably have a viscosity of from 50 to 10000 mPa*s; liquid manual dish wash cleaning compositions (also liquid manual “dish wash compositions”) have a viscosity of preferably from 100 to 10000 mPa*s, more preferably from 200 to 5000 mPa*s and most preferably from 500 to 3000 mPa*s at 20 1/s and 20°C; liquid laundry cleaning compositions have a viscosity of preferably from 50 to 3000 mPa*s, more preferably from 100 to 1500 mPa*s and most preferably from 200 to 1000 mPa*s at 20 1/s and 20°C.

The liquid cleaning compositions of the present invention may have any suitable pH-value. Preferably the pH of the composition is adjusted to between 4 and 14. More preferably the composition has a pH of from 6 to 13, even more preferably from 6 to 10, most preferably from 7 to 9. The pH of the composition can be adjusted using pH modifying ingredients known in the art and is measured as a 10% product concentration in demineralized water at 25°C. For example, NaOH may be used and the actual weight% of NaOH may be varied and trimmed up to the desired pH such as pH 8.0. In one embodiment of the present invention, a pH >7 is adjusted by using amines, preferably alkanolamines, more preferably triethanolamine.

Cleaning compositions such as fabric and home care products and formulations for industrial and institutional cleaning, more specifically such as laundry and manual dish wash detergents, are known to a person skilled in the art. Any composition etc. known to a person skilled in the art, in connection with the respective use, can be employed within the context of the present invention by including at least one inventive polymer, preferably at least one polymer in amounts suitable for ex-

pressing a certain property within such a composition, especially when such a composition is used in its area of use.

One aspect of the present invention is also the use of the inventive polymers as additives for detergent formulations, particularly for liquid detergent formulations, preferably concentrated liquid detergent formulations, or single mono doses for laundry.

The cleaning compositions of the invention may – and preferably do - contain **adjunct cleaning additives** (also abbreviated herein as “**adjuncts**”), such adjuncts being preferably in addition to a surfactant system as defined before.

Suitable **adjunct cleaning additives** include builders, cobuilders, structurants or thickeners, clay soil removal/anti-redeposition agents, polymeric soil release agents, dispersants such as polymeric dispersing agents, polymeric grease cleaning agents, solubilizing agents, chelating agents, enzymes, enzyme stabilizing systems, bleaching compounds, bleaching agents, bleach activators, bleach catalysts, brighteners, malodor control agents, pigments, dyes, opacifiers, hueing agents, dye transfer inhibiting agents, chelating agents, suds boosters, suds suppressors (antifoams), color speckles, silver care, anti-tarnish and/or anti-corrosion agents, alkalinity sources, pH adjusters, pH-buffer agents, hydrotropes, scrubbing particles, antibacterial agents, anti-oxidants, softeners, carriers, processing aids, pro-perfumes, dye fixation agent and perfumes.

Liquid cleaning compositions additionally may comprise – and preferably do comprise at least one of – rheology control/modifying agents, emollients, humectants, skin rejuvenating actives, and solvents.

Solid compositions additionally may comprise - and preferably do comprise at least one of - fillers, bleaches, bleach activators and catalytic materials.

Suitable examples of such cleaning adjuncts and levels of use are found in WO 99/05242, U.S. Patent Nos. 5,576,282, 6,306,812 B1 and 6,326,348 B1.

Those of ordinary skill in the art will understand that a deterative surfactant encompasses any surfactant or mixture of surfactants that provide cleaning, stain removing, or laundering benefit to soiled material.

Hence, the cleaning compositions of the invention such as fabric and home care products, and formulations for industrial and institutional cleaning, more specifically such as laundry and manual dish wash detergents, preferably additionally comprise a surfactant system and, more preferably, also further adjuncts, as the one described above and below in more detail.

The surfactant system may be composed from one surfactant or from a combination of surfactants selected from anionic surfactants, non-ionic surfactants, cationic surfactants, zwitterionic surfactants, amphoteric surfactants, and mixtures thereof. Those of ordinary skill in the art will understand that a surfactant system for detergents encompasses any surfactant or mixture of surfactants that provide cleaning, stain removing, or laundering benefit to soiled material.

The cleaning compositions of the invention preferably comprise a surfactant system in an amount sufficient to provide desired cleaning properties. In some embodiments, the cleaning composition comprises, by weight of the composition, from about 1% to about 70% of a surfactant system. In other embodiments, the liquid cleaning composition comprises, by weight of the composition, from

about 2% to about 60% of the surfactant system. In further embodiments, the cleaning composition comprises, by weight of the composition, from about 5% to about 30% of the surfactant system. The surfactant system may comprise a deterative surfactant selected from anionic surfactants, non-ionic surfactants, cationic surfactants, zwitterionic surfactants, amphoteric surfactants, and mixtures thereof.

(a) Laundry compositions

In laundry formulations, anionic surfactants contribute usually by far the largest share of surfactants within such formulation. Hence, preferably, the inventive cleaning compositions for use in laundry comprise at least one anionic surfactant and optionally further surfactants selected from any of the surfactant classes described herein, preferably from non-ionic surfactants and/or amphoteric surfactants and/or zwitterionic surfactants and/or cationic surfactants.

Nonlimiting examples of **anionic surfactants** – which may be employed also in combinations of more than one surfactant - useful herein include C9-C20 linear alkylbenzenesulfonates (LAS), C10-C20 primary, branched chain and random alkyl sulfates (AS); C10-C18 secondary (2,3) alkyl sulfates; C10-C18 alkyl alkoxy sulfates (AExS) wherein x is from 1 to 30; C10-C18 alkyl alkoxy carboxylates comprising 1 to 5 ethoxy units; mid-chain branched alkyl sulfates as discussed in US 6,020,303 and US 6,060,443; mid-chain branched alkyl alkoxy sulfates as discussed in US 6,008,181 and US 6,020,303; modified alkylbenzene sulfonate (MLAS) as discussed in WO 99/05243, WO 99/05242 and WO 99/05244; methyl ester sulfonate (MES); and alpha-olefin sulfonate (AOS).

Preferred examples of suitable anionic surfactants are alkali metal and ammonium salts of C8-C12-alkyl sulfates, of C12-C18-fatty alcohol ether sulfates, of C12-C18-fatty alcohol polyether sulfates, of sulfuric acid half-esters of ethoxylated C4-C12-alkylphenols (ethoxylation: 3 to 50 mol of ethylene oxide/mol), of C12-C18-alkylsulfonic acids, of C12-C18 sulfo fatty acid alkyl esters, for example of C12-C18 sulfo fatty acid methyl esters, of C10-C18-alkylarylsulfonic acids, preferably of n-C10-C18-alkylbenzene sulfonic acids, of C10-C18 alkyl alkoxy carboxylates and of soaps such as for example C8-C24-carboxylic acids. Preference is given to the alkali metal salts of the aforementioned compounds, particularly preferably the sodium salts.

In one embodiment of the present invention, anionic surfactants are selected from n-C10-C18-alkylbenzene sulfonic acids and from fatty alcohol polyether sulfates, which, within the context of the present invention, are in particular sulfuric acid half-esters of ethoxylated C12-C18-alkanols (ethoxylation: 1 to 50 mol of ethylene oxide/mol), preferably of n-C12-C18-alkanols.

In one embodiment of the present invention, also alcohol polyether sulfates derived from branched (i.e., synthetic) C11-C18-alkanols (ethoxylation: 1 to 50 mol of ethylene oxide/mol) may be employed.

Preferably, the alkoxylation group of both types of alkoxyated alkyl sulfates, based on C12-C18-fatty alcohols or based on branched (i.e., synthetic) C11-C18-alcohols, is an ethoxylation group and an average ethoxylation degree of any of the alkoxyated alkyl sulfates is 1 to 5, preferably 1 to 3.

In a further embodiment of the present invention, anionic surfactants are selected from rhamnolipids and/or sophorolipids.

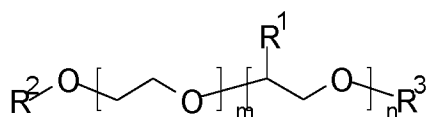
Preferably, the laundry detergent formulation of the present invention comprises from at least 1 wt.-% to 50 wt.-%, preferably in the range from greater than or equal to about 2 wt.-% to equal to or less than about 30 wt.-%, more preferably in the range from greater than or equal to 3 wt.-% to less than or equal to 25 wt.-%, and most preferably in the range from greater than or equal to 5 wt.-% to less than or equal to 25 wt.-% of one or more anionic surfactants as described above, based on the particular overall composition, including other components and water and/or solvents.

In a preferred embodiment of the present invention, anionic surfactants are selected from C10-C15 linear alkylbenzenesulfonates, C10-C18 alkylethersulfates with 1-5 ethoxy units and C10-C18 alkyl-sulfates.

Non-limiting examples of **non-ionic surfactants** – which may be employed also in combinations of more than one other surfactant - include: C8-C18 alkyl ethoxylates, such as, NEODOL® non-ionic surfactants from Shell; ethylenoxide/propylenoxide block alkoxylates as PLURONIC® from BASF; C14-C22 mid-chain branched alkyl alkoxylates, BAEx, wherein x is from 1 to 30, as discussed in US 6,153,577, US 6,020,303 and US 6,093,856; alkylpolysaccharides as discussed in U.S. 4,565,647 Llenado, issued January 26, 1986; specifically alkylpolyglycosides as discussed in US 4,483,780 and US 4,483,779; polyhydroxy fatty acid amides as discussed in US 5,332,528; and ether capped poly(oxyalkylated) alcohol surfactants as discussed in US 6,482,994 and WO 01/42408.

Preferred examples of non-ionic surfactants are in particular alkoxylated alcohols and alkoxylated fatty alcohols, di- and multiblock copolymers of ethylene oxide and propylene oxide and reaction products of sorbitan with ethylene oxide or propylene oxide, furthermore alkylphenol ethoxylates, alkyl glycosides, polyhydroxy fatty acid amides (glucamides).

Preferred examples of alkoxylated alcohols and alkoxylated fatty alcohols are, for example, compounds of the general formula (A)



[formula (A)]

in which the variables are defined as follows:

R¹ is selected from linear C1-C10-alkyl, preferably ethyl and particularly preferably methyl,

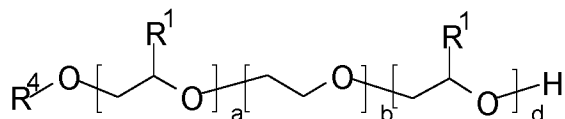
R² is selected from C8-C22-alkyl, for example n-C8H17, n-C10H21, n-C12H25, n-C14H29, n-C16H33 or n-C18H37,

R³ is selected from C1-C10-alkyl, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, isoamyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl or isodecyl,

m and n are in the range from zero to 300, where the sum of n and m is at least one. Preferably, m is in the range from 1 to 100 and n is in the range from 0 to 30.

Here, compounds of the general formula (A) may be block copolymers or random copolymers, preference being given to block copolymers.

Other preferred examples of alkoxyated alcohols and alkoxyated fatty alcohols are, for example, compounds of the general formula (B)



[formula (B)]

in which the variables are defined as follows:

R¹ is identical or different and selected from linear C₁-C₄-alkyl, preferably identical in each case and ethyl and particularly preferably methyl,

R⁴ is selected from C₆-C₂₀-alkyl, in particular n-C₈H₁₇, n-C₁₀H₂₁, n-C₁₂H₂₅, n-C₁₄H₂₉, n-C₁₆H₃₃, n-C₁₈H₃₇,

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

b is a number in the range from zero to 20, preferably 4 to 20,

d is a number in the range from 4 to 25.

Preferably, at least one of a and b is greater than zero.

Here, compounds of the general formula (B) may be block copolymers or random copolymers, preference being given to block copolymers.

Further suitable non-ionic surfactants are selected from di- and multiblock copolymers, composed of ethylene oxide and propylene oxide. Further suitable non-ionic surfactants are selected from ethoxylated or propoxylated sorbitan esters. Alkylphenol ethoxylates or alkyl polyglycosides or polyhydroxy fatty acid amides (glucamides) are likewise suitable. An overview of suitable further non-ionic surfactants can be found in EP-A 0 851 023 and in DE-A 198 19 187.

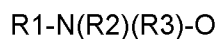
Mixtures of two or more different non-ionic surfactants may of course also be present.

In a preferred embodiment of the present invention, non-ionic surfactants are selected from C₁₂/14 and C₁₆/18 fatty alcoholalkoxylates, C₁₃/15 oxoalkoholalkoxylates, C₁₃-alkoholalkoxylates, and 2-propylheptylalkoholalkoxylates, each of them with 3 – 15 ethoxy units, preferably 4-10 ethoxy units, or with 1-3 propoxy- and 2-15 ethoxy units.

Non-limiting examples of **amphoteric surfactants** - which may be employed also in combinations of more than one other surfactant - include: water-soluble amine oxides containing one alkyl moiety of from about 8 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl moieties and hydroxyalkyl moieties containing from about 1 to about 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and a moiety selected from the group consisting of alkyl moieties and hydroxyalkyl moieties of from about 1 to about 3 carbon atoms. See WO 01/32816, US 4,681,704, and US 4,133,779. Suitable surfactants include thus so-called amine oxides, such as lauryl dimethyl amine oxide ("lauramine oxide").

Preferred examples of amphoteric surfactants are amine oxides. Preferred amine oxides are alkyl dimethyl amine oxides or alkyl amido propyl dimethyl amine oxides, more preferably alkyl dimethyl

amine oxides and especially coco dimethyl amino oxides. Amine oxides may have a linear or mid-branched alkyl moiety. Typical linear amine oxides include water-soluble amine oxides containing one R1 = C8-18 alkyl moiety and two R2 and R3 moieties selected from the group consisting of C1-C3 alkyl groups and C1-C3 hydroxyalkyl groups. Preferably, the amine oxide is characterized by the formula



wherein R1 is a C8-18 alkyl and R2 and R3 are selected from the group consisting of methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 2-hydroxypropyl and 3-hydroxypropyl. The linear amine oxide surfactants in particular may include linear C10-C18 alkyl dimethyl amine oxides and linear C8-C12 alkoxy ethyl dihydroxy ethyl amine oxides. Preferred amine oxides include linear C10, linear C10-C12, and linear C12-C14 alkyl dimethyl amine oxides. As used herein "mid-branched" means that the amine oxide has one alkyl moiety having n1 carbon atoms with one alkyl branch on the alkyl moiety having n2 carbon atoms. The alkyl branch is located on the alpha carbon from the nitrogen on the alkyl moiety. This type of branching for the amine oxide is also known in the art as an internal amine oxide. The total sum of n1 and n2 is from 10 to 24 carbon atoms, preferably from 12 to 20, and more preferably from 10 to 16. The number of carbon atoms for the one alkyl moiety (n1) should be approximately the same number of carbon atoms as the one alkyl branch (n2) such that the one alkyl moiety and the one alkyl branch are symmetric. As used herein "symmetric" means that (n1-n2) is less than or equal to 5, preferably 4, most preferably from 0 to 4 carbon atoms in at least 50 wt.-%, more preferably at least 75 wt.-% to 100 wt.-% of the mid-branched amine oxides for use herein. The amine oxide further comprises two moieties, independently selected from a C1-C3 alkyl, a C1-C3 hydroxyalkyl group, or a polyethylene oxide group containing an average of from about 1 to about 3 ethylene oxide groups. Preferably the two moieties are selected from a C1-C3 alkyl, more preferably both are selected as a C1 alkyl.

In a preferred embodiment of the present invention, amphoteric surfactants are selected from C8-C18 alkyl-dimethyl aminoxides and C8-C18 alkyl-di(hydroxyethyl)aminoxide.

Cleaning compositions may also contain **zwitterionic surfactants** - which may be employed also in combinations of more than one other surfactant.

Suitable zwitterionic surfactants include betaines, such as alkyl betaines, alkylamidobetaine, amidazoliniumbetaine, sulfobetaine (INCI Sultaines) as well as the phosphobetaines. Examples of suitable betaines and sulfobetaines are the following (designated in accordance with INCI): Almond amidopropyl of betaines, Apricotamidopropyl betaines, Avocadamidopropyl of betaines, Babas-suamidopropyl of betaines, Behenamidopropyl betaines, Behenyl of betaines, Canol amidopropyl betaines, Capryl/Capramidopropyl betaines, Carnitine, Cetyl of betaines, Cocamidoethyl of betaines, Cocamidopropyl betaines, Cocamidopropyl Hydroxysultaine, Coco betaines, Coco Hydroxysultaine, Coco/Oleam idopropyl betaines, Coco Sultaine, Decyl of betaines, Dihydroxyethyl Oleyl Glycinate, Dihydroxyethyl Soy Glycinate, Dihydroxyethyl Stearyl Glycinate, Dihydroxyethyl Tallow Glycinate, Dimethicone Propyl of PG-betaines, Erucamidopropyl Hydroxysultaine, Hydrogenated Tallow of betaines, Isostearamidopropyl betaines, Lauramidopropyl betaines, Lauryl of betaines, Lauryl Hydroxy-

sultaine, Lauryl Sultaine, Milkamidopropyl betaines, Minkamidopropyl of betaines, Myristamidopropyl betaines, Myristyl of betaines, Oleamidopropyl betaines, Oleamidopropyl Hydroxysultaine, Oleyl of betaines, Olivamidopropyl of betaines, Palmamidopropyl betaines, Palmitamidopropyl betaines, Palmitoyl Carnitine, Palm Kernelamidopropyl betaines, Polytetrafluoroethylene Acetoxypromyl of betaines, Ricinoleamidopropyl betaines, Sesamidopropyl betaines, Soyamidopropyl betaines, Stearamidopropyl betaines, Stearyl of betaines, Tallowamidopropyl betaines, Tallowamidopropyl Hydroxysultaine, Tallow of betaines, Tallow Dihydroxyethyl of betaines, Undecylenamidopropyl betaines and Wheat Germamidopropyl betaines.

Preferred betaines are, for example, C12-C18-alkylbetaines and sulfobetaines. The zwitterionic surfactant preferably is a betaine surfactant, more preferably a Cocoamidopropylbetaine surfactant.

Non-limiting examples of **cationic surfactants** - which may be employed also in combinations of more than one other surfactant - include: the quaternary ammonium surfactants, which can have up to 26 carbon atoms include: alkoxylated quaternary ammonium (AQA) surfactants as discussed in US 6,136,769; dimethyl hydroxyethyl quaternary ammonium as discussed in US 6,004,922; dimethyl hydroxyethyl lauryl ammonium chloride; polyamine cationic surfactants as discussed in WO 98/35002, WO 98/35003, WO 98/35004, WO 98/35005, and WO 98/35006; cationic ester surfactants as discussed in US patents Nos. 4,228,042, 4,239,660 4,260,529 and US 6,022,844; and amino surfactants as discussed in US 6,221,825 and WO 00/47708, specifically amido propyldimethyl amine (APA).

Compositions according to the invention may comprise at least one **builder**. In the context of the present invention, no distinction will be made between builders and such components elsewhere called "co-builders". Examples of builders are complexing agents, hereinafter also referred to as complexing agents, ion exchange compounds, and precipitating agents. Builders are selected from citrate, phosphates, silicates, carbonates, phosphonates, amino carboxylates and polycarboxylates.

In the context of the present invention, the term citrate includes the mono- and the dialkali metal salts and in particular the mono- and preferably the trisodium salt of citric acid, ammonium or substituted ammonium salts of citric acid as well as citric acid. Citrate can be used as the anhydrous compound or as the hydrate, for example as sodium citrate dihydrate. Quantities of citrate are calculated referring to anhydrous trisodium citrate.

The term phosphate includes sodium metaphosphate, sodium orthophosphate, sodium hydrogenphosphate, sodium pyrophosphate and polyphosphates such as sodium tripolyphosphate. Preferably, however, the composition according to the invention is free from phosphates and polyphosphates, with hydrogenphosphates being subsumed, for example free from trisodium phosphate, pentasodium tripolyphosphate and hexasodium metaphosphate ("phosphate-free"). In connection with phosphates and polyphosphates, "free from" should be understood within the context of the present invention as meaning that the content of phosphate and polyphosphate is in total in the range from 10 ppm to 0.2% by weight of the respective composition, determined by gravimetry.

The term carbonates includes alkali metal carbonates and alkali metal hydrogen carbonates, preferred are the sodium salts. Particularly preferred is Na₂CO₃.

Examples of phosphonates are hydroxyalkanephosphonates and aminoalkanephosphonates.

Among the hydroxyalkanephosphonates, the 1-hydroxyethane-1,1-diphosphonate (HEDP) is of particular importance as builder. It is preferably used as sodium salt, the disodium salt being neutral and the tetrasodium salt being alkaline (pH 9). Suitable aminoalkanephosphonates are preferably ethylene diaminetetramethylenephosphonate (EDTMP), diethylenetriaminepentamethylene-
5 phosphonate (DTPMP), and also their higher homologues. They are preferably used in the form of the neutrally reacting sodium salts, e.g., as hexasodium salt of EDTMP or as hepta- and octa-sodium salts of DTPMP.

Examples of amino carboxylates and polycarboxylates are nitrilotriacetates, ethylene diamine tetraacetate, diethylene triamine pentaacetate, triethylene tetraamine hexaacetate, propylene di-
10 amines tetraacetic acid, ethanol-diglycines, methylglycine diacetate, and glutamine diacetate. The term amino carboxylates and polycarboxylates also include their respective non-substituted or substituted ammonium salts and the alkali metal salts such as the sodium salts, in particular of the respective fully neutralized compound.

15 Silicates in the context of the present invention include in particular sodium disilicate and sodium metasilicate, aluminosilicates such as for example zeolites and sheet silicates, in particular those of the formula α -Na₂Si₂O₅, β -Na₂Si₂O₅, and δ -Na₂Si₂O₅.

Compositions according to the invention may contain one or more builder selected from materials not being mentioned above. Examples of builders are α -hydroxypropionic acid and oxidized starch.

20 In one embodiment of the present invention, builder is selected from polycarboxylates. The term "polycarboxylates" includes non-polymeric polycarboxylates such as succinic acid, C₂-C₁₆-alkyl disuccinates, C₂-C₁₆-alkenyl disuccinates, ethylene diamine N,N'-disuccinic acid, tartaric acid diacetate, alkali metal malonates, tartaric acid monoacetate, propanetricarboxylic acid, butanetetracarboxylic acid and cyclopentanetetracarboxylic acid.

25 Oligomeric or polymeric polycarboxylates are for example polyaspartic acid or in particular alkali metal salts of (meth)acrylic acid homopolymers or (meth)acrylic acid copolymers.

Suitable co-monomers are monoethylenically unsaturated dicarboxylic acids such as maleic acid, fumaric acid, maleic anhydride, itaconic acid and citraconic acid. A suitable polymer is in particular polyacrylic acid, which preferably has a weight-average molecular weight M_w in the range from 2000
30 to 40 000 g/mol, preferably 2000 to 10 000 g/mol, in particular 3000 to 8000 g/mol. Further suitable copolymeric polycarboxylates are in particular those of acrylic acid with methacrylic acid and of acrylic acid or methacrylic acid with maleic acid and/or fumaric acid.

It is also possible to use copolymers of at least one monomer from the group consisting of monoethylenically unsaturated C₃-C₁₀-mono- or C₄-C₁₀-dicarboxylic acids or anhydrides thereof, such as
35 maleic acid, maleic anhydride, acrylic acid, methacrylic acid, fumaric acid, itaconic acid and citraconic acid, with at least one hydrophilically or hydrophobically modified co-monomer as listed below.

Suitable hydrophobic co-monomers are, for example, isobutene, diisobutene, butene, pentene, hexene and styrene, olefins with ten or more carbon atoms or mixtures thereof, such as, for example, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, 1-docosene, 1-

tetracosene and 1-hexacosene, C22- α -olefin, a mixture of C20-C24- α -olefins and polyisobutene having on average 12 to 100 carbon atoms per molecule.

Suitable hydrophilic co-monomers are monomers with sulfonate or phosphonate groups, and also non-ionic monomers with hydroxyl function or alkylene oxide groups. By way of example, mention may be made of: allyl alcohol, isoprenol, methoxypolyethylene glycol (meth)acrylate, methoxypolypropylene glycol (meth)acrylate, methoxypolybutylene glycol (meth)acrylate, methoxypoly(propylene oxide-co-ethylene oxide) (meth)acrylate, ethoxypolyethylene glycol (meth)acrylate, ethoxypolypropylene glycol (meth)acrylate, ethoxypolybutylene glycol (meth)acrylate and ethoxypoly(propylene oxide-co-ethylene oxide) (meth)acrylate. Polyalkylene glycols here can comprise 3 to 50, in particular 5 to 40 and especially 10 to 30 alkylene oxide units per molecule.

Particularly preferred sulfonic-acid-group-containing monomers here are 1-acrylamido-1-propanesulfonic acid, 2-acrylamido-2-propanesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid, 2-methacrylamido-2-methylpropanesulfonic acid, 3-methacrylamido-2-hydroxypropanesulfonic acid, allylsulfonic acid, methallylsulfonic acid, allyloxybenzenesulfonic acid, methallyloxybenzenesulfonic acid, 2-hydroxy-3-(2-propenyloxy)propanesulfonic acid, 2-methyl-2-propene-1-sulfonic acid, styrenesulfonic acid, vinylsulfonic acid, 3-sulfopropyl acrylate, 2-sulfoethyl methacrylate, 3-sulfopropyl methacrylate, sulfomethacrylamide, sulfomethylmethacrylamide, and salts of said acids, such as sodium, potassium or ammonium salts thereof.

Particularly preferred phosphonate-group-containing monomers are vinylphosphonic acid and its salts.

Moreover, amphoteric polymers can also be used as builders.

Compositions according to the invention can comprise, for example, in the range from in total 0.1 to 70% by weight, preferably 10 to 50% by weight, preferably up to 20% by weight, of builder(s), especially in the case of solid formulations. Liquid formulations according to the invention preferably comprise in the range of from 0.1 to 8% by weight of builder.

Formulations according to the invention can comprise one or more **alkali carriers**. Alkali carriers ensure, for example, a pH of at least 9 if an alkaline pH is desired. Of suitability are, for example, the alkali metal carbonates, the alkali metal hydrogen carbonates, and alkali metal metasilicates mentioned above, and, additionally, alkali metal hydroxides. A preferred alkali metal is in each case potassium, particular preference being given to sodium. In one embodiment of the present invention, a pH >7 is adjusted by using amines, preferably alkanolamines, more preferably triethanolamine.

In one embodiment of the present invention, the laundry formulation according to the invention comprises additionally at least one **enzyme**.

In one embodiment, the composition according to the present invention additionally comprises at least one enzyme.

Preferably, the at least one enzyme is a detergent enzyme.

In one embodiment, the enzyme is classified as an oxidoreductase (EC 1), a transferase (EC 2), a hydrolase (EC 3), a lyase (EC 4), an isomerase (EC 5), or a ligase (EC 6). The EC-numbering is according to Enzyme Nomenclature, Recommendations (1992) of the Nomenclature Committee of

the International Union of Biochemistry and Molecular Biology including its supplements published 1993-1999. Preferably, the enzyme is a hydrolase (EC 3).

In a preferred embodiment, the enzyme is selected from the group consisting of

proteases, amylases, lipases, cellulases, mannanases, hemicellulases, phospholipases, esterases,
5 pectinases, lactases, peroxidases, xylanases, cutinases, pectate lyases, keratinases, reductases,
oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases,
malanases, beta-glucanases, arabinosidases, hyaluronidases, chondroitinases, laccases, nucleas-
es, DNase, phosphodiesterases, phytases, carbohydrases, galactanases, xanthanases, xyloglu-
canases, oxidoreductase, perhydrolases, aminopeptidase, asparaginase, carbohydrase, carboxy-
10 peptidase, catalase, chitinase, cyclodextrin glycosyltransferase, alpha-galactosidase, beta-
galactosidase, glucoamylase, alpha-glucosidase, beta-glucosidase, invertase, ribonuclease,
transglutaminase, and dispersins, and combinations of at least two of the foregoing types. More
preferably, the enzyme is selected from the group consisting of proteases, amylases, lipases, cellu-
lases, mannanases, xylanases, DNases, dispersins, pectinases, oxidoreductases, and cutinases,
15 and combinations of at least two of the foregoing types. Most preferably, the enzyme is a protease,
preferably, a serine protease, more preferably, a subtilisin protease.

Preferably, the protease is a protease with at least 90% sequence identity to SEQ ID NO: 22 of
EP1921147B1 and having the amino acid substitution R101E (according to BPN' numbering). Pref-
erably, the amylase is an amylase with at least 90% sequence identity to SEQ ID NO: 54 of
20 WO2021032881A1.

The composition of the present invention can comprise one type of enzyme or more than one en-
zyme of different types, e.g., an amylase and a protease, or more than one enzyme of the same
type, e.g., two or more different proteases, or mixtures thereof, e.g., an amylase and two different
proteases.

25 The enzyme(s) can be incorporated into the composition at levels sufficient to provide an effective
amount for achieving a beneficial effect, preferably for primary washing effects and/or secondary
washing effects, like anti-greying or antipilling effects (e.g., in case of cellulases). Preferably, the
enzyme is present in the composition at levels from about 0.00001% to about 5%, preferably from
about 0.00001% to about 2%, more preferably from about 0.0001% to about 1%, or even more pref-
erably from about 0.001% to about 0.5% enzyme protein by weight of the composition.

Preferably, the enzyme-containing composition further comprises an enzyme stabilizing system.

Preferably, the enzyme-containing composition described herein comprises from about 0.001% to
about 10%, from about 0.005% to about 8%, or from about 0.01% to about 6%, by weight of the
composition, of an enzyme stabilizing system. The enzyme stabilizing system can be any stabilizing
35 system which is compatible with the enzyme.

Preferably, the enzyme stabilizing system comprises at least one compound selected from the group
consisting of polyols (preferably, 1,3-propanediol, ethylene glycol, glycerol, 1,2-propanediol, or sorbi-
tol), inorganic salts (preferably, CaCl₂, MgCl₂, or NaCl), short chain (preferably, C1-C3) carboxylic
acids or salts thereof (preferably, formic acid, formate (preferably, sodium formate), acetic acid, ace-

tate, or lactate), borate, boric acid, boronic acids (preferably, 4-formyl phenylboronic acid (4-FPBA)), peptide aldehydes (preferably, Z-VAL-H or Z-GAY-H), peptide acetals, and peptide aldehyde hydrosulfite adducts. Preferably, the enzyme stabilizing system comprises a combination of at least two of the compounds selected from the group consisting of salts, polyols, and short chain carboxylic acids and preferably one or more of the compounds selected from the group consisting of borate, boric acid, boronic acids (preferably, 4-formyl phenylboronic acid (4-FPBA)), peptide aldehydes, peptide acetals, and peptide aldehyde hydrosulfite adducts. In particular, if proteases are present in the composition, protease inhibitors may be added, preferably selected from borate, boric acid, boronic acids (preferably, 4-FPBA), peptide aldehydes (preferably, peptide aldehydes like Z-VAL-H or Z-GAY-H), peptide acetals, and peptide aldehyde hydrosulfite adducts.

Compositions according to the invention may comprise one or more **bleaching agent (bleaches)**. Preferred bleaches are selected from sodium perborate, anhydrous or, for example, as the monohydrate or as the tetrahydrate or so-called dihydrate, sodium percarbonate, anhydrous or, for example, as the monohydrate, and sodium persulfate, where the term "persulfate" in each case includes the salt of the peracid H_2SO_5 and also the peroxodisulfate.

In this connection, the alkali metal salts can in each case also be alkali metal hydrogen carbonate, alkali metal hydrogen perborate and alkali metal hydrogen persulfate. However, the dialkali metal salts are preferred in each case.

Formulations according to the invention can comprise one or more **bleach catalysts**. Bleach catalysts can be selected from oxaziridinium-based bleach catalysts, bleach-boosting transition metal salts or transition metal complexes such as, for example, manganese-, iron-, cobalt-, ruthenium- or molybdenum-salen complexes or carbonyl complexes. Manganese, iron, cobalt, ruthenium, molybdenum, titanium, vanadium and copper complexes with nitrogen-containing tripod ligands and also cobalt-, iron-, copper- and ruthenium-amine complexes can also be used as bleach catalysts.

Formulations according to the invention can comprise one or more **bleach activators**, for example tetraacetyl ethylene diamine, tetraacetylmethylene diamine, tetraacetylglycoluril, tetraacetylhexylene diamine, acylated phenolsulfonates such as for example n-nonanoyl- or isononanoyloxybenzene sulfonates, (S)NOBS, LOBS, DOBA, PAP, N-methylmorpholinium-acetonitrile salts ("MMA salts"), trimethylammonium acetonitrile salts, N-acylimides such as, for example, N-nonanoylsuccinimide, 1,5-diacetyl-2,2-dioxohexahydro-1,3,5-triazine ("DADHT") or nitrile quats (trimethylammonium acetonitrile salts).

As precursors of H_2O_2 peroxides come into consideration. i. e. every compound which is capable of yielding hydrogen peroxide in aqueous solutions, for example, the organic and inorganic peroxides known in the literature and available commercially that bleach textile materials at conventional washing temperatures, for example at from 10 to 95°C.

Preferably, however, inorganic peroxides are used, for example persulfates, perborates, percarbonates and/or persilicates. They are typically used in an amount of 2-80 wt-%, preferably of 4-30 wt-%, based on the weight of the composition.

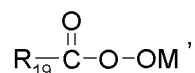
Typically, the compound of formula (1)
$$\text{R}_{19}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{OM}$$
, as described in more detail below, is present

in the composition in an amount of 0.05-15 wt-%, preferably from 0.1 to 10 wt-%, based on the weight of the total composition.

5 Examples of suitable inorganic peroxides are sodium perborate tetrahydrate or sodium perborate monohydrate, sodium percarbonate, inorganic peroxyacid compounds, such as for example potassium monopersulphate (MPS). If organic or inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2-80 wt-%, preferably from 4-30 wt-%, based on the weight of the composition.

10 The organic peroxides are, for example, mono- or poly-peroxides, urea peroxides, a combination of a C1-C4alkanol oxidase and C1-C4alkanol (Such as methanol oxidase and ethanol as described in WO95/07972), alkylhydroxy peroxides, such as cumene hydroperoxide and t-butyl hydroperoxide. The peroxides may be in a variety of crystalline forms and have different water contents, and they may also be used together with other inorganic or organic compounds in order to improve their storage stability.

15 As oxidants, peroxy acids can also be used. One example are organic mono peracids of formula (1)



wherein

M signifies hydrogen or a cation,

20 R₁₉ signifies unsubstituted C1-C18alkyl; substituted C1-C18alkyl; unsubstituted aryl; substituted aryl; -(C1-C6alkylene)-aryl, wherein the alkylene and/or the alkyl group may be substituted; and phthalimidoC1-C8alkylene, wherein the phthalimido and/or the alkylene group may be substituted.

Preferred mono organic peroxy acids and their salts are those of formula
$$\text{R}'_{19}-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{O}-\text{OM}$$
,

wherein

M signifies hydrogen or an alkali metal, and

25 R'₁₉ signifies unsubstituted C₁-C₄alkyl; phenyl;-C₁-C₂alkylene-phenyl or phthalimidoC₁-C₈alkylene.

Especially preferred is CH₃COOOH and its alkali salts.

Especially preferred is also ε-phthalimido peroxy hexanoic acid and its alkali salts (PAP).

30 Also suitable are diperoxyacids, for example, 1,12-diperoxydodecanedioic acid (DPDA), 1,9-diperoxyazelaic acid, diperoxybrassicic acid, diperoxysebasic acid, diperoxyisophthalic acid, 2-decyldiperoxybutane-1,4-dioic acid and 4,4'-sulphonylbisperoxybenzoic acid.

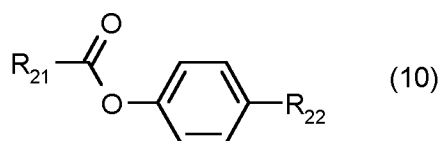
In some cases, the use of an additional bleach activator may be of advantage.

The term bleach activator is frequently used as a synonym for peroxyacid bleach precursor. All the above mentioned peroxy compounds may be utilized alone or in conjunction with a peroxyacid bleach precursor.

Such precursors are the corresponding carboxylic acid or the corresponding carboxyanhydride or the corresponding carbonylchloride, or amides, or esters, which can form the peroxy acids on perhydrolysis. Such reactions are commonly known.

Peroxyacid bleach precursors are known and amply described in literature, such as in the British Patents 836988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; and U.S. Pat. Nos. 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393.

Suitable bleach activators include the bleach activators, that carry O- and/or N-acyl groups and/or unsubstituted or substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetylenediamine (TAED); acylated glycolurils, especially tetraacetyl glycol urea (TAGU), N,N-diacetyl-N,N-dimethylurea (DDU); sodium-4-benzoyloxy benzene sulphonate (SBOBS); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoyloxy benzoate; trimethyl ammonium toluoyloxy-benzene sulphonate; acylated triazine derivatives, especially 1,5-diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT); compounds of formula (10):



wherein R_{22} is a sulfonate group, a carboxylic acid group or a carboxylate group, and wherein R_{21} is linear or branched (C_7 - C_{15})alkyl, especially activators known under the names SNOBS, SLOBS and DOBA; acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate and 2,5-diacetoxy-2,5-dihydrofuran; and also acetylated sorbitol and mannitol and acetylated sugar derivatives, especially pentaacetylglucose (PAG), sucrose polyacetate (SUPA), pentaacetylfructose, tetraacetylxylose and octaacetyllactose as well as acetylated, optionally N-alkylated glucamine and gluconolactone. It is also possible to use the combinations of conventional bleach activators known from German Patent Application DE-A-44 43 177. Nitrile compounds that form perimine acids with peroxides also come into consideration as bleach activators.

Another useful class of peroxyacid bleach precursors is that of the cationic i.e. quaternary ammonium substituted peroxyacid precursors as disclosed in US Pat. Nos. 4,751,015 and 4,397,757, in EP-A0284292 and EP-A-331,229. Examples of peroxyacid bleach precursors of this class are: 2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphonphenyl carbonate chloride - (SPCC), N-octyl,N,N-dimethyl-N10 -carbophenoxy decyl ammonium chloride - (ODC), 3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate and N,N,N-trimethyl ammonium toluoyloxy benzene sulphonate.

It is also possible to use additional bleach catalysts, which are commonly known, for example transition metal complexes as disclosed in EP 1194514, EP 1383857 or WO04/007657.

Formulations according to the invention can comprise one or more **corrosion inhibitors**. In the present case, this is to be understood as including those compounds which inhibit the corrosion of metal. Examples of suitable corrosion inhibitors are triazoles, in particular benzotriazoles, bisbenzotriazoles, aminotriazoles, alkylaminotriazoles, also phenol derivatives such as, for example, hydroquinone, pyrocatechol, hydroxyhydroquinone, gallic acid, phloroglucinol or pyrogallol.

In one embodiment of the present invention, formulations according to the invention comprise in total in the range from 0.1 to 1.5% by weight of corrosion inhibitor.

Formulations according to the invention may also comprise further **cleaning polymers and/or soil release polymers**.

The additional cleaning polymers may include, without limitation, "multifunctional alkoxyated polyethylene imines" (for example BASF's Sokalan® HP20), "multifunctional alkoxyated diamines" (for example BASF's Sokalan® HP96), BASF's Sokalan® SR400 A and also terephthalic acid-based polyesters like Clariant's TexCare®, such as TexCare® SRN 170, TexCare® SRN 172, TexCare® SRN 260, TexCare® SRN 260 SG Terra and TexCare® SRA 300 as well as distinct combinations of all of the before mentioned polymers.

Suitable multifunctional alkoxyated polyethylene imines are typically ethoxylated polyethylene imines with a weight-average molecular weight M_w in the range from 3000 to 250000, preferably 5000 to 200000, more preferably 8000 to 100000, more preferably 8000 to 50000, more preferably 10000 to 30000, and most preferably 10000 to 20000 g/mol. Suitable multifunctional ethoxylated polyethylene imines have 80 wt.-% to 99 wt.-%, preferably 85 wt.-% to 99 wt.-%, more preferably 90 wt.-% to 98 wt.-%, most preferably 93 wt.-% to 97 wt.-% or 94 wt.-% to 96 wt.-% ethylene oxide side chains, based on the total weight of the materials. Ethoxylated polyethylene imines are typically based on a polyethylene imine core and a polyethylene oxide shell. Suitable polyethylene imine core molecules are polyethylene imines with a weight-average molecular weight M_w in the range of 500 to 5000 g/mol. Preferably employed is a molecular weight from 500 to 1000 g/mol, even more preferred is a M_w of 600 to 800 g/mol. The ethoxylated polymer then has on average 5 to 50, preferably 10 to 35 and even more preferably 20 to 35 ethylene oxide (EO) units per NH-functional group.

Suitable multifunctional alkoxyated diamines are typically ethoxylated C2 to C12 alkylene diamines, preferably hexamethylene diamine, which are further quaternized and optionally sulfated. Typical multifunctional alkoxyated diamines have a weight-average molecular weight M_w in the range from 2000 to 10000, more preferably 3000 to 8000, and most preferably 4000 to 6000 g/mol. In a preferred embodiment of the invention, ethoxylated hexamethylene diamine, furthermore quaternized and sulfated, may be employed, which contains on average 10 to 50, preferably 15 to 40 and even more preferably 20 to 30 ethylene oxide (EO) groups per NH-functional group, and which preferably bears two cationic ammonium groups and two anionic sulfate groups.

In a preferred embodiment of the present invention, the cleaning compositions may contain at least one multifunctional alkoxyated polyethylene imine and/or at least one multifunctional alkoxyated di-

amine to improve the cleaning performance, such as preferably improve the stain removal ability, especially the primary detergency of particulate stains on polyester fabrics of laundry detergents. The multifunctional polyethylene imines or multifunctional diamines or mixtures thereof according to the descriptions above may be added to the laundry detergents and cleaning compositions in

5 amounts of generally from 0.05 to 15 wt.-%, preferably from 0.1 to 10 wt.-% and more preferably from 0.25 to 5 wt.-% and even as low as up to 2 wt.%, based on the particular overall composition, including other components and water and/or solvents.

In another preferred embodiment of the present invention, the cleaning compositions may contain at least one terephthalic acid-based polyester, employed as soil release polymer, to improve the white-

10 ness of the fabrics after the wash, especially the whiteness of polyester fabrics.

Thus, one aspect of the present invention is a laundry detergent composition, in particular a liquid laundry detergent, comprising (i) at least one inventive polymer and (ii) at least one compound selected from multifunctional alkoxyated polyethylene imines, multifunctional alkoxyated diamines and terephthalic acid-based polyesters, and mixtures thereof.

15 In one embodiment of the present invention, the ratio of the at least one inventive polymer and (ii) the at least one compound selected from multifunctional alkoxyated polyethylene imines, multifunctional alkoxyated diamines and terephthalic acid-based polyesters, and mixtures thereof, is from 10:1 to 1:10, preferably from 5:1 to 1:5 and more preferably from 3:1 to 1:3.

Laundry formulations comprising the inventive polymer may also comprise at least one **antimicrobial agent** (also often named **preservatives**).

20

The composition may contain one or more antimicrobial agents and/or preservatives as listed in patent WO2021/115912 A1 on pages 35 to 39.

Especially of interest are the following antimicrobial agents and/or preservatives:

4,4'-dichloro 2-hydroxydiphenyl ether (CAS-No. 3380-30-1), further names: 5-chloro-2-(4-chlorophenoxy) phenol, Diclosan, DCP, which is commercially available as a solution of 30 wt% of

25 4,4'-dichloro 2-hydroxydiphenyl ether in 1,2 propylene glycol under the trade name Tinosan® HP 100 (BASF); 2-Phenoxyethanol (CAS-no. 122-99-6, further names: Phenoxyethanol, Methylphenylglycol, Phenoxetol, ethylene glycol phenyl ether, Ethylene glycol monophenyl ether, Protectol® PE); 2-bromo-2-nitropropane-1,3-diol (CAS-No. 52-51-7, further names: 2-bromo-2-nitro-1,3-propanediol, Bronopol®, Protectol® BN, Myacide AS); Glutaraldehyde (CAS-No. 111-30-8, further names: 1-5-pentandial, pentane-1,5-dial, glutaral, glutardialdehyde, Protectol® GA, Protectol® GA 50, Myacide® GA); Glyoxal (CAS No. 107-22-2; further names: ethandial, oxylaldehyde, 1,2-ethandial, Protectol® GL); 2-butyl-benzo[d]isothiazol-3-one (BBIT, CAS No. 4299-07-4); 2-methyl-2H-isothiazol-3-one (MIT, CAS No 2682-20-4); 2-octyl-2H-isothiazol-3-one (OIT, CAS No. 26530-20-1); 5-Chloro-2-

30 methyl-2H-isothiazol-3-one (CIT, CMIT, CAS No. 26172-55-4); Mixture of 5-chloro-2-methyl-2H-isothiazol-3-one (CMIT, EINECS 247-500-7) and 2-methyl-2H-isothiazol-3-one (MIT, EINECS 220-239-6) (Mixture of CMIT/MIT, CAS No. 55965-84-9); 1,2-benzisothiazol-3(2H)-one (BIT, CAS No. 2634-33-5); Hexa-2,4-dienoic acid (Sorbic acid, CAS No. 110-44-1) and its salts, e.g. calcium sorbate, sodium sorbate, potassium (E,E)-hexa-2,4-dienoate (Potassium Sorbate, CAS No. 24634-61-5);

Lactic acid and its salts; L-(+)-lactic acid (CAS No. 79-33-4); Benzoic acid and its sodium salt (CAS No 65-85-0, CAS No. 532-32-1) and salts of benzoic acid e.g. ammonium benzoate, calcium benzoate, magnesium benzoate, MEA-benzoate, potassium benzoate; Salicylic acid and its salts, e.g. calcium salicylate, magnesium salicylate, MEA sa-licylate, sodium salicylate, potassium salicylate, TEA salicylate; Benzalkonium chloride, bromide and saccharinate, e.g. benzalkonium chloride, benzalkonium bromide, benzalkonium saccharinate (CAS Nos 8001-54-5, 63449-41-2, 91080-29-4, 68989-01-5, 68424-85-1, 68391-01-5, 61789-y71-7, 85409-22-9); Didecyldimethylammonium chloride (DDAC, CAS No. 68424-95-3 and CAS No. 7173-51-5); N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine (Diamine, CAS No. 2372-82-9); Peracetic acid (CAS No. 79-21-0); Hydrogen peroxide (CAS No. 7722-84-1).

The antimicrobial agent is added to the composition in a concentration of 0.001 to 10% relative to the total weight of the composition.

Preferably, the composition contains 2-Phenoxyethanol in a concentration of 0.1 to 2% or 4,4'-dichloro 2-hydroxydiphenyl ether (DCPP) in a concentration of 0.005 to 0.6%.

The invention thus further encompasses a method of preserving an aqueous composition according to the invention against microbial contamination or growth, which method comprises addition of 2-Phenoxyethanol. The invention thus further encompasses a method of providing an antimicrobial effect on textiles after treatment with a solid laundry detergent e.g., powders, granulates, capsules, tablets, bars etc.), a liquid laundry detergent, a softener or an after rinse containing 4,4'-dichloro 2-hydroxydiphenyl ether (DCPP).

In a further embodiment, this invention also encompasses a composition comprising an inventive polymer as described herein before, further comprises an antimicrobial agent as disclosed hereinafter, preferably selected from the group consisting of 2-phenoxyethanol, more preferably comprising said antimicrobial agent in an amount ranging from 2ppm to 5% by weight of the composition; even more preferably comprising 0.1 to 2% of phenoxyethanol.

In a further embodiment, this invention also encompasses a method of preserving an aqueous composition against microbial contamination or growth, such composition comprising an inventive polymer as described herein before, such composition being preferably a detergent composition, such method comprising adding at least one antimicrobial agent selected from the disclosed antimicrobial agents as disclosed hereinafter, such antimicrobial agent preferably being 2-phenoxyethanol.

In a further embodiment, this invention also encompasses a composition, preferably a cleaning composition, more preferably a liquid laundry detergent composition or a liquid hand dish composition, even more preferably a liquid laundry detergent composition, or a liquid softener composition for use in laundry, such composition comprising an inventive polymer as described herein before, such composition further comprising 4,4'-dichoro 2-hydroxydiphenylether in a concentration from 0.001 to 3%, preferably 0.002 to 1%, more preferably 0.01 to 0.6%, each by weight of the composition.

In a further embodiment, this invention also encompasses a method of laundering fabric or of cleaning hard surfaces, which method comprises treating a fabric or a hard surface with a cleaning com-

position, more preferably a liquid laundry detergent composition or a liquid hand dish composition, even more preferably a liquid laundry detergent composition, or a liquid softener composition for use in laundry, such composition comprising an inventive polymer as described herein before, such composition further comprising 4,4'-dichloro 2-hydroxydiphenylether.

5 The term „**dye fixation agent**”, as used herein, relates to compounds that attenuate or even terminate dye bleeding of colored fabrics during the washing process. Dye fixation agents include, but are not limited to cationic dye fixation agents, crosslinking fixation agents and formaldehyde-based fixation agents. The skilled person is well-aware of these compounds and may purchase commercially available products from BASF SE, Huntsman, Archroma, Fineotex, Biotex Malaysia or Dystar. Exemplified, but not limiting dye fixation agents are Basilen Fixing Agent F-RP, Albafix ECO, Finofix NF, poly DADMAC, Polyamine (DCDA-DETA, Epichloro-DMA, Epichloro-DETA, etc.).

10 Formulations according to the invention may also comprise **water** and/or additional **organic solvents**, e.g., ethanol or propylene glycol.

Further optional ingredients may be but are not limited to viscosity modifiers, foam boosting or

15 foam reducing agents, perfumes, dyes, optical brighteners, and dye transfer inhibiting agents.

(b) General cleaning compositions and formulations

The liquid formulations disclosed in this chapter may comprise 0 to 2 % 2-phenoxyethanol, preferably about 1 %, in addition to all other mentioned ingredients.

20 The above and below disclosed liquid formulations may comprise 0-0,2% 4,4'-dichloro 2-hydroxydiphenylether, preferably about 0,15 %, in addition to all other mentioned ingredients. The bleach-free solid laundry compositions may comprise 0-0,2% 4,4'-dichloro 2-hydroxydiphenylether, preferably about 0,15 %, in addition to all other mentioned ingredients.

The formulations disclosed in this chapter may – in addition to all other mentioned ingredients –

25 comprise one or more enzymes selected from those disclosed herein above, more preferably a protease and/or an amylase, wherein even more preferably the protease is a protease with at least 90% sequence identity to SEQ ID NO: 22 of EP1921147B1 and having the amino acid substitution R101E (according to BPN' numbering) and wherein the amylase is an amylase with at least 90% sequence identity to SEQ ID NO: 54 of WO2021032881A1, such enzyme(s) preferably being present in the

30 formulations at levels from about 0.00001% to about 5%, preferably from about 0.00001% to about 2%, more preferably from about 0.0001% to about 1%, or even more preferably from about 0.001% to about 0.5% enzyme protein by weight of the composition.

The following compositions shown below including those in the tables disclose general cleaning compositions of certain types, which correspond to typical compositions correlating with typical

35 washing conditions as typically employed in various regions and countries of the world. The at least one inventive polymer may be added to such formulation(s) in suitable amounts as outlined herein. When the shown composition does not comprise an inventive polymer, such composition is a comparative composition. When it comprises an inventive polymer, especially in the amounts that are

described herein as preferred, more preferred etc. ranges, such compositions are considered to fall within the scope of the present invention.

In a preferred embodiment the at least one modified hyperbranched alkoxyated polyalkylene imine (as defined in any of the embodiments herein, especially the Embodiments 1 to 17; modified hyper-

5 branched alkoxyated polyalkylene imines in this section also named "inventive polymer") is used in a laundry detergent.

Liquid laundry detergents according to the present invention are composed of:

	0,05 – 20%	of at least one inventive polymer
	1 – 50%	of surfactants
10	0,1 – 40%	of builders, cobuilders and/or chelating agents
	0,1 – 50%	other adjuncts
	water	to add up 100%.

Preferred liquid laundry detergents according to the present invention are composed of:

15	0,2 – 6%	of at least one inventive polymer
	5 – 40%	of anionic surfactants selected from C10-C15- LAS and C10-C18 alkyl ether sul-
		fates containing 1-5 ethoxy-units
	1,5 – 10%	of nonionic surfactants selected from C10-C18-alkyl ethoxylates containing 3 – 10
		ethoxy-units
20	2 – 20%	of soluble organic builders/ cobuilders selected from C10-C18 fatty acids, di- and
		tricarboxylic acids, hydroxy-di- and hydroxytricarboxylic acids and polycarboxylic ac-
		ids
	0,05 – 5%	of an enzyme system containing at least one enzyme suitable for detergent use and
		preferably also an enzyme stabilizing system
25	0,5 – 20%	of mono- or diols selected from ethanol, isopropanol, ethylene glycol, or propylene
		glycolol
	0,1 – 20%	other adjuncts
	water	to add up to 100%.

30 Solid laundry detergents (like e.g., powders, granules or tablets) according to the present invention are composed of:

	0,05 – 20%	of at least one inventive polymer
	1 – 50%	of surfactants
	0,1 – 80%	of builders, cobuilders and/or chelating agents
35	0-50%	fillers
	0 – 40%	bleach actives
	0,1 – 30%	other adjuncts and/or water
	wherein the sum of the ingredients adds up 100%.	

Preferred solid laundry detergents according to the present invention are composed of:

- 0,2 – 6% of at least one inventive polymer
- 5 – 30% of anionic surfactants selected from C10-C15- LAS, C10-C18 alkyl sulfates and C10-C18 alkyl ether sulfates containing 1-5 ethoxy-units
- 5 1,5 – 7,5% of non-ionic surfactants selected from C10-C18-alkyl ethoxylates containing 3 – 10 ethoxy-units
- 5 – 50% of inorganic builders selected from sodium carbonate, sodium bicarbonate, zeolites, soluble silicates, sodium sulfate
- 0,5 - 15% of cobuilders selected from C10-C18 fatty acids, di- and tricarboxylic acids, hydroxydi- and hydroxytricarboxylic acids and polycarboxylic acids
- 10 0,1 – 5% of an enzyme system containing at least one enzyme suitable for detergent use and preferably also an enzyme stabilizing system
- 0,1 – 20% other adjuncts
- water to add up to 100%

15

In a preferred embodiment the polymer according to the present invention is used in a manual dish wash detergent.

Liquid manual dish wash detergents according to the present invention are composed of:

- 0,05 – 10% of at least one inventive polymer
- 20 1 – 50% of surfactants
- 0,1 – 50% of other adjuncts
- water to add up 100%.

Preferred liquid manual dish wash detergents according to the present invention are composed of:

- 0,2 – 5% of at least one inventive polymer
- 25 5 – 40% of anionic surfactants selected from C10-C15- LAS, C10-C18 alkyl ether sulfates containing 1-5 ethoxy-units, and C10-C18 alkyl sulfates
- 0 - 10% of Cocamidopropylbetaine
- 0 – 10% of Lauramine oxide
- 0 – 2% of a non-ionic surfactant, preferably a C10-Guerbet alcohol alkoxyate
- 30 0 – 5% of an enzyme, preferably Amylase, and preferably also an enzyme stabilizing system
- 0,5 – 20% of mono- or diols selected from ethanol, isopropanol, ethylenglycol, or propylenglycol
- 0,1 – 20% other adjuncts
- 35 water to add up to 100%

As the polyalkylene imine polymers of the invention are biodegradable, and especially the cleaning formulations typically have a pH of about 7 or higher, and additionally often contain also enzymes - which are included into such cleaning formulations to degrade biodegradable stuff such as grease,

proteins, polysaccharides etc. which are present in the stains and dirt which shall be removed by the cleaning compositions – some consideration is needed to be taken to formulate those bio-degradable polymers of the invention. Such formulations suitable are in principle known, and include the formulation in solids – where the enzymes and the polymers can be separated by coatings or adding them in separate particles which are mixed – and liquids and semi-liquids, where the polymers and the enzymes can be separated by formulating them in different compartments, such as different compartments of multi-chamber-pouches or bottles having different chambers, from which the liquids are poured out at the same time in a predefined amount to assure the application of the right amount per individual point of use of each component from each chamber. Such multi-compartment-pouches and bottles etc. are known to a person of skill as well.

The following table shows general cleaning compositions of certain types, which correspond to typical compositions correlating with typical washing conditions as typically employed in various regions and countries of the world. The at least one inventive polymer may be added to such formulation(s) in suitable amounts as outlined herein.

Table 1: General formula for laundry detergent compositions according to the invention:

Ingredient	Ranges of Ingredient in Liquid frame formulations
Linear alkyl benzene sulphonic acid	0 to 30%
Coco fatty acid	1 to 12%
Fatty alcohol ether sulphate	0 to 25%
NaOH or mono- or triethanolamine	Up to pH 7,5 to 9,0
Alcohol ethoxylate	3 to 10%
1,2-Propylene glycol	1 to 10%
Ethanol	0 to 4%
Sodium citrate	0 to 8%
water	Up to 100%

Table 2: Liquid laundry frame formulations according to the invention:

active						
(numbers:% active)	F1	F2	F3	F4	F5	F6
alcohol ethoxylate 7EO	5.40	10.80	12.40	7.30	1.60	7.60
Coco fatty acid K12-18	2.40	3.10	3.20	3.20	3.50	6.40
Fatty alcohol ether sulphate	5.40	8.80	7.10	7.10	5.40	14.00
Linear alkyl benzene sulphonic acid	5.50	0.00	14.50	15.50	10.70	0.00

active						
1,2 Propane diol	6.00	3.50	8.70	8.70	1.10	7.80
Triethanolamine						
Monoethanolamine			4.00	4.30	0.30	
NaOH	2.20	1.10				1.00
Glycerol		0.80	3.00	2.80		
Ethanol	2.00				0.38	0.39
Na citrate	3.00	2.80	3.40	2.10	7.40	5.40
Inventive Polymer (s) (total) *	0 - 5	0 - 5	0 - 5	0 - 5	0 - 5	0 - 5
Protease	0 - 1	0 - 1	0 - 1	0 - 1	0 - 1	0 - 1
Amylase	0 - 0,5	0 - 0,5	0 - 0,5	0 - 0,5	0 - 0,5	0 - 0,5
Cellulase	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3
Lipase	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2
Mannanase	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2
Pectat Lyase	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3
water	to 100	to 100	to 100	to 100	to 100	to 100

*Without inventive polymer the formulations are comparative examples.

Table 2 - continued: Liquid laundry frame formulations according to the invention:

active								
(numbers:% active)	F7	F8	F9	F10	F11	F12	F13	F14
alcohol ethoxylate 7EO	3.80	0.30	13.30	8.00	5.70	20.00	9.20	29.00
Coco fatty acid K12-18	2.80	3.00	1.70	1.80	2.50	5.00	8.60	10.40
Fatty alcohol ether sulphate	2.80	4.50	3.90	4.10		10.00	22.20	
Linear alkyl benzene sulphon- ic acid	6.30	5.43	11.45	5.90	10.10	10.00	28.00	27.00
1,2 Propane diol	0.50		2.50	0.40	6.00	10.00	7.00	7.00
Triethanolamine				8.10				
Monoethanolamine	0.40	1.80					8.00	7.00
NaOH			2.20		3.30	1.50		
Glycerol		0.60	0.20	1.90			7.00	10.00
Ethanol			1.84					
Na citrate	4.60	3.30	3.30	1.40		1.50		

Inventive Polymer (s) (total)*	0 - 5	0 - 5	0 - 5	0 - 5	0 - 5	0 - 5	0 - 5	0 - 5
Protease	0 - 1	0 - 1	0 - 1	0 - 1	0 - 1	0 - 3	0 - 3	0 - 3
Amylase	0 - 0,5	0 - 0,5	0 - 0,5	0 - 0,5	0 - 0,5	0 - 0,5	0 - 0,5	0 - 0,5
Cellulase	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3
Lipase	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2
Mannanase	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2	0 - 0,2
Pectat Lyase	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3	0 - 0,3
water	to 100	to 100	to 100	to 100	to 100	to 100	to 100	to 100

*Without inventive polymer the formulations are comparative examples.

Table 3: Laundry powder frame formulations according to the invention:

	Bleach free Powder					
Alcohol ethoxylate 7EO	0.6	0	1	0	0	5.2
Coco fatty acid K12-18	1.2	0	0	0	0	0
Fatty alcohol ether sulphate	1.5	0	0	0	0	6
Linear alkyl benzene sulphonic acid	12.1	11.2	13.6	21.9	18.7	12.7
Bleach activator	0	0	0	0	0	0
Percarbonate	0	0	0	0	0	0
AcetateNa	0	0	0	0.1	0	0.1
CitrateNa	0	0	0	0	0	14
Na Silicate	27.9	5.8	6.6	2	15	20.3
Na Carbonate	17.2	35	37.3	30.1	37	1
Na Phosphate	0	0	0	14	0.3	0
Na Hydrogencarbonate	0.7	0.9	0.5	2.7	0.4	10.5
Zeolite4A	4.2	0.1	5.1	10.2	1.8	11.6
HEDP	0	0	0	0	0	0.13
MGDA	0	1.1	0	0	0	0
Cellulase	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5
Lipase	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4
Mannanase	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4
Protease	0 - 1.5	0 - 1.5	0 - 1.5	0 - 1.5	0 - 1.5	0 - 1.5
Amylase	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5
Na Sulfate	30.8	1.3	33	11	22	3

	Bleach free Powder					
Na Chloride	0.2	43	0.1	0	0.1	0.1
optical brightener	0.02	0		0.1	0.06	
Inventive Polymer(s) (total)	1	1	0.2	2	0.5	3

Table 3 - continued: Laundry powder frame formulations according to the invention:

	Bleach containing Powder					
Alcohol ethoxylate 7EO	1.2	5	4	0.5	0.5	0
Coco fatty acid K12-18	0	0	0	0.3	0	0.6
Fatty alcohol ether sulphate	0	3.9	4.4	1.6	0	0
Linear alkyl benzene sulphonic acid	7.6	12.1	11.5	12.2	6.5	10.4
Bleach activator	0.2	9.5	9.5	0.5	0.8	2.2
Percarbonate	3.6	19.4	16.6	2.2	11.5	5.8
AcetateNa	0	6.7	7.1	0.3	1	0.7
CitrateNa	0	1.6	8.2	0.3	0.9	1.7
Na Silicate	3.6	11.3	16.4	10.2	9.1	16.5
Na Carbonate	21.6	8.7	1.4	8	22.9	14.8
Na Phosphate	0	0	0	0	0	0
Na Hydrogencarbonate	0.2	2.8	1.6	0.8	0.5	0.5
Zeolite4A	1.6	1.4	2.4	1.6	1.8	2.3
HEDP	0	0.27	0.16	0	0	0.17
MGDA	0	0	0	0	0	0
Cellulase	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5
Lipase	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4
Mannanase	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4	0 - 0.4
Protease	0 - 1.5	0 - 1.5	0 - 1.5	0 - 1.5	0 - 1.5	0 - 1.5
Amylase	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5	0 - 0.5
Na Sulfate	51	4	6	57	38	37
Na Chloride	1	1	0.5	1.2	0.2	1
optical brightener		0.29	0.1	0.23	0.13	0.19
Inventive Polymer(s) (total)	2.2	9.2	2.2	0.7	1	0.4

Table 4: Liquid manual dish wash frame formulations according to the invention:

Ingredients	MDW.1	MDW.2	MDW.3	MDW.4	MDW.5	MDW.6	MDW.7	MDW.8
Linear C ₁₂ -C ₁₄ -alkyl-benzenesulfonic acid	8	0	6	0	6	0	6	0
C ₁₂ -C ₁₄ -fatty alcohol x 2 EO sulfate	8	16	6	12	6	12	6	12
Cocamidopropyl betaine	0	0	4	4	0	0	2	2
Lauramine oxide	0	0	0	0	4	4	2	2
2-Propylheptanol x 4 EO	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Inventive Polymer (s) (total)	1	1	1	1	1	1	1	1
Ethanol	2	2	2	2	2	2	2	2
2-Phenoxyethanol (pre-servative)	1	1	1	1	1	1	1	1
Sodium chloride	1	1	1	1	1	1	1	1
Demin. water	add 100	add 100	add 100	add 100	add 100	add 100	add 100	add 100
Sodium hydroxide	add pH 8	add pH 8	add pH 8	add pH 8	add pH 8	add pH 8	add pH 8	add pH 8

The following examples shall further illustrate the present invention without restricting the scope of the invention.

The specific embodiments as described throughout this disclosure are encompassed by the present invention as part of this invention; the various further options being disclosed in this present specification as “optional”, “preferred”, “more preferred”, “even more preferred” or “most preferred” (or “preferably” etc.) options of a specific embodiment may be individually and independently (unless such independent selection is not possible by virtue of the nature of that feature or if such independent selection is explicitly excluded) selected and then combined within any of the other embodiments (where other such options and preferences can be also selected individually and independently unless such independent selection is not possible by virtue of the nature of that feature or if such independent selection is explicitly excluded), with each and any and all such possible combinations being included as part of this invention as individual embodiments.

Examples

In the following, "CL/NH" means caprolactone (CL) repeating units per NH-functionality of the (backbone-modified) polyalkylene imine, "EO/NH" means ethylene oxide (EO) repeating units per NH-functionality of the (backbone-modified) polyalkylene imine, "PO/NH" means propylene oxide (PO) repeating units per NH-functionality of the (backbone-modified) polyalkylene imine.

The amount of ϵ -caprolactone, ethylene oxide and propylene oxide added in the below described reactions is calculated based on the determined OH number of the precursor polymer. In the Tables below, the amount of ϵ -caprolactone, ethylene oxide and propylene oxide is recalculated to obtain the equivalents of ϵ -caprolactone, ethylene oxide and propylene oxide added per NH-functionality of the (backbone-modified) hyperbranched poly(ethylene imine) to ensure consistency with the definitions chosen in the claims and throughout this patent application.

Abbreviations used, in particular in the Tables: n.d. = not determined; PDI = polydispersity index; MW = molecular weight as determined by multi-angle light scattering (MALLS or LS); EDA = ethylene diamine; TPTA = tripropylene tetramine; KDA = ketaldiamine according to Formula (II); EI = ethylene imine, A = amine; *hb*PEI = hyperbranched poly(ethylene imine); PDA = 1,3-propylene diamine; HMDA = hexamethylene diamine; CL = ϵ -caprolactone; EO = ethylene oxide; PO = propylene oxide; BO = butylene oxide; EC130 = Baxxodur® EC130 = 4,7,10-Trioxa-tridecane-1,13-diamine (TTD); HP20 = Sokalan® HP20 = ethoxylated PEI; LOM = launder-o-meter.

1) Synthesis examples

a) Synthesis of backbone-modified poly(ethylene imine)s according to the present invention

An overview of the prepared examples can be found in Table 5.

Table 5: Overview of prepared backbone-modified poly(ethylene imine)s

Polymer	Amine (A)	Employed A / EI molar ratio	MW (g/mol, LS)	PDI	Biodegradability (% , 28d, OECD 301F)	Biodegradability (% , 56d, OECD 301F)
Ref.1	EDA	1 / 10	900	1,2	0	n.d.
Ref.2	EDA	1 / 5	500	1,2	0	n.d.
1.1	TPTA	1 / 3	1000	1,2	11	n.d.
1.2	TPTA	1 / 2	1000	1,1	21	n.d.
1.3	KDA	1 / 4	~800	1,3	16	19
1.4	KDA	1 / 3	~600	1,3	23	26
1.5	KDA	1 / 2	<500	1,2	34	40

i) Ring-opening polymerization of ethylene imine in presence of amine A (polymers 1.1-1.5)

The amine is mixed or dissolved in distilled water and placed in the reactor and an equimolar amount of carbon dioxide to the amine (dry ice) are added as catalyst. The reactor mixture is heated

to a temperature of 90 °C after which a 60% aqueous solution of ethylene imine is added over 2 hours using an automated dosimeter. The solid content of the aqueous reaction mixture is targeted to be 50%. After polymerization, a post-reaction of up to two hours at a temperature close to 100 °C is carried out to remove any residual ethylene imine. Residual ethylene imine values were typically <1 ppm. The residual ethylene imine values are analyzed using a solid phase microextraction (SPME) technique. After confirmation of the low residual ethylene imine values, the solvent is distilled off to result in a viscous yellowish product. Typically yields are >90%.

ii) Comparative examples (Ref.1 and Ref.2)

The comparative example is carried out in the exact same manner as described above, while using ethylene diamine as amine A.

iii) Test results of all examples on backbone-modified poly(ethylene imine)s

The use of EDA to prepare commercially available poly(ethylene imine), such as Lupasol® FG (Ref.1, commercially available from BASF SE, Ludwigshafen, Germany) results in a non-biodegradable polymer. A reduction of the molecular weight of the poly(ethylene imine) did not improve the biodegradability. Exchanging EDA with TPTA or KDA however resulted in a novel backbone-modified poly(ethylene imine) with biodegradability values in OECD 301F from 11 to 40% after 28-56 days.

b) Alkoxylation of the backbone-modified poly(ethylene imine)s with a first alkylene oxide

i) Synthesis of KDA/EI 1/4 – 0,9 EO/NH

200 g of KDA/EI 1/4 are charged to a steel pressure reactor. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is then heated to 100 °C and 190 g of ethylene oxide are dosed into the reactor within 4 hours. After that, the reaction mixture is kept at 100 °C for post reaction. Volatile compounds are removed under vacuum and 366 g (94% yield) of a yellow and highly viscous product is isolated from the reactor.

ii) Synthesis of Baxxodur® EC130/EI 1/4 – 0,9 PO/NH

180 g of Baxxodur® EC130/EI 1/4 are charged to a steel pressure reactor. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is then heated to 100 °C and 167 g of propylene oxide are dosed into the reactor within 4 hours. After that, the reaction mixture is kept at 100 °C for post reaction. Volatile compounds are removed under vacuum and 326 g (94% yield) of a yellow and highly viscous product is isolated from the reactor.

iii) Synthesis of TPTA/EI 1/4 – 0,9 EO/NH

200 g of TPTA/EI 1/4 and 20 g distilled water are charged to a steel pressure reactor. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is then heated to 100 °C and 220 g of ethylene oxide are dosed into the reactor within 4 hours. After that, the reaction mixture is kept at 100 °C for post reaction. Volatile compounds are removed under vacuum and 416 g (99% yield) of a dark orange and highly viscous product is isolated from the reactor.

c) Caprolactone-modification of the backbone-modified poly(ethylene imine)s

An overview of the prepared examples can be found in Table 6.

Table 6: Caprolactone-modification of the backbone-modified poly(ethylene imine)s

#	Chemistry	MW (g/mol, LS)	PDI	Biodegradability (%, 28 d, OECD 301F)
Ref.3	hbPEI800 – 2 CL/NH	3.600	1,9	57
Ref.4	hbPEI500 – 2 CL/NH	2.000	2,0	58
2.1	(PDA/EI 1/4,5) - 2 CL/NH	n.d.	2,5	69
2.2	(HMDA/EI 1/5) - 2 CL/NH	n.d.	2,8	66
2.3	(HMDA/EI 1/5) - 3 CL/NH	3.100	1,8	71
2.4	(HMDA/EI 1/4) - 2 CL/NH	2.400	2,0	63
2.5	(HMDA/EI 1/3) - 2 CL/NH	1.700	2,0	62
2.6	(TPTA/EI 1/4) – 2 CL/NH	3.100	1,6	62

5 i) Synthesis of polymers 2.1-2.6

40 g of the backbone-modified poly(ethylene imine) are charged into a four-necked round bottom flask equipped with a cooler and a dripping funnel under nitrogen atmosphere. The product is heated to 80 °C and the respective volume of caprolactone per NH-functionality of the backbone-modified poly(ethylene imine) is added slowly at 80 °C. After caprolactone addition, the temperature is increased slowly to 160 °C and the mixture is allowed to post-react sixteen hours at 160 °C to remove any residual caprolactone. 235 g (90% yield) of a typically light brown, highly viscous liquid were obtained.

ii) Comparative examples (Ref.3 and Ref.4)

The comparative examples were prepared according to the same method as described above, using poly(ethylene imine) with a molecular weight of either 900 g/mol or 500 g/mol (determined by LS).

iii) Test results of all examples on caprolactone-modified backbone-modified poly(ethylene imine)s

The biodegradation of all backbone-modified poly(ethylene imine)s (polymer 2.1-2.6) was increased after 28 days in OECD 301F versus both comparative examples (Ref.3 and Ref.4).

d) Alkoxylation with a second alkylene oxide (AO2)

1) Alkoxylation of intermediate 2 with a second alkoxide

An overview of the prepared examples can be found in Table 7.

Table 7: Alkoxylation of intermediate 2 with a second alkylene oxide

Polymer	Chemistry	MW (g/mol, LS)	PDI	Biodegradability (%, 28 d, OECD 301 F)
Ref.5	Sokalan® HP20	10.200	1,3	<5
Ref.6	<i>hb</i> PEI500 – 0,9 EO/NH – 19,1 EO/NH	5.700	1,5	9
3.1	(TPTA/EI 1/4) – 0,9 EO/NH – 19,1 EO/NH	5.500	1,5	24
3.2	(TPTA/EI 1/3) – 0,9 EO/NH – 19,1 EO/NH	4.300	1,8	25
3.3	(TPTA/EI 1/2) – 0,9 EO/NH – 19,1 EO/NH	4.100	1,7	27

i) Synthesis of polymers 3.1 – 3.3.

100 g of the previously obtained TPTA/EI 1/X – 0,9 EO/NH (as described under section 1b), with X =
 4, 3 or 2) are filled into a steel pressure reactor and 7.5 g of potassium methanolate (32.5 wt% in
 methanol) are added. Methanol is removed at 20 mbar at 80 °C. The reactor is purged with nitrogen
 to remove air and a nitrogen pressure of 2 bar is set. The reactor is heated to 120 °C and 1134 g of
 ethylene oxide are dosed into the reactor within eight hours. The mixture is allowed to post-react for
 six hours at 120 °C to remove any residual ethylene oxide. 1225 g (99% yield) of a light brown, high-
 ly viscous liquid were obtained.

ii) Comparative examples

Sokalan® HP20 (Ref.5) was obtained commercially from BASF SE, while Ref.6 was obtained using
 the same procedure as described above.

iii) Test results of polymer examples 3.1-3.3

The biodegradation of the backbone-modified poly(ethylene imine) samples 3.1-3.3 was significantly
 improved vs. the reference samples

2) Alkoxylation of intermediate 2 with a mixture of an alkoxide and a lactone

An overview of the prepared examples can be found in Table 8.

Table 8: Alkoxylation of intermediate 2 with a mixture of an alkoxide and a lactone

Polymer	Chemistry	MW (g/mol, LS)	PDI	Biodegradability (%, 28 d, OECD 301F)
Ref.7	<i>hb</i> PEI800-0,9 PO/NH - (1CL-mix-20 EO)/NH)	8.500	1,5	30
4.1	(TPTA/EI 1/3) – 0,9 EO/NH – (1CL-mix-20 EO)/NH	4.700	1,6	51
4.2	(TPTA/EI 1/2) – 0,9 PO/NH – (1CL-mix-20 EO)/NH	4.600	1,6	44
4.3	(KDA/EI 1/4) – 0,9 PO/NH – (1CL-mix-20 EO)/NH	4.300	1,8	54
4.4	(EC130 / EI 1 / 4) – 0,9 PO/NH - (1CL-mix-20 EO)/NH	5.800	1,9	53

i) Synthesis of polymer 4.1

1) Synthesis of TPTA/EI 1/3 – 0,9 EO/NH

5 100 g of polymer 1.1 and 10 g distilled water are charged to a steel pressure reactor. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is then heated to 100 °C and 113 g of ethylene oxide are dosed into the reactor within 8 hours. After that, the reaction mixture is kept at 100 °C for post reaction. Volatile compounds are removed under vacuum and 185 g (87% yield) of a dark orange and highly viscous product is isolated from the reactor.

10 2) Synthesis of TPTA/EI 1/3 – 0,9 EO/NH – (1CL-mix-20EO)/NH

100 g of TPTA/EI 1/3 – 0,9 EO/NH are filled into a steel pressure reactor and 7,3 g of potassium methanolate (32,5 wt% in methanol) are added. Methanol is removed at 20 mbar at 80 °C. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is heated to 120 °C and a mixture of 961 g of ethylene oxide and 130 g caprolactone are dosed into the reactor within nineteen hours. The mixture is allowed to post-react for six hours at 120 °C to remove any residual ethylene oxide and caprolactone. 1191 g (100% yield) of a dark orange solid product were obtained.

ii) Synthesis of polymer 4.2

1) Synthesis of TPTA/EI 1/2 – 0,9 PO/NH

20 101 g of polymer 1.2 and 10,1 g distilled water are charged to a steel pressure reactor. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is then heated to 100 °C and 155 g of propylene oxide are dosed into the reactor within 4 hours. After that, the reaction mixture is kept at 100 °C for post reaction. Volatile compounds are removed under vacuum and 230 g (90% yield) of a dark orange and highly viscous product is isolated from the reactor.

2) Synthesis of TPTA/EI 1/2 – 0,9 PO/NH – (1CL-mix-20EO)/NH

100 g of TPTA/EI 1/2 – 0,9 PO/NH are filled into a steel pressure reactor and 7,4 g of potassium methanolate (32,5 wt% in methanol) are added. Methanol is removed at 20 mbar at 80 °C. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is heated to 120 °C and a mixture of 972 g of ethylene oxide and 132 g caprolactone are dosed into the reactor within twelve hours. The mixture is allowed to post-react for six hours at 120 °C to remove any residual ethylene oxide and caprolactone. 1201 g (100% yield) of a dark orange solid product were obtained.

iii) Synthesis of polymer 4.3**1) Synthesis of KDA/EI 1/4 – 0,9 PO/NH**

172 g of polymer 1.3 are charged to a steel pressure reactor. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is then heated to 100 °C and 216 g of propylene oxide are dosed into the reactor within twelve hours. After that, the reaction mixture is kept at 100 °C for post reaction. Volatile compounds are removed under vacuum and 371 g (95% yield) of a yellowish solid product is isolated from the reactor.

2) Synthesis of KDA/EI 1/4 – 0,9 PO/NH – (1CL-mix-20EO)/NH

60 g of KDA/EI 1/4 – 0,9 PO/NH are filled into a steel pressure reactor and 0,5 g of potassium methanolate (100 t%) are added. Methanol is removed at 20 mbar at 80 °C. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is heated to 120 °C and a mixture of 562 g of ethylene oxide and 73 g caprolactone are dosed into the reactor within twelve hours. The mixture is allowed to post-react for six hours at 120 °C to remove any residual ethylene oxide and caprolactone. 674 g (97% yield) of a dark orange solid product were obtained.

iv) Synthesis of polymer 4.4**1) Synthesis of EC130/EI 1/4 – 0,9 PO/NH**

EC130/EI 1/4 – 0,9 PO/NH was prepared as described under section b ii).

2) Synthesis of EC130/EI 1/4 – 0,9 PO/NH – (1CL-mix-20EO)/NH

70 g of EC130/EI 1/4 – 0,9 PO/NH are filled into a steel pressure reactor and 1,5 g of potassium methanolate (100%) are added. Methanol is removed at 20 mbar at 80 °C. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is heated to 120 °C and a mixture of 605 g of ethylene oxide and 83 g caprolactone are dosed into the reactor within eight hours. The mixture is allowed to post-react for six hours at 120 °C to remove any residual ethylene oxide and caprolactone. 749 g (99% yield) of a dark orange solid product were obtained.

v) Comparative example

Ref.7 was prepared using the same procedure as for polymers 4.2-4.4, starting from Lupasol® FG, commercially available from BASF SE, Ludwigshafen, Germany.

vi) Test results on polymers 4.1 – 4.4.

The biodegradation of the backbone-modified poly(ethylene imine) samples 4.1-4.4 was significantly improved vs. the reference sample.

3) Alkoxylation of intermediate 3 with a second alkoxide

5 An overview of the prepared examples can be found in Table 9.

Table 9: Alkoxylation of intermediate 3 with a second alkylene oxide

Polymer	Chemistry	MW (g/mol, LS)	PDI	Biodegradability (%, 28 d, OECD 301 F)
Ref.8	<i>hb</i> PEI800 – 2CL/NH – 19 EO/NH	8.900	2,4	50
Ref.9	<i>hb</i> PEI500 – 2CL/NH – 20 EO/NH	6.400	1,8	48
5.1	(HMDA/EI 1/5) - 2 CL/NH - 17 EO/NH	6.200	2,0	57

i) Synthesis of polymer 5.1.

100 g of polymer 2.2. (prepared as described under section c) are filled into a steel pressure reactor and 2.3 g of potassium methanolate (32.5 wt% in methanol) are added. Methanol is removed at 20 mbar at 80 °C. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is heated to 120 °C and 267 g of ethylene oxide are added into the reactor within five hours. The amount of ethylene oxide added is calculated based on the determined OH number of the educt and is targeted to be 25 EO per OH-functionality of the caprolactone-modified backbone-modified hyperbranched poly(ethylene imine). In Table 9, the amount of ethylene oxide is recalculated to obtain the equivalents of ethylene oxide added per NH-functionality of the backbone-modified hyperbranched poly(ethylene imine). The mixture is allowed to post-react for six hours at 120 °C to remove any residual ethylene oxide. 355 g (99% yield) of a dark brown, viscous liquid were obtained.

ii) Comparative examples

Ref.8 and Ref.9 were prepared via the same procedure as described above, starting from Ref.3 and Ref.4, respectively. Also here, the amount of ethylene oxide added is calculated based on the determined OH number of the precursor polymer and is targeted to be 25 EO per OH-functionality of the caprolactone-modified hyperbranched poly(ethylene imine). In Table 9, the amount of ethylene oxide is recalculated to obtain the equivalents of ethylene oxide added per NH-functionality of the hyperbranched poly(ethylene imine).

iii) Test results of results on polymer 5.1

The biodegradability of polymer 5.1. was significantly improved as compared to Ref.8 and Ref.9.

e) Alkoxylation with a third alkylene oxide (AO3)

An overview of the prepared examples can be found in Table 10.

Table 10: Alkoxylation with a third alkylene oxide

Polymer	Chemistry	Biodegradability (%, 56 d, OECD 301 F)
Ref.10	<i>hb</i> PEI800 – 1,1 BO/NH – 2 CL/NH – 27 EO/NH – 28 PO/NH	57
6.1	(HMDA/EI 1/10) – 1,1 BO/NH - 2 CL/NH – 28 EO/NH – 28 PO/NH	64

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i) Synthesis of polymer 6.1**1) Synthesis of (HMDA/EI 1/10)**

116 g of HMDA are dissolved in 481 distilled water and placed in the reactor. 44 g of carbon dioxide (dry ice) are then added as catalyst. The reactor mixture is heated to a temperature of 90 °C after which 430 g ethylene imine (100%) is added over 2 hours using an automated dosimeter. After polymerization, a post-reaction of one to two hours at a temperature slightly above 100 °C is carried out to remove any residual ethylene imine. Residual ethylene imine values were < 1 ppm. The residual ethylene imine values are analyzed using a solid phase microextraction (SPME) technique. After confirmation of the low residual ethylene imine values, the solvent is distilled off to result in 450 g (99%) of a viscous yellowish product.

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2) Synthesis of (HMDA/EI 1/10) - 1,1 BO/NH

150 g of HMDA/EI 1/10 and 15 g distilled water are charged to a steel pressure reactor. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is then heated to 100 °C and 288 g of butylene oxide are dosed into the reactor within 3 hours. After that, the reaction mixture is kept at 100 °C for post reaction. Volatile compounds are removed under vacuum and 425 g (97% yield) of a yellow, viscous product is isolated from the reactor.

20

3) Synthesis of (HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/NH

120 g of (HMDA/EI 1/10) – 1,1 BO/NH are charged into a four-necked round bottom flask equipped with a cooler and a dripping funnel under nitrogen atmosphere. The product is heated to 80 °C and 215,5 g of ϵ -caprolactone are added slowly at 80 °C. The amount of ϵ -caprolactone added is calculated based on the determined OH number of the educt and is targeted to be 2 CL per OH-functionality of (HMDA/EI 1/10) – 1,1 BO/NH. In Table 10, the amount of ϵ -caprolactone is recalculated to obtain the equivalents of ϵ -caprolactone added per NH-functionality of the backbone-modified hyperbranched poly(ethylene imine). After caprolactone addition, the temperature is in-

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creased slowly to 160 °C and the mixture is allowed to post-react sixteen hours at 160 °C to remove any residual caprolactone. 328 g (98% yield) of a light brown, viscous liquid were obtained.

(HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/NH is equal to (HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/OH.

4) Synthesis of (HMDA/EI 1/10) – 1,1 BO/NH – 1 CL/NH – 17 EO/NH

5 120 g (HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/NH are filled into a steel pressure reactor and 3,3 g of potassium methanolate (32.5 wt% in methanol) are added. Methanol is removed at 20 mbar at 80 °C. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is heated to 120 °C and 420 g of ethylene oxide are dosed into the reactor within seven hours. The amount of ethylene oxide added is calculated based on the determined OH number of
10 the educt and is targeted to be 20 EO per OH-functionality of (HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/NH. In Table 10, the amount of ethylene oxide is recalculated to obtain the equivalents of ethylene oxide added per NH-functionality of the backbone-modified hyperbranched poly(ethylene imine). The mixture is allowed to post-react for six hours at 120 °C to remove any residual ethylene oxide. 536 g (99% yield) of a dark brown, viscous liquid were obtained.

15 (HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/NH – 17 EO/NH is equal to (HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/OH – 20 EO/OH.

5) Synthesis of (HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/NH – 28 EO/NH – 28 PO/NH

150 g (HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/NH – 17 EO/NH are filled into a steel pressure reactor and 2,3 g of potassium methanolate (32.5 wt% in methanol) are added. Methanol is removed at 20
20 mbar at 80 °C. The reactor is purged with nitrogen to remove air and a nitrogen pressure of 2 bar is set. The reactor is heated to 130 °C and 74 g of ethylene oxide are dosed into the reactor within one hour. The mixture is allowed to post-react for three hours at 130 °C to remove any residual ethylene oxide. Then, 294 g of propylene oxide are dosed into the reactor within six hours. The mixture is allowed to post-react for six hours at 130 °C to remove any residual propylene oxide. The amount of
25 ethylene oxide and propylene oxide added is calculated based on the determined OH number of the educt and is targeted to be 30 EO and 30 PO, respectively, per OH-functionality of (HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/OH – 20 EO/OH. In Table 10, the amount of ethylene oxide and propylene oxide is recalculated to obtain the equivalents of ethylene oxide and propylene oxide added per NH-functionality of the backbone-modified hyperbranched poly(ethylene imine). 518 g (100% yield) of a
30 dark orange, viscous liquid were obtained.

(HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/NH – 28 EO/NH – 28 PO/NH is equal to (HMDA/EI 1/10) – 1,1 BO/NH – 2 CL/OH – 30 EO/OH – 30 PO/OH.

ii) Comparative example

Ref.10 was prepared via the same procedure as described above (steps 1 to 5), however starting
35 from Lupasol® FG, commercially available from BASF SE, Ludwigshafen, Germany. Also here, the amount of ε-caprolactone, ethylene oxide and propylene oxide added is calculated based on the determined OH number of the precursor polymer and is targeted to be 2 CL, 30 EO and 30 PO per

OH-functionality of the respective precursor. In Table 10, the amount of ϵ -caprolactone, ethylene oxide and propylene oxide is recalculated to obtain the equivalents of ϵ -caprolactone, ethylene oxide and propylene oxide added per NH-functionality of the hyperbranched poly(ethylene imine). Herein, *hbPEI*800 – 1,1 BO/NH – 2 CL/NH – 27 EO/NH – 28 PO/NH is equal to *hbPEI*800 – 1,1 BO/NH – 2 CL/OH – 30 EO/OH – 30 PO/OH.

iii) Test results of results on polymer 6.1

The biodegradability of polymer 6.1. was significantly improved as compared to Ref.10.

2) Characterization of the inventive polymers and the comparative examples

The identity of the obtained inventive polymers was confirmed by ¹H- and ¹³C-NMR spectroscopy in deuterated methanol. ¹H-NMR spectra are recorded with a Bruker AV-401 instrument at room temperature. ¹³C-NMR spectra are recorded with a Bruker AV-401 instrument at room temperature. Molecular weights of the inventive polymers and the comparative examples may be determined by gel permeation chromatography (GPC). The measurements may be carried on a combination of two columns (styrene-divinylbenzene and polyester copolymer, both 25 cm in length and 4,6 mm in diameter), using 0.05 wt% potassium trifluoroacetate in hexafluoroisopropanol as eluent. The molecular weights may be obtained by using an RI detector and PEO standards (Polymer Laboratories/Agilent, USA) for calibration. In addition, the absolute molar mass may be determined by multi angle light scattering (MALLS).

OH numbers of the inventive polymers and their intermediates were determined according to a BASF internal procedure in alignment with the respective ISO standard.

Amine numbers were determined according to the method described in DIN 16945.

3) Biodegradation data

Biodegradation in wastewater was tested in triplicate using the OECD 301F manometric respirometry method. OECD 301F is an aerobic test that measures biodegradation of a sample by measuring the consumption of oxygen. To a measured volume of medium, 100 mg/L test substance, which is the nominal sole source of carbon is added along with the inoculum (30 mg/L, aerated sludge taken from Mannheim wastewater treatment plant). This is stirred in a closed flask at a constant temperature (20°C or 25°C) for 28 or 56 days, respectively. The consumption of oxygen is determined by measuring the change in pressure in the apparatus using an OxiTop® C (Xylem 35 Analytics Germany Sales GmbH & Co KG). Evolved carbon dioxide is absorbed in a solution of sodium hydroxide. Nitrification inhibitors are added to the flask to prevent usage of oxygen due to nitrification. The amount of oxygen taken up by the microbial population during biodegradation of the test substance (corrected for uptake by blank inoculum, run in parallel) is expressed as a percentage of ThOD (Theoretical oxygen demand, which is measured by the elemental analysis of the compound). A positive control Glucose/Glucosamine is run along with the test samples for each cabinet.

4) Application experiments

Table 11 shows the base liquid laundry detergent w/o any polymer (LLD.1) that has been used to carry out the application tests to determine the impact of the inventive polymers on the primary cleaning performance.

5

Table 11. Composition of the base liquid laundry detergent.

Ingredients	LLD.1 *
Linear C ₁₂ C ₁₄ -alkylbenzenesulfonic acid	5.50
C ₁₂ -fatty alcohol x 2 EO sulfate	5.40
C ₁₂ C ₁₅ -fatty alcohol x 7 EO	5.40
Coconut C12-C18 fatty acid	2.40
Sodium hydroxide	2.20
1,2-Propylene glycol	6.00
Ethanol	2.00
Sodium citrate	3.00
Demin. water	add 100
pH value	8.5

*) All data are wt% active ingredient, independent of the respective product form.

Primary cleaning performance on particulate stains

- 10 To determine the primary detergency, the cleaning performance on 4 different particulate stains on a polyester fabric (CFT, Vlaardingen, The Netherlands) was measured by determining the color difference (delta E) between the stains after wash and the unsoiled white fabric using a reflectometer (Mach5 plus, a multi area color measurement instrument from ColourConsult). Each experiment containing the 4 different circular particulate stains (Clay ground soil, Standard clay, Red pottery
- 15 clay, Tennis court clay; All 4 stains on one polyester fabric, 2 of those fabrics per wash) was repeated 3 times, and the obtained data was used to calculate the average delta E value.
- By using these delta E values, the so-called "standardized cleaning performance" (delta delta E) has been calculated for each individual stain. The "standardized cleaning performance" (delta delta E) is the difference of the performance of the laundry detergent including the inventive modified hyper-
- 20 branched alkoxyated polyalkylene imine or the comparative polymer, respectively, vs. the laundry detergent w/o any modified hyperbranched alkoxyated polyalkylene imine or comparative polymer, respectively.

- Table 12 shows the washing test conditions and Table 3 summarizes the obtained standardized cleaning performance. The standardized cleaning performance shown in Table 13 is the sum of the
- 25 standardized cleaning performance of all 4 stains. The bigger the sum of the delta delta E value, the bigger the positive contribution of the inventive modified hyperbranched alkoxyated polyalkylene imine or the comparative polymer, respectively, vs. the laundry detergent w/o any modified hyper-

branched alkoxyated polyalkylene imine or comparative polymer, respectively, on the cleaning performance.

Table 12. Washing conditions for evaluation of primary cleaning performance on particulate stains.

Washing conditions	
Device	Launder-O-Meter from SDL Atlas, Rock Hill, USA
Washing liquor	250 mL
Washing time	30 minutes
Washing temperature	30 °C
Detergent concentration	3.0 g/L
Water hardness (Ca:Mg:HCO ₃)	1.2 mmol/L (4:1:8) (7 °dH)
Fabric to liquor ratio	1:10
Modified hyperbranched alkoxyated poly-alkylene imine or comparative polymer, respectively	3% by weight (vs. liquid laundry detergent) of the polymer, 100% active ingredient
Test fabric *	4 different circular particulate stains (P-H018, P-H115, P-H144, P-H145) (CFT, Vlaardingen, The Netherlands) on one polyester fabric; 2 stained fabrics per wash
Ballast fabric	2.5 g SBL 2004 (Soil Ballast Fabric 'Formula 2004' that simulates sebum grease stains; WFK Testgewebe GmbH, Brueggen, Germany); + additional white cotton ballast

- 5 *) After the washing experiment, the test fabrics were rinsed with tap water followed by drying at ambient room temperature overnight, prior to the measurement with the Mach5 plus.

Table 13. Results from washing tests (primary cleaning performance on particulate stains).

Detergent	Polymer	Concentration of polymeric additive *	Standardized cleaning performance (sum delta delta E)
LLD.1	3.1	3 wt%	14.4
LLD.1	3.2	3 wt%	16.9
LLD.1	3.3	3 wt%	10.8
LLD.1	4.1	3 wt%	13.5
LLD.1	4.2	3 wt%	11.6
LLD.1	4.3	3 wt%	10.6
LLD.1	4.4	3 wt%	11.3

Detergent	Polymer	Concentration of poly- meric additive *	Standardized cleaning performance (sum delta delta E)
LLD.1	5.1	3 wt%	11.5
LLD.1	Ref.5	3 wt%	12.8
LLD.1	Ref.6	3 wt%	10.4
LLD.1	Ref.7	3 wt%	11.4
LLD.1	Ref.8	3 wt%	9.7
LLD.1	Ref.9	3 wt%	12.1

*) All data are wt% active ingredient, independent of the respective product form.

Test results:

The error of the measurement is +/- 2 delta delta E units. Therefore, any value >2 (sum delta delta E) means that the respective polymer exhibits a directional and visible contribution to the overall cleaning performance of the respective detergent formulation; Any value >4 (sum delta delta E) means that the respective polymer exhibits even a significant contribution to the overall cleaning performance, i.e., the respective polymer leads to a significant improvement of the formulation. All polymers (inventive and comparative) exhibit significant cleaning benefits on particulate stains.

The wash performance of the backbone-modified poly(ethylene imine) samples 3.1-3.3, 4.1-4.4 and 5.1 was comparable to Sokalan® HP20 (Ref.5), considering the error of the measurement.

Primary cleaning performance on oily/fatty stains

To determine the primary detergency, the cleaning performance on 16 different oily/fatty stains on cotton, polycotton and polyester fabrics (CFT, Vlaardingen, The Netherlands) was measured by determining the color difference (delta E) between the stains after wash and the unsoiled white fabric using a reflectometer (Mach5 plus, a multi area color measurement instrument from ColourConsult). Each experiment containing the 16 different circular oily/fatty stains (Lipstick, Make-Up, Beef Fat, Frying Fat, Burnt Butter, Palm Oil, Sebum BEY, Sebum Tefo, Collar Stain; All on different fabrics) was repeated 6 times, and the obtained data was used to calculate the average delta E value. By using these delta E values, the so-called "standardized cleaning performance" (delta delta E) has been calculated for each individual stain. The "standardized cleaning performance" (delta delta E) is the difference of the performance of the laundry detergent including the inventive modified hyperbranched alkoxyated polyalkylene imine or the comparative polymer, respectively, vs. the laundry detergent w/o any modified hyperbranched alkoxyated polyalkylene imine or comparative polymer, respectively.

Table 14 shows the washing test conditions and Table 5 summarizes the obtained standardized cleaning performance. The standardized cleaning performance shown in Table 5 is the sum of the standardized cleaning performance of all 16 stains. The bigger the sum of the delta delta E value, the bigger the positive contribution of the inventive modified hyperbranched alkoxyated polyalkylene

imine or the comparative polymer, respectively, vs. the laundry detergent w/o any modified hyper-branched alkoxyated polyalkylene imine or comparative polymer, respectively, on the cleaning performance.

5 Table 14. Washing conditions for evaluation of primary cleaning performance on oily/fatty stains.

Washing conditions	
Device	Laundry-O-Meter from SDL Atlas, Rock Hill, USA
Washing liquor	250 mL
Washing time	60 minutes
Washing temperature	30 °C
Detergent concentration	3.0 g/L
Water hardness (Ca:Mg:HCO3)	2.5 mmol/L (4:1:8) (14 °dH)
Fabric to liquor ratio	1:10
Modified hyperbranched alkoxyat- ed polyalkylene imine or compara- tive polymer, respectively	2.83% by weight (vs. liquid laundry detergent) of the poly- mer, 100% active ingredient
Test fabric *	16 different circular oily/fatty stains (KC-H122, KC-H176, KC-H015, KC-H187, PC-H082, PC-H212, PC-H210, PC- H252, P-H122, P-H129, P-H015, P-H187, P-H082, P-H212, P-H210, P-H252) (CFT, Vlaardingen, The Netherlands)
Ballast fabric	Polyester and cotton ballast, to yield a 1:1 ratio of polyes- ter/cotton fabric per experiment

*) After the washing experiment, the test fabrics were rinsed with 14 °dH water (2 times), followed by drying at ambient room temperature overnight, prior to the measurement with the Mach5 plus.

Table 15. Results from washing tests (primary cleaning performance on oily/fatty stains).

Detergent	Polymer	Concentration of poly- meric additive *	Standardized cleaning performance (sum delta delta E)
LLD.1	6.1	2.83 wt%	66.7
LLD.1	Ref.10	2.83 wt%	60.8

10 *) All data are wt% active ingredient, independent of the respective product form.

Test results:

The error of the measurement is +/- 10 delta delta E units. Therefore, any value >10 (sum delta delta E) means that the respective polymer exhibits a directional and visible contribution to the overall cleaning performance of the respective detergent formulation; Any value >20 (sum delta delta E) means that the respective polymer exhibits even a significant contribution to the overall cleaning

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performance, i.e., the respective polymer leads to a significant improvement of the formulation. All polymers (inventive and comparative) exhibit significant cleaning benefits on oily/fatty stains.

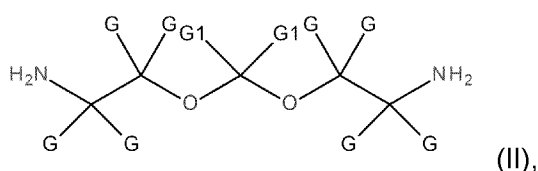
The wash performance of the backbone-modified poly(ethylene imine) sample 6.1 was comparable to the reference sample Ref.10 with lower biodegradability, considering the error of the measure-

5 ment.

Claims

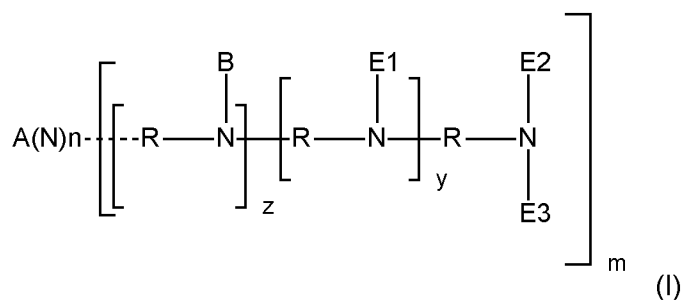
1. A modified hyperbranched alkoxyated polyalkylene imine obtainable by a process comprising the following steps:
- a) reaction of (i) at least one amine (A) with (ii) at least one alkylene imine to obtain a first intermediate (I1), wherein the amine (A) comprises at least one carbon atom more than the imine,
- b) optionally reaction of the first intermediate (I1) with at least one first alkylene oxide (AO1), wherein at least 0.5 mol of first alkylene oxide (AO1) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain second intermediate (I2),
- c) optionally reaction of the first intermediate (I1) or the second intermediate (I2) with at least one first lactone (LA1) and/or at least one first hydroxy carbon acid (HA1), wherein 0.25 to 10 mol of first lactone (LA1) and/or first hydroxy carbon acid (HA1) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain third intermediate (I3)
- d) reaction of the first (I1), second (I2) or third intermediate (I3) (i) with at least one second alkylene oxide (AO2) or (ii) with a mixture of 1) at least one second alkylene oxide (AO2) with 2) at least one second lactone (LA2) and/or at least one second hydroxy carbon acid (HA2), wherein at least 5.0 mol of second alkylene oxide (AO2) and for the mixture additionally at least 1.0 mol of second lactone (LA2) and/or second hydroxy carbon acid (HA2) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain a fourth intermediate (I4),
- e) optionally reaction of the fourth intermediate (I4) (i) with at least one third alkylene oxide (AO3) or (ii) with a mixture of 1) at least one third alkylene oxide (AO3) with 2) at least one third lactone (LA3) and/or at least one third hydroxy carbon acid (HA3), wherein at least 5.0 mol of third alkylene oxide (AO3) and for the mixture additionally at least 1.0 mol of third lactone (LA3) and/or third hydroxy carbon acid (HA3) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain a fifth intermediate (I5),
- f) optionally reaction of the fifth intermediate (I5) or fourth intermediate (I4) with at least one fourth lactone (LA4) and/or at least one fourth hydroxy carbon acid (HA4), wherein at least 1.0 mol of fourth lactone (LA4) and/or fourth hydroxy carbon acid (HA4) is employed per mol of NH-functionality of first intermediate (I1), in order to obtain a sixth intermediate (I6),
- g) optionally reaction of the fourth intermediate (I4), fifth intermediate (I5) or sixth intermediate (I6) with at least one C1-C18 alkylation or esterification reagent,
- in order to obtain the modified hyperbranched alkoxyated polyalkylene imine.
2. The modified hyperbranched alkoxyated polyalkylene imine according to claim 1, wherein the at least one amine (A)

- (i) has 1, 2, 3 or 4 amino groups, preferably 2, 3 or 4 amino groups;
- (ii) has at least three carbon atoms, preferably 3 to 12 carbon atoms, more preferably 3 to 9 carbon atoms;
- (iii) comprises at least one primary and/or at least one secondary amino group, preferably at least two primary amino groups; and/or
- (iv) is selected from the group consisting of propylenediamine (PDA), tetramethylenediamine (TMDA), pentamethylenediamine (PMDA), hexamethylenediamine (HMDA), heptamethylenediamine, octamethylenediamine (OMDA), dipropylene-triamine (DPTA), tripropylene-tetramine (TPTA), 4,7,10-Trioxa-tridecane-1,13-diamine (TTD), 4,9-Dioxado-decane-1,12-diamine (DODA), Poly-(propylenglykol)-bis-(2-aminopropylether), oligo or poly(alkylene glycol) di- and triamines and a compound as defined according to formula (II)



wherein G represents identical or different alkyl groups or H, preferably H, a methyl or ethyl group, more preferably all G are H and G1 represents identical or different alkyl groups or H, preferably both G1 are methyl groups.

3. The modified hyperbranched alkoxyated polyalkylene imine according to claim 1 or 2, wherein the at least one alkylene imine is ethylene imine or propylene imine, preferably ethylene imine.
4. The modified hyperbranched alkoxyated polyalkylene imine according to any of claims 1 to 3, wherein the alkylene oxides AO1 to AO3 are independently of each other selected from the group consisting of C₂-C₁₂-alkylene oxides, preferably ethylene oxide, propylene oxide and butylene oxide.
5. The modified hyperbranched alkoxyated polyalkylene imine according to any of claims 1 to 4, wherein said modified hyperbranched alkoxyated polyalkylene imine is defined according to general formula (I)



wherein the variables are defined as follows:

R represents identical or different, linear or branched C₂-C₁₂-alkylene radicals, preferably C₂- or C₃-alkylene radicals;

5 y is an integer having a value in the range of 0 to 150, preferably of 0 to 10;

z is an integer having a value in the range of 0 to 150, preferably of 0 to 10;

10 A is the amine comprising n NH-functionalities, wherein n is an integer between 1 to 8, preferably 3 to 8, wherein the dotted line indicates the bond between the NH-functionalities and the structure in brackets of Formula (I) and wherein m indicates the total number of polyalkylene imine side chains attached to the amine, with the proviso that $m \leq n$;

15 B represents a continuation of the polyalkylene imine by branching;

E1-3 represent independent of each other

i) -(R1-O)_p-H, wherein p is an integer having a value of 1 to 150, preferably 15 to 90; or

20 ii) any mixture of -(R1-O)- and -(C(O)-R2-O)-, wherein total number of -(R1-O)- is an integer having a value of 1 to 150 and of -(C(O)-R2-O)- is an integer having a value of 1 to 10, arranged in any order and having a terminal -H, wherein R1 represents identical or different, linear or branched C₂-C₁₂-alkylene radicals, preferably C₂-, C₃ or C₄-alkylene radicals and R2 represents identical or different, linear or branched C₂-C₁₀-alkylene radicals, preferably linear or branched C₂-C₅-alkylene radicals;

6. The modified hyperbranched alkoxyated polyalkylene imine according to claim 5, wherein the total number of -(R1-O)- is an integer having a value of 5 to 120, preferably 20 to 90; and/or
30 the total number of -(C(O)-R2-O)- is an integer having a value of 2, 3, 4, 5, 6, 7 or 8.

7. The modified hyperbranched alkoxyated polyalkylene imine according to any of claims 1 to 6, wherein

35 i) steps b) for AO1 between 0,5 and 1,2 per mol NH-functionality in I1, c) (ii), d) (ii) and/or e) are carried out as a one-step reaction, optionally in the presence of water and/or a catalyst, and/or

ii) steps b) for AO1 larger than 1,2 per mol NH-functionality in I1, and/or d) (i), in case steps b) and c) are absent, are carried out as a two-step reaction, wherein the first step

is carried out optionally in the presence of water and the second step is carried out without any water, but in the presence of a catalyst, and/or

- 5 iii) the weight average molecular weight (Mw) of the first intermediate (I1) lies in the range of 50 to 10 000 g/mol, preferably in the range of 150 to 5 000 g/mol, more preferably in the range of 200 to 2500 g/mol.
- 10 8. The modified hyperbranched alkoxyated polyalkylene imine according to any one of claims 1 to 7, wherein up to 100% of the nitrogen atoms present in the modified hyperbranched alkoxyated polyalkylene imine are further quaternized, preferably the degree of quaternization of the nitrogen atoms present in the modified hyperbranched alkoxyated polyalkylene imine lies in the range of 5% to 95%.
- 15 9. The modified hyperbranched alkoxyated polyalkylene imine according to any of claims 1 to 8, wherein
- 20 i) in steps b), d) and/or e)) the alkylene oxide (AO1, AO2 and/or AO3,) is independent of each other at least one C₂-C₁₂-epoxide, preferably ethylene oxide and/or propylene oxide and/or butylene oxide, and/or
- ii) in steps c), d), e) and/or f) the lactone (LA1, LA2, LA3 and/or LA4) is independent of each other caprolactone, γ - or δ -valerolactone, or lactide, and/or
- iii) in steps c), d), e) and/or f) the hydroxy carbon acid (HA1, HA2, HA3 and/or HA4) is independent of each other lactic acid or glycolic acid.
- 25 10. The modified hyperbranched alkoxyated polyalkylene imine according to any of claims 1 to 9, wherein
- 30 i) in steps b), d) and/or e) in total 5 to 100 mol, preferably 10 to 80 mol, more preferably 12 to 60 mol, most preferably 15 to 40 mol of alkylene oxide (AO1, AO2 and/or AO3) is employed per mol of NH-functionality of first intermediate (I1), wherein more than 70 mol%, preferably more than 90 mol% of the alkylene oxide is based on ethylene oxide, and/or
- 35 ii) in steps c), d), e) and/or f) in total 1 to 10 mol, preferably 1 to 6 mol, more preferably 2 to 5 mol of lactone (LA1, LA2, LA3 and/or LA4) and/or 1 to 20 mol, preferably 2 to 15 mol, more preferably 3 to 10 mol of hydroxy carbon acid (HA1, HA2, HA3 and/or HA4) is employed per mol of NH-functionality of first intermediate (I1).

11. The modified hyperbranched alkoxyated polyalkylene imine according to any of claims 1 to 9, wherein
- 5 i) in steps b), d) and/or e) in total 25 to 120 mol, preferably 30 to 110 mol, more preferably 35 to 100 mol, most preferably 40 to 90 mol of alkylene oxide (AO1, AO2 and/or AO3) is employed per mol of NH-functionality of first intermediate (I1), whereas less than 70 mol%, preferably less than 60 mol% of the alkylene oxide is based on ethylene oxide, and/or
- 10 ii) in steps c), d), e) and/or f) in total 1 to 10 mol, preferably 2 to 8 mol, more preferably 3 to 7 mol of lactone (LA1, LA2, LA3 and/or LA4) and/or 1 to 20 mol, preferably 2 to 15 mol, more preferably 3 to 10 mol of hydroxy carbon acid (HA1, HA2, HA3 and/or HA4) is employed per mol of NH-functionality of first intermediate (I1).
12. The modified hyperbranched alkoxyated polyalkylene imine according to any of claims 1 to 11, wherein
- 15 i) in steps b), d) and/or e) the alkylene oxide (AO1, AO2 and/or AO3) is ethylene oxide and/or propylene oxide and/or butylene oxide and/or
- ii) in steps c), d), e) and/or f) the lactone (LA1, LA2, LA3 and/or LA4) is in at least one step caprolactone.
- 20 13. The modified hyperbranched alkoxyated polyalkylene imine according to any of claims 1 to 12, wherein
- (1) in step a) the amine (A) is TPTA and the alkylene imine is ethylene imine reacted in a 1:4 molar ratio; and
- 25 in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- (2) in step a) the amine (A) is TPTA and the alkylene imine is ethylene imine reacted in a 1:3 molar ratio; and
- in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- 30 (3) in step a) the amine (A) is TPTA and the alkylene imine is ethylene imine reacted in a 1:2 molar ratio; and
- in d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- 35 (4) in step a) the amine (A) is TPTA and the alkylene imine is ethylene imine reacted in a 1:4 molar ratio;
- in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
- in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or

- (5) in step a) the amine (A) is PDA and the alkylene imine is ethylene imine reacted in a 1:4.5 molar ratio;
in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
5 in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- (6) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:10 molar ratio;
in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
10 in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- (7) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:5 molar ratio;
15 in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- (8) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:5 molar ratio;
20 in step c) at least 3 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- (9) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:4 molar ratio;
25 in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
30
- (10) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:3 molar ratio;
in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
35 in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
- (11) in step a) the amine (A) is HMDA and the alkylene imine is ethylene imine reacted in a 1:10 molar ratio;

- in step b) at least 1.1 mol of butylene oxide is employed per mol of NH-functionality of first intermediate (I1); and
in step c) at least 2 mol of caprolactone is employed per mol of NH-functionality of first intermediate (I1); and
5 in step d) at least 15 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); and
in step e) at least 15 mol of propylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
(12) in step a) the amine (A) is the compound of formula (II), wherein all G are H and both
10 G1 are methyl groups and the alkylene imine is ethylene imine reacted in a 1:4 molar ratio; and
in step d) at least 10 mol of ethylene oxide is employed per mol of NH-functionality of first intermediate (I1); or
(13) in step a) the amine (A) is the compound of formula (II), wherein all G are H and both
15 G1 are methyl groups and the alkylene imine is ethylene imine reacted in a 1:4 molar ratio; and
in step b) at least 0.9 mol of propylene oxide is employed per mol of NH-functionality of first intermediate (I1);
in step d) a mixture of at least 10 mol of ethylene oxide and at least 1 mol of capro-
20 lactone is employed per mol of NH-functionality of first intermediate (I1).
14. The modified hyperbranched alkoxyated polyalkylene imine according to any of claims 1 to 13, wherein said modified hyperbranched alkoxyated polyalkylene imine demonstrates at
25 least 20%, preferably at least 40% or more preferably at least 60% biodegradability according to standard OECD 301F within 56 days, preferably within 28 days.
15. A process to prepare a modified hyperbranched alkoxyated polyalkylene imine according to any one of claims 1 to 14 comprising carrying out the process steps according to any one of
30 claims 1 to 14.
16. A compound that is the first intermediate (I1) according to claim 1, step a).
17. Use of the modified hyperbranched alkoxyated polyalkylene imine according to any one of
35 claims 1 to 14 in cleaning compositions, in fabric and home care products, in cosmetic formulations, as crude oil emulsion breaker, in pigment dispersions for ink jet inks, in formulations for electro plating, in cementitious compositions, as dispersant for agrochemical formulations and/or as an additive for the papermaking industry, for example for acceleration of dewatering,

elimination of contraries and/or neutralization of charge, and for paper coating as a multifunctional additive.

18. The use according to claim 17 in cleaning compositions and/or in fabric and home care products, preferably in cleaning compositions for

- i) clay removal, and/or
- ii) improved removal of oily/fatty stains, and/or
- iii) soil removal of particulate stains, and/or
- iv) dispersion and/or emulsification of soils, and/or
- v) modification of treated surface to improve removal upon later re-soiling, and/or
- vi) whiteness improvement and/or
- vii) – when at least one enzyme selected from the list consisting of lipases, hydrolases, amylases, DNases, proteases, cellulases, hemicellulases, phospholipases, esterases, mannanases, xylanases, dispersins, oxidoreductases, cutinases, pectate lyases, pectinases, lactases and peroxidases, and combinations of at least two of the foregoing types, preferably selected from one or more lipases, hydrolases, amylases, proteases, cellulases, and combinations of at least two of the foregoing types, more preferably at least one enzyme being selected from proteases, is present – additionally for improvement of removal of oily/fatty stains, food stain removal and/or removal of complex stains,

most preferably in cleaning compositions for

- i) clay removal and/or ii) removal of oily/fatty stains,

each of the before mentioned options i) to vii) preferably for use in a laundry detergent formulation and/or a manual dish wash detergent formulation and/or in a formulation suitable for (pre)-treatment of textiles and/or soap bars, more preferably in a liquid laundry detergent formulation and/or a liquid manual dish wash detergent formulation.

19. Use of a compound that is the first intermediate (I1) according to claim 1, step a), in solid automatic dish wash compositions, for preventing the corrosion of glass.
20. Cleaning composition, fabric and home care product, industrial and institutional cleaning product, cosmetic formulation, crude oil emulsion breaker, pigment dispersion for ink jet inks, formulation for electro plating, cementitious composition, dispersant for agrochemical formulations, papermaking solutions and/or paper coatings, comprising at least one modified hyperbranched alkoxylated polyalkylene imine according to any of claims 1 to 14,

preferably cleaning composition and/or fabric and home care product and/or industrial and institutional cleaning product, comprising at least one modified hyperbranched alkoxyated polyalkylene imine according to any of claims 1 to 14.

- 5 21. Cleaning composition according to claim 20 in a liquid laundry detergent formulation and/or a liquid manual dish wash detergent formulation comprising
- 10 a) the at least one modified hyperbranched alkoxyated polyalkylene imine according to any of claims 1 to 14;
- b) at least one anionic surfactant; and
- c) water.
22. Cleaning composition in a solid automatic dish wash formulation comprising
- 15 a) a compound that is the first intermediate (I1) according to claim 1, step a), and
- b) at least one chelating agent selected from methylglycinediaceticacid (MGDA), glutamic acid diacetate (GLDA), citric acid and salts thereof.
23. Cleaning compositions according to (a) claim 20 or 21 or (b) claim 22 comprising additionally at least one enzyme selected from the list consisting of lipases, hydrolases, amylases, DNases, proteases, cellulases, hemicellulases, phospholipases, esterases, mannanases, xy-
- 20 lanases, dispersins, oxidoreductases, cutinases, pectate lyases, pectinases, lactases and peroxidases, and combinations of at least two of the foregoing types, preferably selected from one or more lipases, hydrolases, amylases, proteases, cellulases, and combinations of at least two of the foregoing types, more preferably at least one enzyme being selected from proteases.
- 25 24. The composition according to any one of claims 20 to 23(a) or claim 22 or 23(b) further comprising an antimicrobial agent selected from the group consisting of 2-phenoxyethanol and 4,4'-dichoro 2-hydroxydiphenylether; preferably comprising 2-phenoxyethanol in an amount ranging from 2ppm to 5% by weight of the composition; more preferably comprising 0.1 to 2% of phenoxyethanol or preferably comprising 4,4'-dichoro 2-hydroxydiphenylether in a concentration from 0.001 to 3%, more preferably 0.002 to 1%, even more preferably 0.01 to 0.6%, each by weight of the composition.
- 30

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/053495**A. CLASSIFICATION OF SUBJECT MATTER****INV.** C08G73/02 C08G63/664 C08G63/685 C08G65/26 C11D3/37
C11D11/00**ADD.**

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)

C08G C11D C09J

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	WO 2022/136408 A1 (BASF SE [DE]) 30 June 2022 (2022-06-30) page 57, table 6, ex. 8, 11; claim 2; page 14, lines 6-10; page 52, table 4, ex. 8, 11; pages 22-24, section: description of cleaning compositions; page 54, table 5, ex. 8, 11 -----	1-24



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"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

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"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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2024/053495

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WO 2022136408 A1	30-06-2022	CN 116348524 A	27-06-2023
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