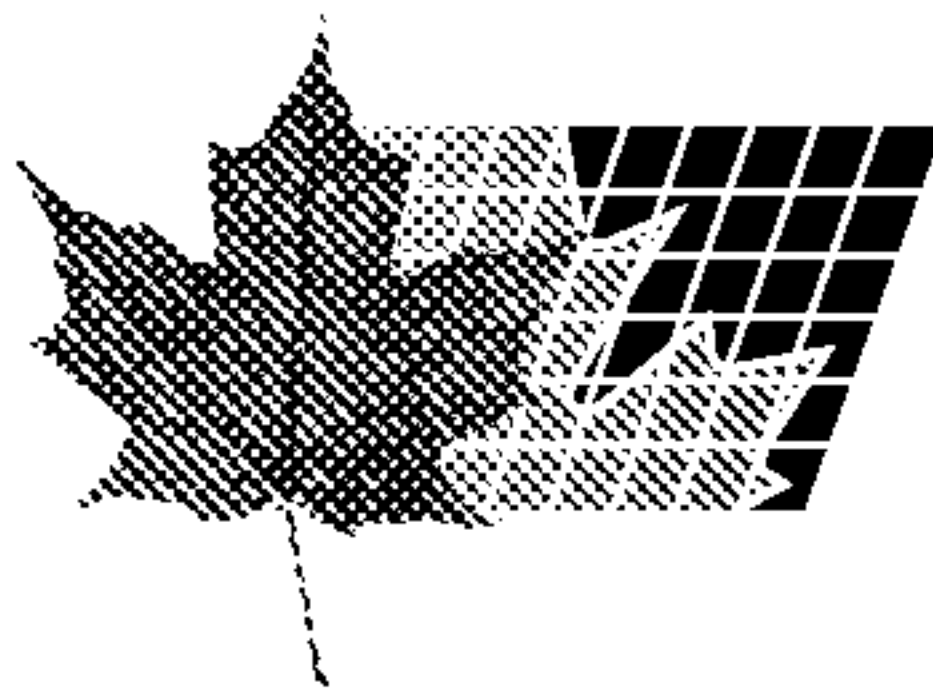




- (72) SMETS, JOHAN, BE
(72) BETTIOL, JEAN-LUC PHILIPPE, BE
(72) LAUDAMIEL, CHRISTOPHE, BE
(72) BOYER, STANTON LANE, US
(72) BAECK, ANDRE CESAR, BE
(72) HERBOTS, IVAN MAURICE ALFONS JAN, BE
(71) THE PROCTER & GAMBLE COMPANY, US
(51) Int.Cl.⁶ C12N 9/42, C11D 3/386, D06M 16/00
(54) **COMPOSITIONS DE DETERGENTS POUR LESSIVE ET/OU
POUR LE SOIN DES TISSUS COMPRENANT DES
COMPOSANTS CHIMIQUES LIES A UN DOMAINE DE
LIAISON DE LA CELLULOSE**
(54) **LAUNDRY DETERGENT AND/OR FABRIC CARE
COMPOSITIONS COMPRISING CHEMICAL COMPONENTS
LINKED TO A CELLULOSE BINDING DOMAIN**

(57) The present invention relates to a chemical entity comprising more than one chemical components linked to a cellulose binding domain. The present invention further relates to a laundry detergent and/or fabric care composition comprising one or more of these chemical entities. The laundry detergent and/or fabric care compositions of the present invention when comprising these chemical entities provide a higher effective concentration of the chemical component at the fabric surface and therefore, improved benefits.

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C12N 9/42, C11D 3/386, D06M 16/00	A1	(11) International Publication Number: WO 00/18897 (43) International Publication Date: 6 April 2000 (06.04.00)
(21) International Application Number: PCT/US98/20491 (22) International Filing Date: 30 September 1998 (30.09.98) (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): SMETS, Johan [BE/BE]; Bollenberg 79, B-3210 Lubbeek (BE). BETTIOL, Jean-Luc, Philippe [FR/BE]; 93 Avenue Slegers, B-1200 Brussels (BE). LAUDAMIEL, Christophe [FR/BE]; 20A Rue de la Violette, B-1000 Brussels (BE). BOYER, Stanton, Lane [US/US]; 12 Fall River Court, Fairfield, OH 45014 (US). BAECK, Andre, Cesar [BE/BE]; Putsesteenweg 273, B-2820 Bonheiden (BE). HERBOTS, Ivan, Maurice, Alfons, Jan [BE/BE]; Hollegat 11, B-9230 Wetteren (BE). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).		(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BE, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: LAUNDRY DETERGENT AND/OR FABRIC CARE COMPOSITIONS COMPRISING CHEMICAL COMPONENTS LINKED TO A CELLULOSE BINDING DOMAIN (57) Abstract The present invention relates to a chemical entity comprising more than one chemical components linked to a cellulose binding domain. The present invention further relates to a laundry detergent and/or fabric care composition comprising one or more of these chemical entities. The laundry detergent and/or fabric care compositions of the present invention when comprising these chemical entities provide a higher effective concentration of the chemical component at the fabric surface and therefore, improved benefits.		

LAUNDRY DETERGENT AND/OR FABRIC CARE COMPOSITIONS COMPRISING CHEMICAL
COMPONENTS LINKED TO A CELLULOSE BINDING DOMAIN

5

10

Field of the Invention

15

The present invention relates to a chemical entity comprising more than one chemical components linked to a Cellulose Binding Domain (CBD).

20

Background of the invention

Modern laundry detergent and/or fabric care compositions contain various detergent ingredients having one or more purposes in obtaining fabrics which are not only clean, fresh and sanitised but also have retained appearance and integrity. Therefore, detergent components such as perfumes, soil release agents, fabric brightening agents, fabric softeners, chelants, bleaching agents and catalysts, dye fixatives and enzymes, have been incorporated in laundry detergent and/or fabric care compositions. In using such detergent components, it is important that some of these compounds deposit on the fabrics so as to be effective during or after the laundering and/or fabric care process.

30

One specific example is the use of cellulase enzymes for the treatment of cotton-containing fabrics which largely consist of cellulose. The cellulose structures are depolymerized or cleaved by cellulases into smaller and thereby more soluble or dispersible fractions. This activity in particular on fabrics provides a cleaning, rejuvenation, softening and generally improved handfeel characteristics to the

35

5 fabric structure. However, it has been difficult to incorporate cellulase enzymes into modern detergents in an effective manner. In that regard, those skilled in the art have sought to use minimal amounts of cellulase to their fullest effectiveness by ensuring that most, if not all, of the cellulase enzyme comprised in the detergent composition deposits on the fabric. For example, optimum cellulases would generally have a binding domain especially suitable for celluloses. In this way, most of the cellulase enzyme included in the detergent composition deposits or otherwise binds to the fabric during the laundering cycle to achieve its desired results.

10

Similarly, it would be desirable to have laundry detergent and/or fabric care compositions in which chemical components are also modified to ensure deposition onto the fabrics for improved and/or new performances.

15

Accordingly, there remains a need to formulate laundry detergent and/or fabric care compositions wherein the chemical components have improved deposition on fabrics, which results in improved performance during typical washing / fabric care cycles. There is also a need to ensure that chemical components remain on the fabric or fibre during the additional steps of rinsing and during wear. There also remains a need for such components to be formulated in an cost-effective manner.

20

The above objectives have been met by formulating laundry detergent and/or fabric care compositions comprising a chemical entity comprising more than one chemical components linked to a cellulose binding domain. It has been surprisingly found that such chemical entities more readily affix or otherwise come into contact with the fabric, thereby resulting in new, increased, enhanced and/or more cost-effective performance of the chemical component at the fabric surface or when released during or after the laundry and/or fabric care process.

25
30

Enzymes linked to Cellulose Binding Domains are described in the art : WO 91/10732 describes novel derivatives of cellulase enzymes combining a core region derived from an endoglucanase producible by a strain of *Bacillus* spp., NICMB 40250 with a CBD derived from another cellulase enzyme, or combining a core region derived from another cellulase enzyme with a CBD derived from said endoglucanase, for improved binding properties. WO94/07998 describes

35

cellulase variants of a cellulase classified in family 45, comprising a CBD, a Catalytically Active Domain (CAD) and a region linking the CBD to the CAD, wherein one or more amino acid residues have been added, deleted or substituted and /or another CBD is added at the opposite end of the CAD.

5 WO95/16782 relates to the cloning and high level expression of novel truncated cellulase proteins or derivatives thereof in *Trichoderma longibrachiatum* comprising different core regions with several CBDs. WO97/01629 describes cellulolytic enzyme preparation wherein the mobility of the cellulase component may be reduced by adsorption to an insoluble or soluble carrier e.g. via the

10 existing or newly introduced CBD. WO97/28243 describes a process for removal or bleaching or soiling or stains from cellulosic fabrics wherein the fabric is contacted in aqueous medium with a modified enzyme which comprises a catalytically active amino acid sequence of a non-cellulolytic enzyme selected from amylases, proteases, lipases, pectinases and oxidoreductases, linked to an

15 amino acid sequence comprising a cellulose binding domain and a detergent composition comprising such modified enzyme and a surfactant. WO98/00500 discloses a composition comprising a protein deposition aid having a high affinity for fibres or a surface and having a benefit agent attached / adsorbed thereto.

20 However, none of these documents disclose a chemical entity comprising more than one chemical components linked to a cellulose binding domain, for providing new, increased, enhanced and/or more cost-effective performance of the chemical components.

25

Summary of the invention

30

The present invention relates to a chemical entity comprising more than one chemical components linked to an amino acid sequence comprising a Cellulose Binding Domain.

35

The present invention further relates to laundry detergent and/or fabric care compositions comprising one or more of such chemical entities. These compositions provide new, increased, enhanced and/or more cost-effective performance of the chemical components.

The present invention also relates to a method of treating a fabric with a chemical entity, comprising the steps of :

- (i) selecting a chemical component to be attached to a cellulose binding domain;
- 5 (ii) applying the chemical entity to the fabric.

The present invention further relates to the use of a cellulose binding domain to deposit a chemical component onto a fabric wherein the chemical component is attached to the cellulose binding domain.

10

The present invention finally relates to a process for attaching a chemical component to a cellulose binding domain comprising the steps of in any order :

- (i) reacting the chemical components to the linking region; and/or
- (ii) reacting the linking region with the cellulose binding domain.

15

Detailed description of the invention

The object of the present invention is to increase and/or enhance the performance and cost effectiveness of chemical components. This object is achieved by the formulation of a chemical entity which comprise more than one chemical components linked to an amino acid sequence comprising a cellulose binding domain. It has been surprisingly found that such chemical entities more readily affix or otherwise come into contact with the fabric, thereby resulting in new, increased and/or enhanced performance of the chemical component at the fabric surface or when released during or after the laundry and/or fabric care process. Accordingly, this allows to formulate compositions in a more cost-effective manner.

30 The present invention relates to a chemical entity having a ratio of chemical components to Cellulose Binding Domain unit (CBD) higher than 1. This can be achieved by :

- The linking of all chemical components directly to a selected cellulose binding domain. Said cellulose binding domain is selected to comprise in its amino acid sequence, at least one Lysine amino acid. Lysine amino acid(s) and the terminal amino acid will provide suitable attachment points for chemical components.

35

- The linking of at least one chemical component directly to the cellulose binding domain and at least one chemical component indirectly to said cellulose binding domain via a linking region. In this instance, at least one chemical will be attached to the reactive group of an amino acid comprised in the sequence of the cellulose binding domain. At least another chemical component will be linked to said CBD via a linking region.
- The linking of all chemical components indirectly to a cellulose binding domain via a linking region comprising more than one reactive site suitable for the linking of a chemical component, hereinafter referred to as "polyreactive linking region".

10

Also encompassed in the present invention are combinations of these different options, i.e., chemical entities wherein the chemical components are linked directly and/or indirectly via a linking region and/or polyreactive linking region to one or more cellulose binding domains and/or one or more selected cellulose binding domains, i.e. :

15

- A chemical entity wherein all the chemical components are linked directly to the CBD;
- A chemical entity wherein at least one chemical is linked indirectly via a linking region to the CBD;
- A chemical entity wherein at least one chemical component is linked directly to the CBD and at least one chemical component is linked indirectly via a linking region to the CBD;
- A chemical entity wherein all the chemical components are linked indirectly via a linking region to the CBD;
- A chemical entity wherein said linking region is a polyreactive linking region;
- A chemical entity wherein said amino acid sequence comprising a cellulose binding domain comprises at least one Lysine amino acid.

20

25

30

35

Depending on the intended activity of the attached chemical component, said chemical components can be linked permanently or temporarily to the CBD, linking region and/or the polyreactive linking region. Therefore, the present invention further encompasses chemical entities wherein the chemical component is linked to the CBD, linking region and/or polyreactive linking region by a weak bond. Said weak bonds are cleaved during or after the wash or fabric care process, allowing the release of the attached chemical component(s).

Preferably, the perfume component, insect control agent, hygiene agent will be linked via a weak bond.

5 Identical or different chemical components can be linked to a CBD. The chemical components encompassed in the present invention are preferably selected from the group consisting of perfumes, hygiene agents, insect control agent, softener compounds, soil release polymers, bleaching agents, dye fixatives agents, brighteners and/or mixtures thereof. More preferred components are the perfume components, insect control agents, hygiene agents and/or bleaching agents.

10

In addition to these chemical entities, the compositions of the present invention can comprise the same chemical components unmodified.

15 The linking region

The term "linking region" is intended to indicate a region that adjoins the CBD and connects it to the chemical components. The linking region is an intermediate between the chemical components and the amino acid sequence
20 comprising a cellulose binding domain. This linking region comprises a moiety that will covalently bind to the CBD and one or more reactive group available to attach a chemical component.

If encompassed in the chemical entity of the present invention, suitable are the
25 linking regions characterised by having at least one attachment point for a chemical component and at least one attachment point to the cellulose binding domain. Preferably, the linking regions of the present invention will encompass at least one attachment point to the cellulose binding domain and more than one reactive group available to attach a chemical component, hereinafter referred to
30 as "polyreactive linking region".

Suitable linking regions are :

- The polyethylene glycol derivatives described in the Shearwater polymers, Inc. catalogue of January 1996, such as the nucleophilic PEGs, the carboxyl PEGs,
35 the electrophilically activated PEGs, the sulfhydryl-selective PEGs, the heterofunctional PEGs, the biotin PEGs, the vinyl derivatives, the PEG silanes

and the PEG phospholipids. Particularly suitable specifically substituted polymers are the heterofunctional PEG, (X-PEG-Y) polymers from Shearwater such as PEG(NPC)₂, PEG-(NH₂)₂, t-BOC-NH-PEG-NH₂, t-BOC-NH-PEG-CO₂NHS, OH-PEG-NH-tBOC, Fmoc-NH-PEG-CO₂NHS or PEG(NPC)₂ MW 3400 from Sigma.

5 Preferred polymers are PEG(NPC)₂, (NH₂)₂-PEG, t-BOC-NH-PEG-NH₂ polymers, more preferred is t-BOC-NH-PEG-NH₂ polymer from Shearwater.

- Glutaric dialdehyde 50 wt% solution in water from Aldrich, disuccinimidyl suberate (DSS) from Sigma, γ -maleimidobutyric acid N-hydroxysuccinimide ester (GMBS) from Sigma, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide
10 hydrochloride (EDC) from Sigma and dimethyl suberimidate hydrochloride (DMS) from Sigma.

- 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide, N-ethyl-5-phenylisoaxolium-3-sulphonate, 1-cyclohexyl-3(2morpholinoethyl) carbodide metho-p-toluene sulphonate, N-ethoxycarbonyl-2-ethoxy 1,2, dihydroquinoline or glutaraldehyde.

15

Suitable linking regions, in particular polyreactive linking regions include the polyacrylic acid/ maleic acid polymer, polyvinyl alcohol polymer, amino-containing compounds and/or mixtures thereof such as described below. The amine-containing compounds include the amino aryl derivatives, the polyamines, the
20 substituted amines and amides, the glucamines, the dendrimers / chitosan saccharides and amine derivatives polysaccharides and the peptidic polymers.

1) Poly acrylic acid/ maleic acid and/or mixtures thereof wherein one of the acid moiety is covalently bond to a NH₂ group present in the amino acid sequence of
25 the CBD. The other acid units are the reactive groups available as potential attachment groups for chemical components via their alcohol/amine groups.

2) Poly vinyl alcohol polymers. These polymers can still comprise or not the moiety containing the polymerisation initiator.

30

- Without the acid moiety containing initiator of polymerisation, this polymer can be linked for example, to the reactive group of aspartic or glutamic acid present in the amino acid sequence of the CBD via an esterification reaction. The poly vinyl alcohol polymer does further
35 comprise hydroxyl reactive groups available for attachment of acid/aldehyde containing chemical components.

- With an acid moiety containing initiator of polymerisation, this acid moiety of the initiator of polymerisation of the polymer for example, can be linked for example, to a NH₂ group present in the amino acid CBD sequence. The poly vinyl alcohol polymer does further comprise hydroxyl reactive groups available for attachment of acid/aldehyde containing chemical components.

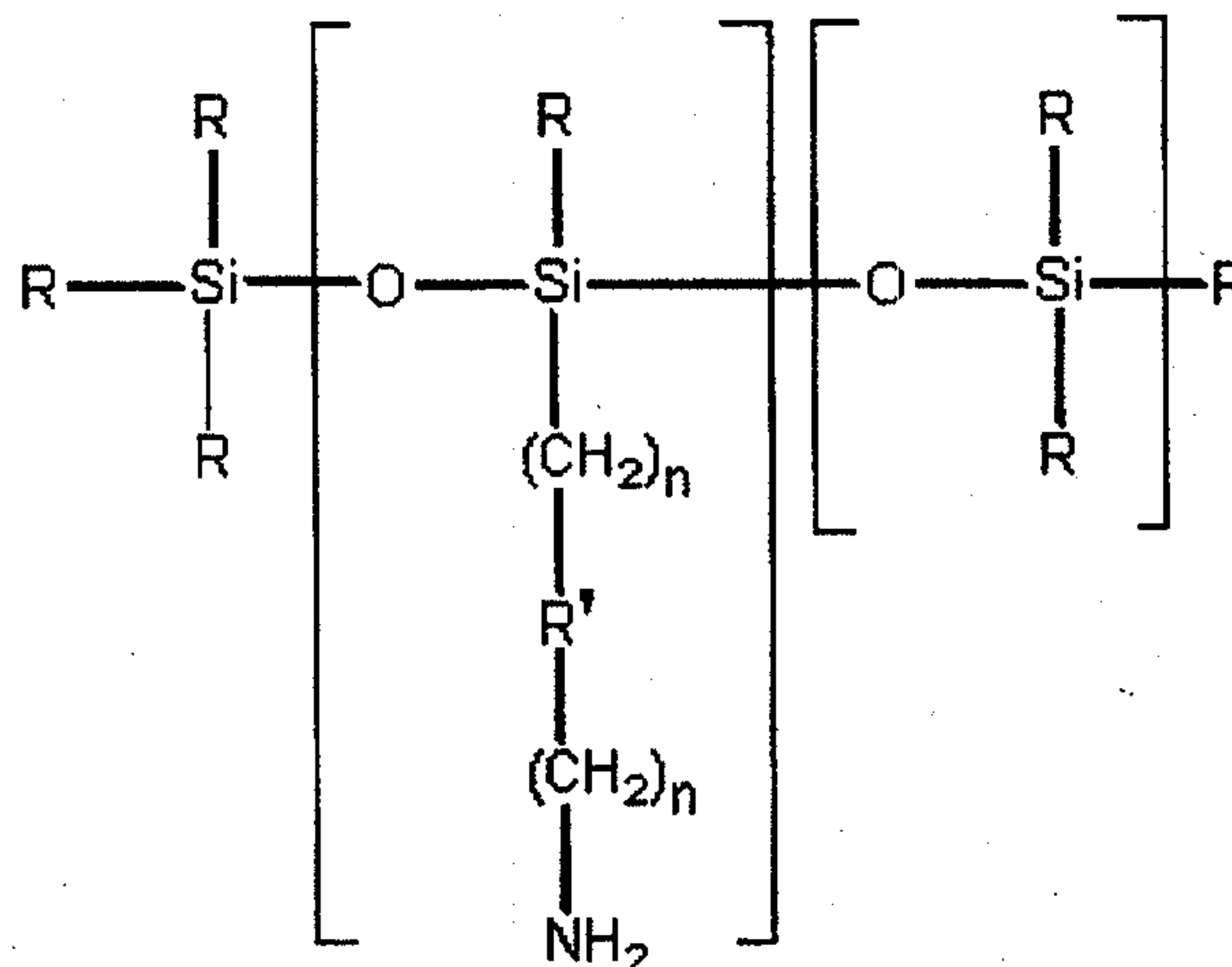
3) Also suitable are amine-containing compounds having the following general structure : B-(NH₂)_n; wherein B is a carrier material, and n is an index of value of at least 1. Preferred B carriers are inorganic or organic carriers.

By "inorganic carrier", it is meant carrier which are non- or substantially non carbon based backbones. Among the inorganic carriers, preferred inorganic carriers are mono or polymers or organic-organosilicon copolymers of amino derivatised organo silane, siloxane, silazane, alumane, aluminum siloxane, or aluminum silicate compounds. Typical examples of such carriers are: organosiloxanes with at least one primary amine moiety like the diaminoalkylsiloxane [H₂NCH₂(CH₃)₂Si]_nO, or the organoaminosilane (C₆H₅)₃SiNH₂ described in: Chemistry and Technology of Silicone, W. Noll, Academic Press Inc. 1998, London, pp 209, 106).

Mono or polymer or organic-organosilicon copolymers containing one or more organosilylhydrazine moiety are also preferred. A typical example of such a class of carrier material is the N,N'-bis(trimethylsilyl)hydrazine (Me₃Si)₂NNH₂ described in: The OrganoSilicon Chemistry Second international Symposium, Pure and Applied Chemistry, Vol, 19 Nos 3-4, (1969).

The following are also preferred mono or poly silazanes and which are exemplified by the 1,1,1,3,3,3,-hexamethyl-2-phenyldiaminosilyldisilasane [(CH₃)₃Si]₂NSi(C₆H₅)NH₂)₂ described in: OrganoSilicon Compounds, 1965, V. Bazant and al. Academic Press). Still other preferred examples of polymer silicone derivatives are the cyclic 1,1,5,5,7,7,7,11,11-Octamethyl-3-9-bis-[2-(2-aminoethylamino)-ethyl]-1,5,7,11-tetrasiloxane-3,9-diaza-6,12-dioxacyclododecane and the Hexaethoxydiamino cyclotetrasiloxane (C₆H₅)₂(NH₂)₂Si₄O₄, id, Vol 2 part 2, p 474, p454).

Preferred amino functionalized inorganic polymeric carriers for use herein are polyaminoalkyl polysiloxanes. Typical disclosure can be found in JP 79,131,096, and EP 058 493. Still other inorganic polymeric carriers suitable for use herein are the amino functionalized polydi-alkylsiloxanes, as described in EP 150 867 and having the general formula:



Wherein $\text{R} = \text{C}_{1-16}$ preferentially C_{1-4} alkyl; n is an integer from 0 to 16 preferentially from 1 to 6, $\text{R}' = \text{nil}, \text{O}, \text{C}=\text{O}, \text{COO}, \text{NC}=\text{O}, \text{C}=\text{O}-\text{NR}, \text{NR}, \text{SO}_m$, $m=2,3$.

By organic carriers, it meant carriers having essentially carbon bond backbones. Typical amines having organic carrier include aminoaryl derivatives, polyamines, aminofunctional polymers, aminoacids and derivatives, substituted mono-, oligo- and poly amino saccharides, substituted amines and amides, dendrimers, and glucamines.

Of course, the amine compound can be interrupted or substituted by linkers or cellulose substantive group. A general formula for this amine compound may be represented as follows:



wherein each m is an index of value 0 or at least 1, and n is an index of value of at least 1 as defined herein before. As can be seen above, the amine group is linked to a carrier molecule as defined by classes hereinafter described. The

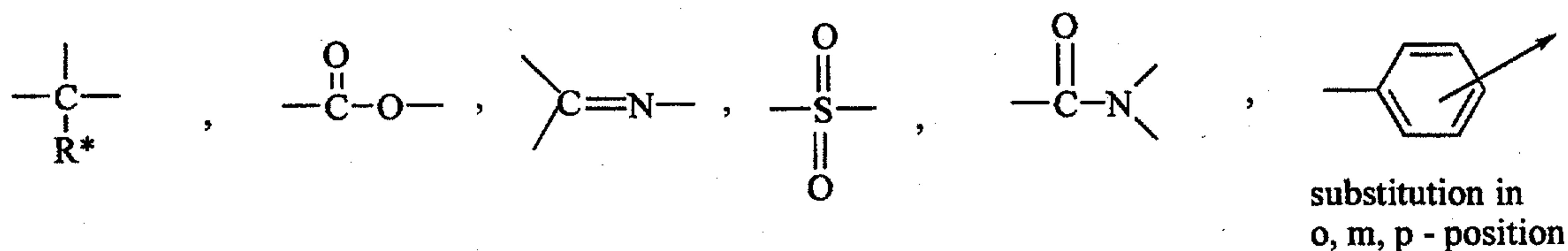
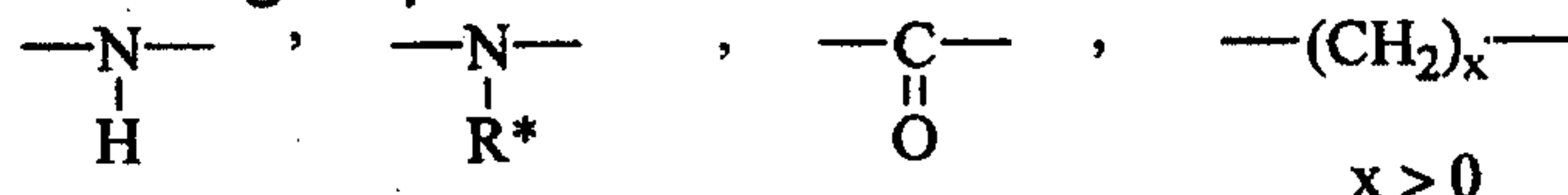
primary amine group is either directly linked to the carrier group or via a linker group L. The carrier can also be substituted by a R* substituent, and R* can be linked to the carrier either directly or via a linker group L. Of course, R* can also contain branching groups like e.g. tertiary amine and amide groups.

5

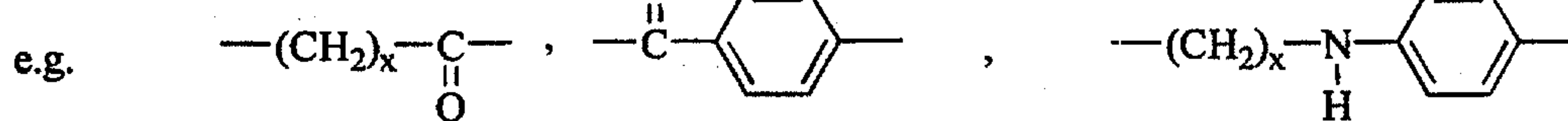
It is important for the purpose of the invention that the amine compound comprises at least one primary amine group to react with a chemical component of the present invention to form the reaction products. Of course, the amine compound is not limited to having only one amine function. Indeed, more preferably, the amine compound comprises more than one amine function, thereby enabling the amine compound to react with several chemical components of the present invention. For example, reaction products carrying mixed perfumes aldehyde(s) and/or ketone(s) can be achieved, thereby resulting in a mixed release of such fragrances.

10

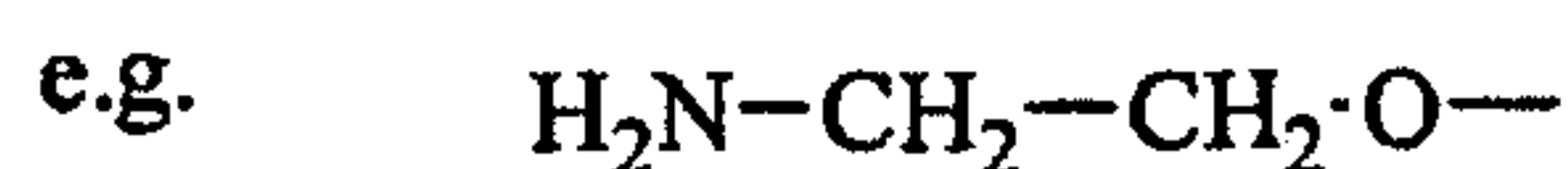
Typical linker group include:



L can also be a combination



L can also contain —O— if this group is not directly linked to N



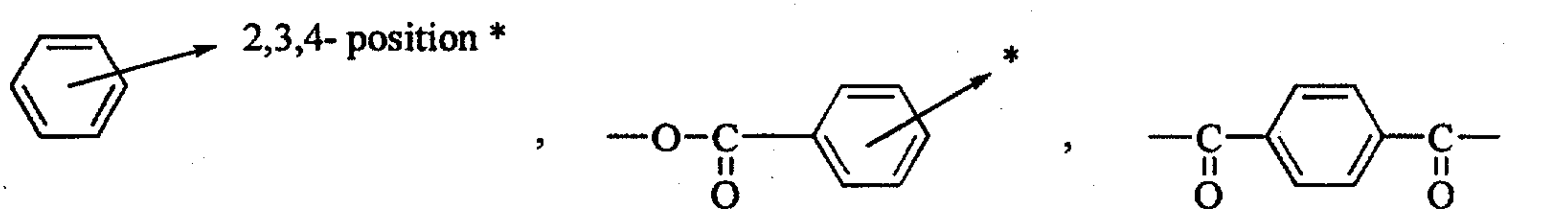
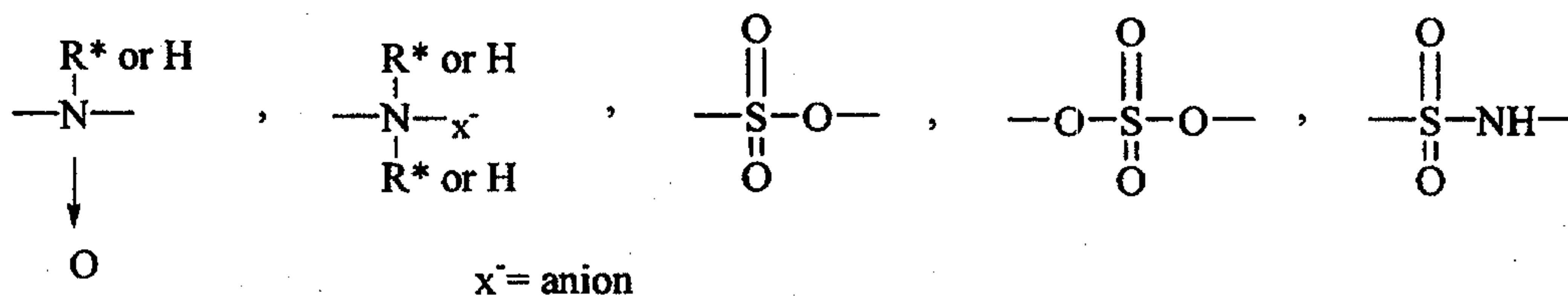
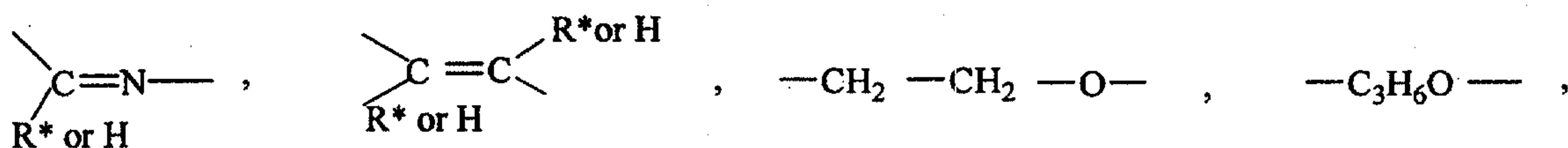
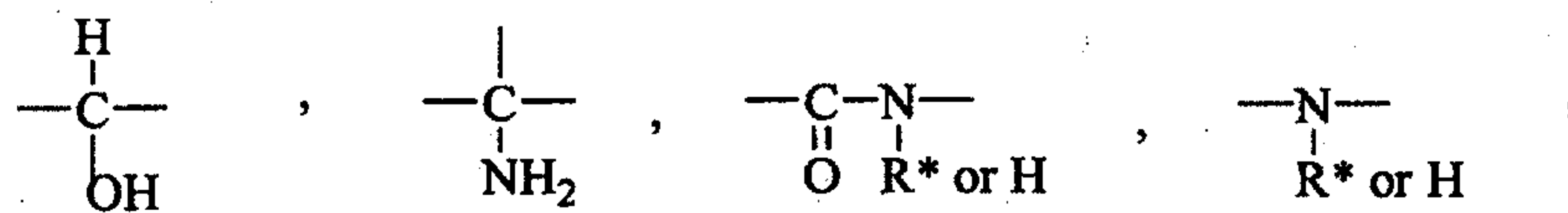
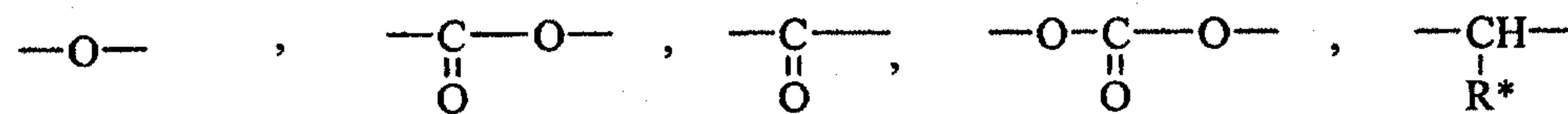
20

Most of the compounds described in the classes of amine compounds hereinafter will contain at least one substituent group classified as R*.

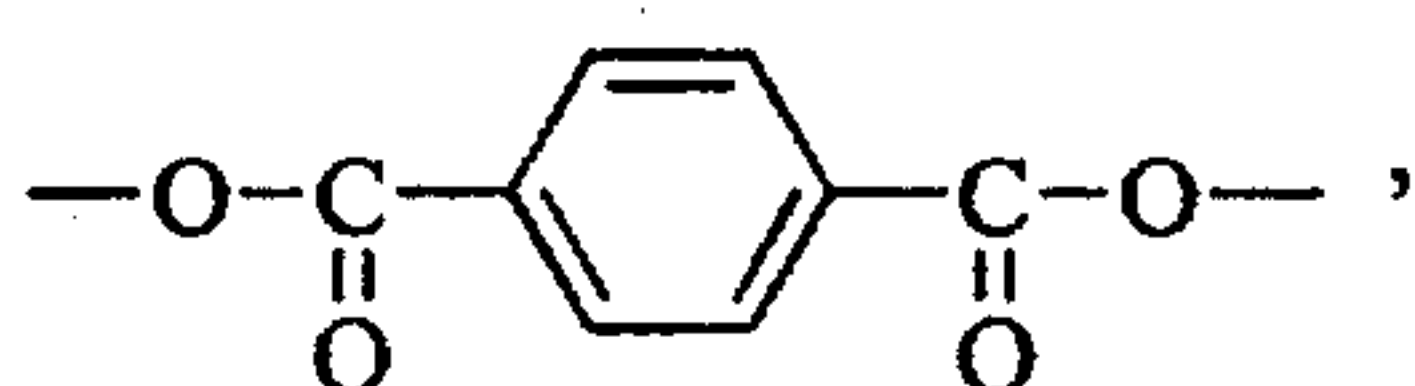
R* contains 1 to 22 carbon atoms in the main chain and optionally can be an alkyl, alkenyl, or alkylbenzene chain. It can also contain alicyclic, aromatic, heteroaromatic or heterocyclic systems, either inserted into the main chain or by substitution of an H atom of the main chain. Further, R* can either be linked to
5 the carrier B material or via a linker L, as defined herein before. In this instance, L can also be -O-.

The main chain can contain from 1 to up to 15 R* groups.

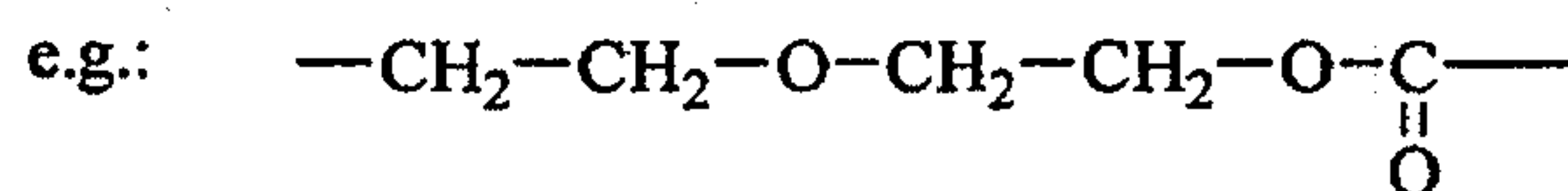
Typical R* insertion groups include:



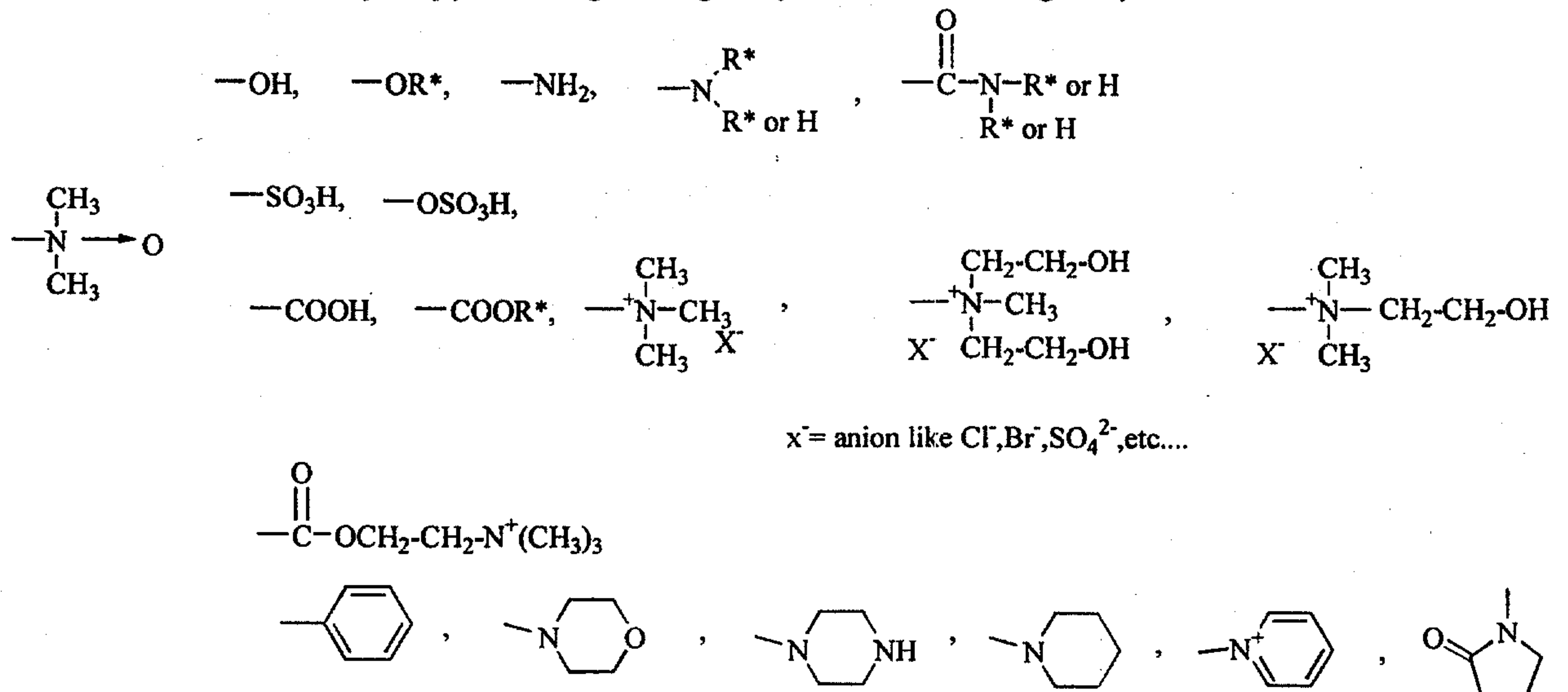
* the arrow indicates upto 3 substitutions in position 2,3,4



R* can also contain several insertion groups linked together: e.g.



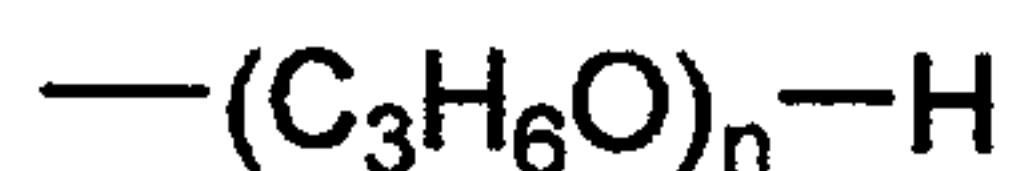
Furthermore, R^* can carry a functional end group E that provides additional surface substantivity. Typical organic groups of this end group E include



E can also be an aromatic, alicyclic, heteroaromatic, or heterocyclic group including mono-, oligo-, polysaccharides

- 5 In addition, the R^* group can also be modified via substitution of one or more H atoms in the main chain. The substitution group can either be E or the insertion groups as defined above where the insertion group is terminated by any of H, E, or R^* .

10 R^* can also be a group made of ethoxy or epoxy groups with n ranging from 1 to 15, including groups like:

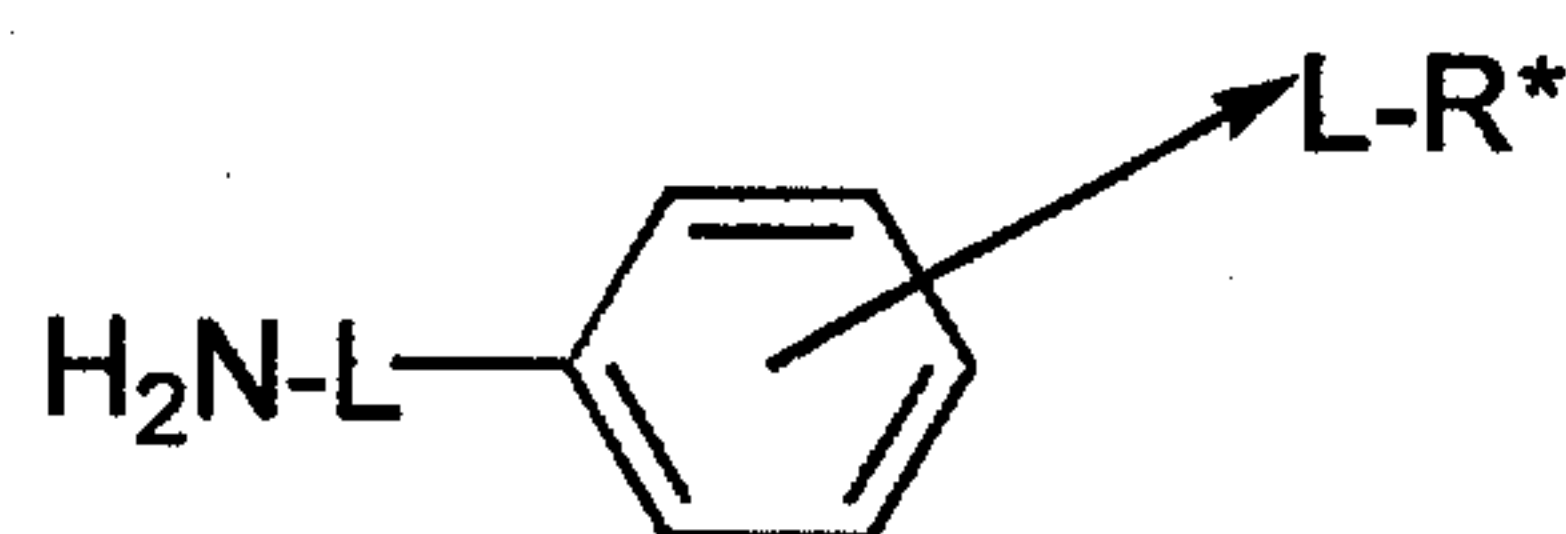


15 As defined herein before, preferred amine having organic carrier material B may be selected from aminoaryl derivatives, polyamines, aminoacids and derivatives, substituted amines and amides, and glucamines.

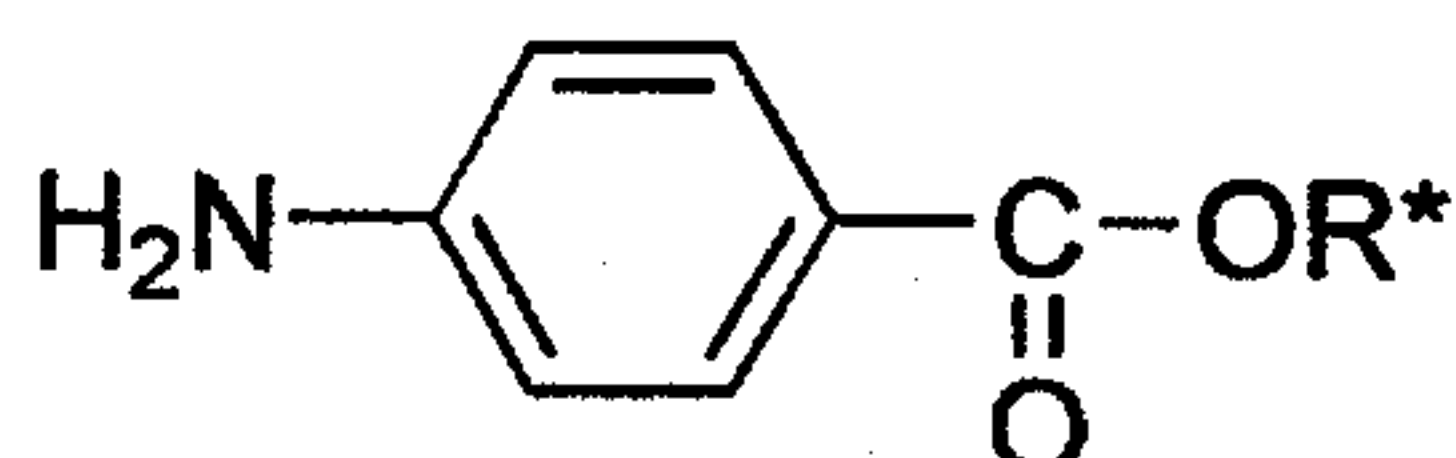
3.1-Amino aryl derivatives

In this class of compounds, the amino group is preferably attached to a benzene ring. The benzene ring is further substituted in the para- and/or meta-position with R* as defined herein before. R* can be attached to the benzene ring via a linker L. The benzene ring can be substituted by other aromatic ring systems including naphthalene, indole, benzimidazole, pyrimidine, purine, and mixtures thereof. Preferably, the R* is attached to the benzene ring in its para position.

Typical amino-benzene derivatives have the following formula:



Preferred amino-benzene derivatives have the following formula:



Preferred amino-benzene derivatives are alkyl esters of 4-amino benzoate compounds, preferably selected from ethyl-4-amino benzoate, phenylethyl-4-aminobenzoate, phenyl-4-aminobenzoate, 4-amino-N'-(3-aminopropyl)-benzamide, and mixtures thereof.

3.2-Polyamines

The polyamines of the invention need to have at least one, preferably more than one free and unmodified primary amine group, to react with a chemical component of the present invention. In the polyamines, H can be substituted by R*, optionally via a linker group L. Additionally, the primary amine group can be linked to the polymer end via a linker group L.

The polyamines compounds suitable for use in the present invention are water-soluble or dispersible, polyamines. Typically, the amino-functional polymers for use herein have a molecular weight between 150 and 2×10^6 , preferably between 400 and 10^6 , most preferably between 5000 and 10^6 . These polyamines comprise backbones that can be either linear or cyclic. The polyamine

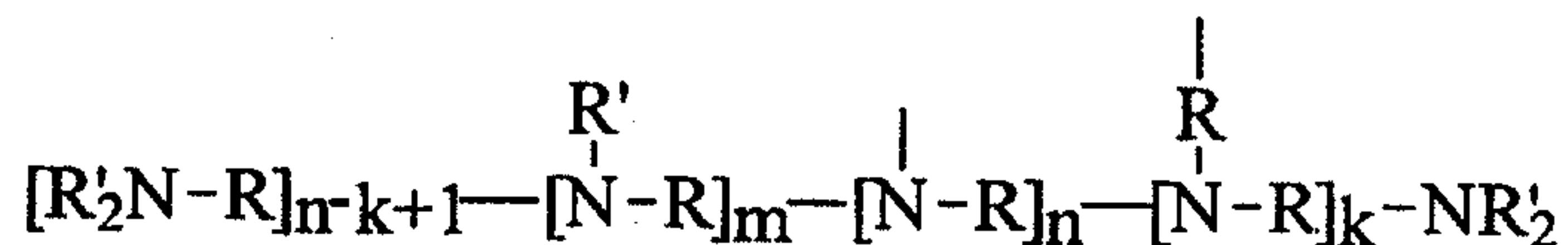
backbones can also comprise polyamine branching chains to a greater or lesser degree. Preferably, the polyamine backbones described herein are modified in such a manner that at least one, preferably each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

For the purposes of the present invention the term "modification" as it relates to the chemical structure of the polyamines is defined as replacing a backbone -NH hydrogen atom by an R' unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidised). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an R' unit. Quaternization or oxidation may take place in some circumstances without substitution, but substitution is preferably accompanied by oxidation or quaternization of at least one backbone nitrogen.

The linear or non-cyclic polyamine backbones that comprise the amino-functional polymer have the general formula:



The cyclic polyamine backbones that comprise the amino-functional polymer have the general formula:



The above backbones prior to optional but preferred subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units.

For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the end of the main polyamine backbone or branching chain having the structure



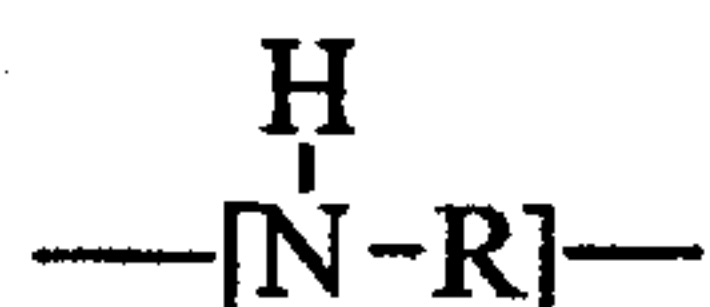
is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified

subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure

5 -NH₂

is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

10 In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure



15 is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

20

In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure



25

is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all of the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

30

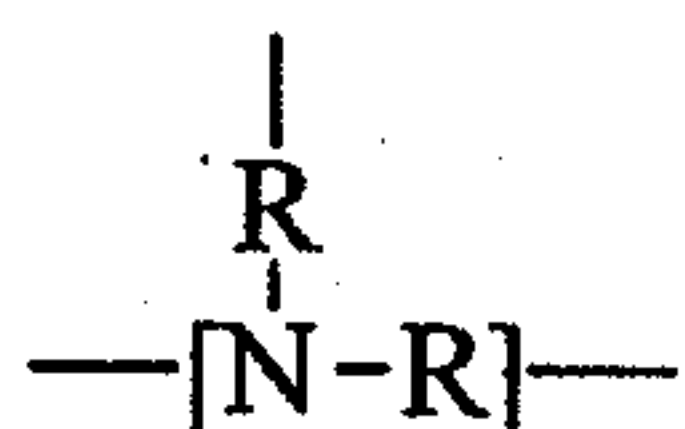
The final modified structure of the polyamines of the present invention can be therefore represented by the general formula



for linear amino-functional polymer and by the general formula



for cyclic amino-functional polymer. For the case of polyamines comprising rings, a Y' unit of the formula



serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula



that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula

15



therefore comprising no Z terminal unit and having the formula $V_{n-k}W_mY_nY'_k$ wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

20

In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula : VW_mZ that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 2 to 700, preferably 4 to 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

25

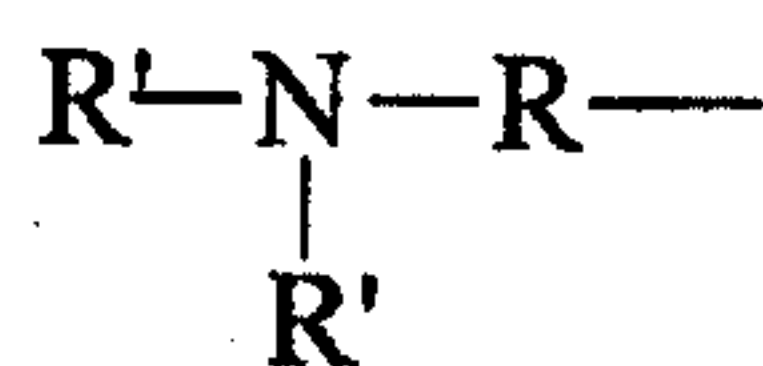
Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, Y' or Z units

30

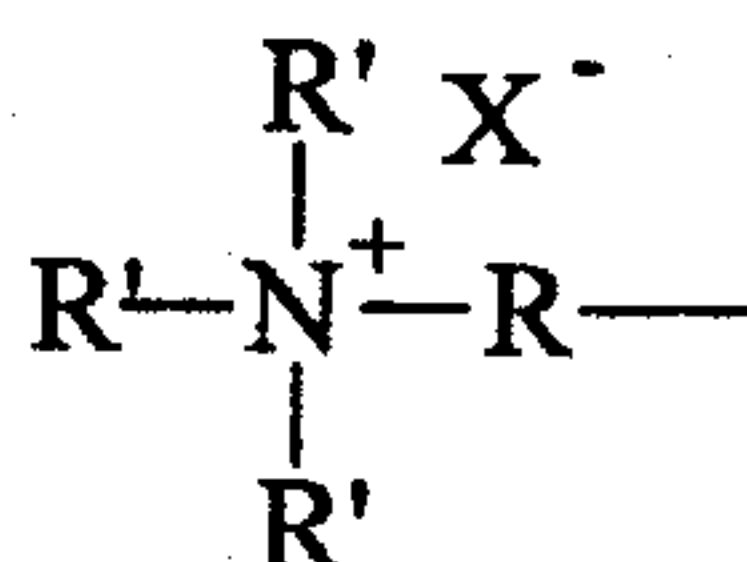
depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units or Y' units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

5

Modified primary amine moieties are defined as V "terminal" units having one of three forms: a) simple substituted units having the structure:



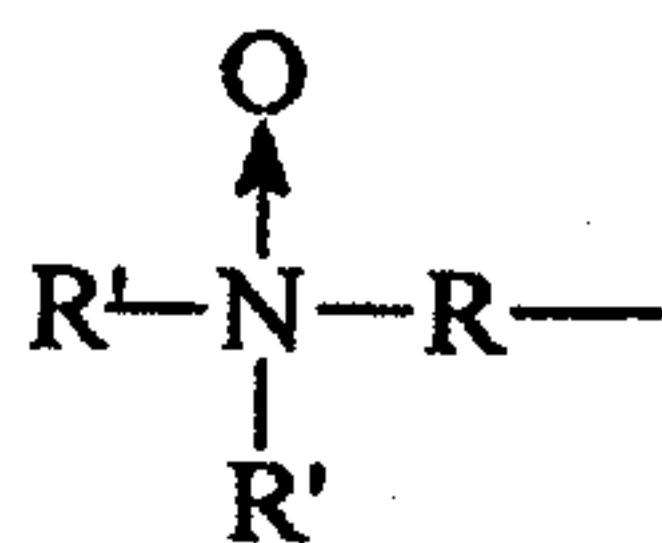
b) quaternized units having the structure:



10

wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:



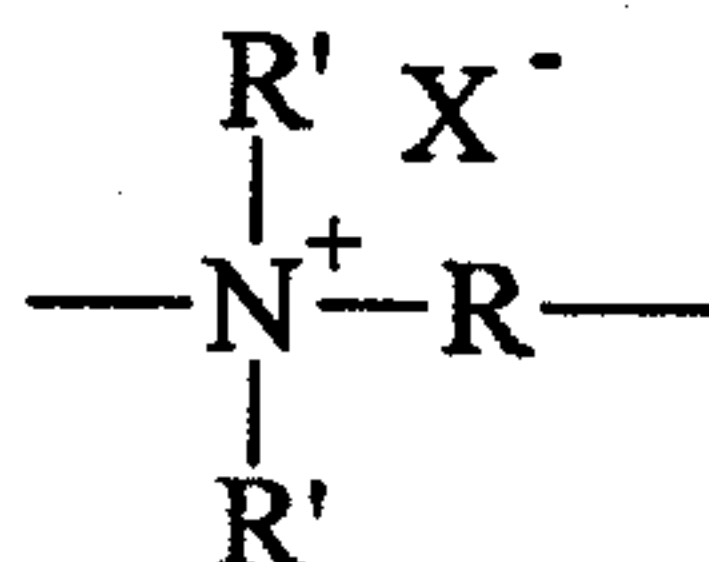
15

Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

a) simple substituted units having the structure:



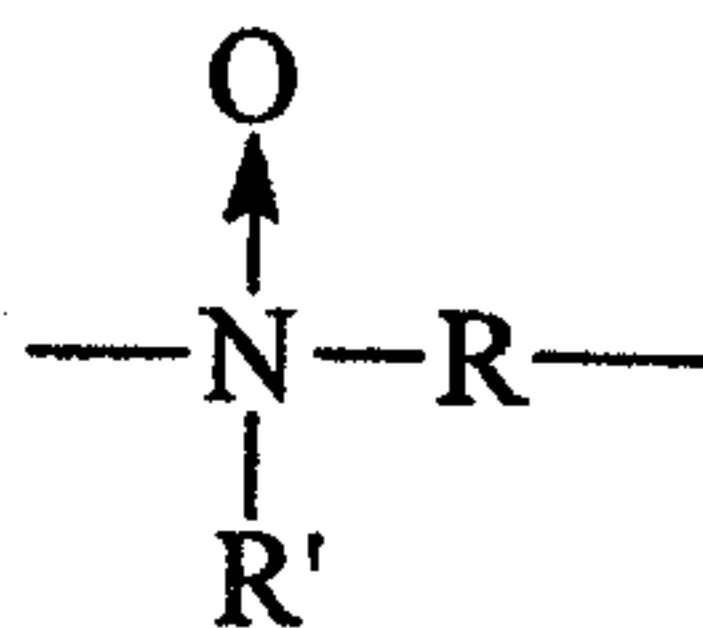
b) quaternized units having the structure:



20

wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

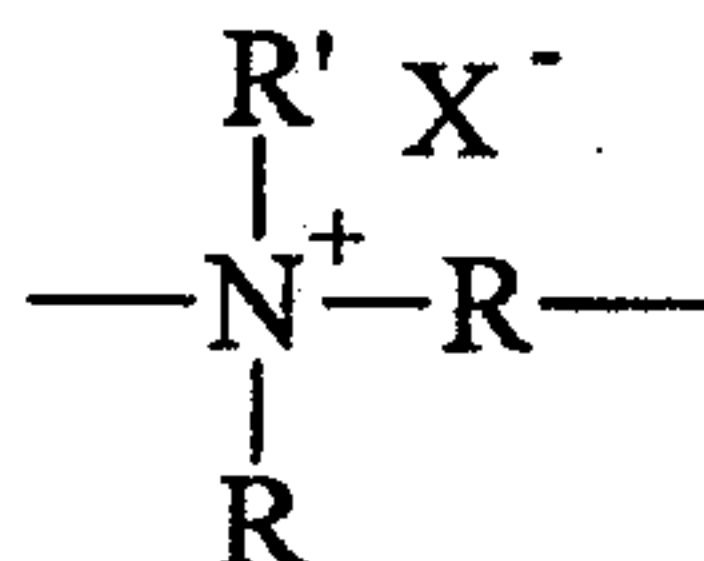


Other modified secondary amine moieties are defined as Y' units having one of three forms: a) simple substituted units having the structure:

25



b) quaternized units having the structure:

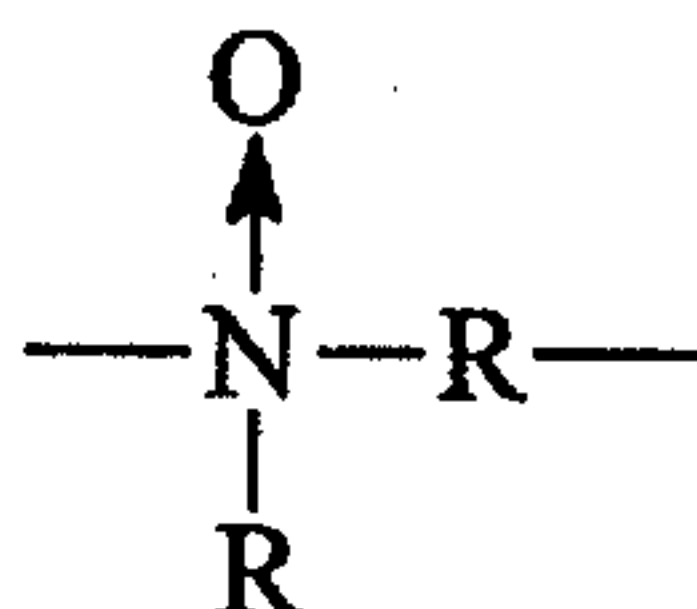


5

c)

wherein X is a suitable counter ion providing charge balance; and

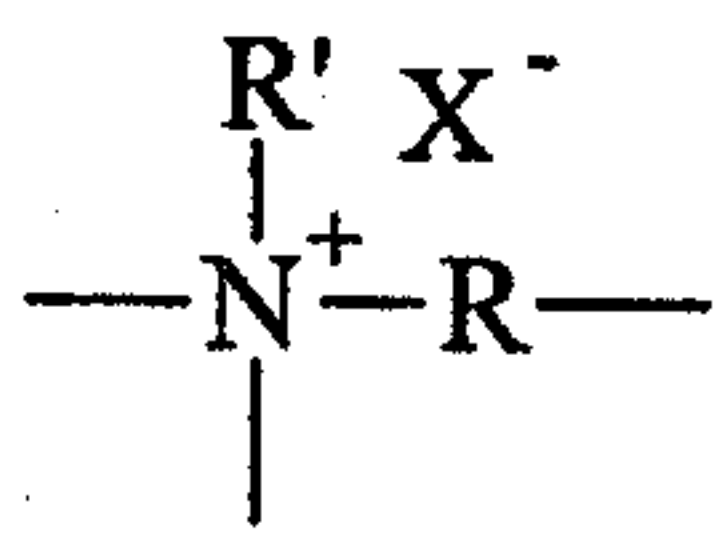
c) oxidized units having the structure:



10 Modified tertiary amine moieties are defined as Y "branching" units having one of three forms: a) unmodified units having the structure:

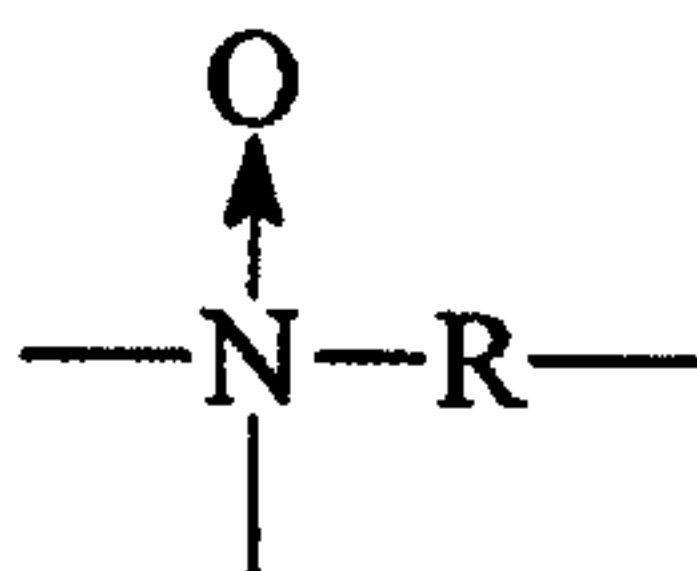


b) quaternized units having the structure:



15 wherein X is a suitable counter ion providing charge balance; and

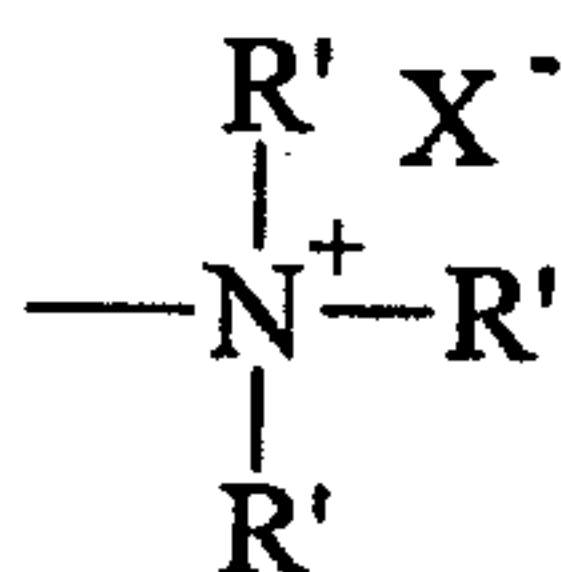
c) oxidized units having the structure:



20 Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms: a) simple substituted units having the structure:

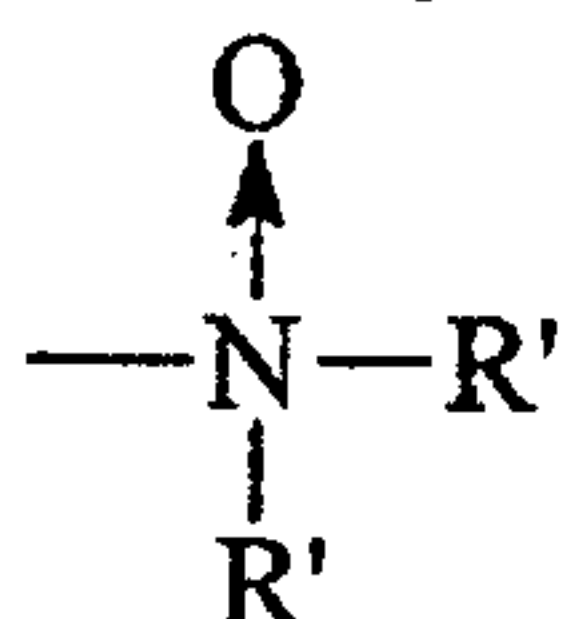


b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

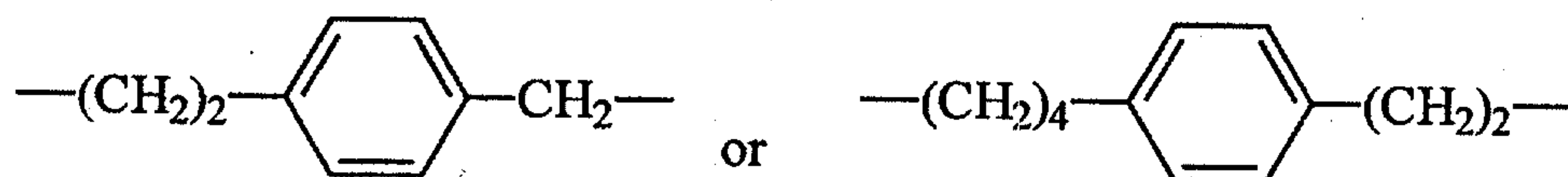
c) oxidized units having the structure:



When any position on a nitrogen is unsubstituted or unmodified, it is understood that hydrogen will substitute for R'. For example, a primary amine unit comprising one R' unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula (HOCH₂CH₂)HN-.

For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure -NH₂. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the R' units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore R' cannot be a hydrogen.

The polyamines of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C₂-C₁₂ alkylene, C₄-C₁₂ alkenylene, C₃-C₁₂ hydroxyalkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C₄-C₁₂ dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; C₈-C₁₂ dialkylarylene which for the purpose of the present invention are arylene moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula



although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted C2-C12 alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise -
 5 (R1O)xR5(OR1)x-, -CH2CH(OR2)CH2O)z(R1O)yR1(OCH2CH(OR2)CH2)w-, -CH2CH(OR2)CH2-, -(R1O)xR1-, and mixtures thereof. Preferred R units are selected from the group consisting of C2-C12 alkylene, C3-C12 hydroxyalkylene, C4-C12 dihydroxyalkylene, C8-C12 dialkylarylene, -(R1O)xR1-, -CH2CH(OR2)CH2-, -(CH2CH(OH)CH2O)z(R1O)yR1(OCH2CH-(OH)CH2)w-, -
 10 (R1O)xR5(OR1)x-, more preferred R units are C2-C12 alkylene, C3-C12 hydroxy-alkylene, C4-C12 dihydroxyalkylene, -(R1O)xR1-, -(R1O)xR5(OR1)x-, -(CH2CH(OH)CH2O)z(R1O)yR1(OCH2CH-(OH)CH2)w-, and mixtures thereof, even more preferred R units are C2-C12 alkylene, C3 hydroxyalkylene, and mixtures thereof, most preferred are C2-C6 alkylene. The most preferred
 15 backbones of the present invention comprise at least 50% R units that are ethylene.

R1 units are C2-C6 alkylene, and mixtures thereof, preferably ethylene.

R2 is hydrogen, and -(R1O)xB, preferably hydrogen.

20 R3 is C1-C18 alkyl, C7-C12 arylalkylene, C7-C12 alkyl substituted aryl, C6-C12 aryl, and mixtures thereof, preferably C1-C12 alkyl, C7-C12 arylalkylene, more preferably C1-C12 alkyl, most preferably methyl. R3 units serve as part of R' units described herein below.

R4 is C1-C12 alkylene, C4-C12 alkenylene, C8-C12 arylalkylene, C6-C10
 25 arylene, preferably C1-C10 alkylene, C8-C12 arylalkylene, more preferably C2-C8 alkylene, most preferably ethylene or butylene.

R5 is C1-C12 alkylene, C3-C12 hydroxyalkylene, C4-C12 dihydroxyalkylene, C8-C12 dialkylarylene, -C(O)-, -C(O)NHR6NHC(O)-, -C(O)(R4)rC(O)-, -R1(OR1)-, -CH2CH(OH)CH2O(R1O)yR1OCH2CH(OH)CH2-, -C(O)(R4)rC(O)-, -
 30 CH2CH(OH)CH2- R5 is preferably ethylene, -C(O)-, -C(O)NHR6NHC(O)-, -R1(OR1)-, -CH2CH(OH)CH2-, -CH2CH(OH)CH2O(R1O)yR1OCH2CH-(OH)CH2-, more preferably -CH2CH(OH)CH2-.

R6 is C2-C12 alkylene or C6-C12 arylene.

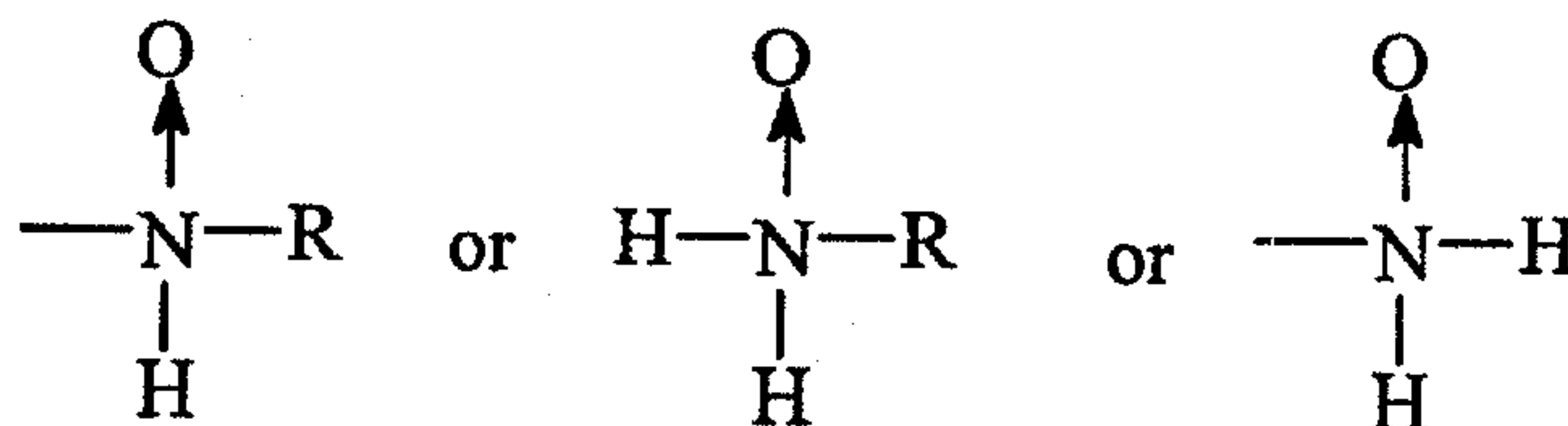
35 The preferred "oxy" R units are further defined in terms of the R1, R2, and R5 units. Preferred "oxy" R units comprise the preferred R1, R2, and R5 units. The

preferred polyamines of the present invention comprise at least 50% R1 units that are ethylene. Preferred R1, R2, and R5 units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

- 5 i) Substituting more preferred R5 into $-(\text{CH}_2\text{CH}_2\text{O})_x\text{R}_5(\text{OCH}_2\text{CH}_2)_x-$ yields $-(\text{CH}_2\text{CH}_2\text{O})_x\text{CH}_2\text{CHOHCH}_2(\text{OCH}_2\text{CH}_2)_x-$.
- ii) Substituting preferred R1 and R2 into $-(\text{CH}_2\text{CH}(\text{OR}_2)\text{CH}_2\text{O})_z(\text{R}_1\text{O})_y\text{R}_1\text{O}(\text{CH}_2\text{CH}(\text{OR}_2)\text{CH}_2)_w-$ yields $-(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{O})_z(\text{CH}_2\text{CH}_2\text{O})_y\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}(\text{OH})\text{CH}_2)_w-$.
- 10 iii) Substituting preferred R2 into $-\text{CH}_2\text{CH}(\text{OR}_2)\text{CH}_2-$ yields $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-$.

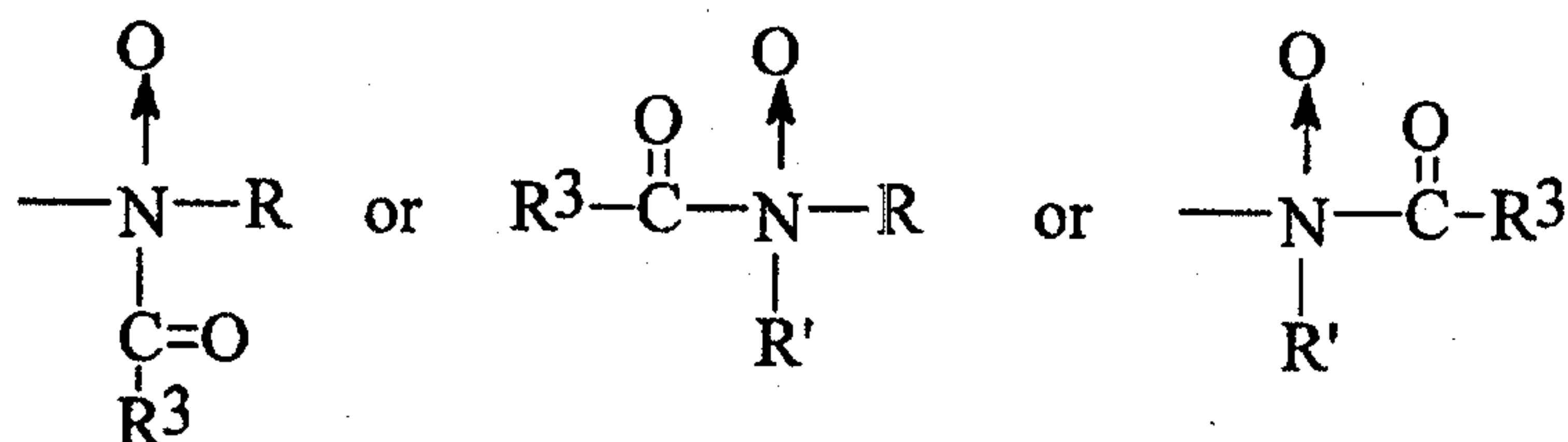
R' units are selected from the group consisting of hydrogen, C1-C22 alkyl, C3-C22 alkenyl, C7-C22 arylalkyl, C2-C22 hydroxyalkyl, $-(\text{CH}_2)_p\text{CO}_2\text{M}$, $-(\text{CH}_2)_q\text{SO}_3\text{M}$, $-\text{CH}(\text{CH}_2\text{CO}_2\text{M})\text{CO}_2\text{M}$, $-(\text{CH}_2)_p\text{PO}_3\text{M}$, $-(\text{R}_1\text{O})_m\text{B}$, $-\text{C}(\text{O})\text{R}_3$,
 15 preferably hydrogen, C2-C22 hydroxyalkylene, benzyl, C1-C22 alkylene, $-(\text{R}_1\text{O})_m\text{B}$, $-\text{C}(\text{O})\text{R}_3$, $-(\text{CH}_2)_p\text{CO}_2\text{M}$, $-(\text{CH}_2)_q\text{SO}_3\text{M}$, $-\text{CH}(\text{CH}_2\text{CO}_2\text{M})\text{CO}_2\text{M}$, more preferably C1-C22 alkylene, $-(\text{R}_1\text{O})_x\text{B}$, $-\text{C}(\text{O})\text{R}_3$, $-(\text{CH}_2)_p\text{CO}_2\text{M}$, $-(\text{CH}_2)_q\text{SO}_3\text{M}$, $-\text{CH}(\text{CH}_2\text{CO}_2\text{M})\text{CO}_2\text{M}$, most preferably C1-C22 alkylene, $-(\text{R}_1\text{O})_x\text{B}$, and $-\text{C}(\text{O})\text{R}_3$. When no modification or substitution is made on a nitrogen then
 20 hydrogen atom will remain as the moiety representing R'. A most preferred R' unit is $(\text{R}_1\text{O})_x\text{B}$.

R' units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



25

Additionally, R' units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According to the present invention, the R' unit $-\text{C}(\text{O})\text{R}_3$ moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides
 30 having the structure



or combinations thereof.

B is hydrogen, C1-C6 alkyl, $-(\text{CH}_2)_q\text{SO}_3\text{M}$, $-(\text{CH}_2)_p\text{CO}_2\text{M}$, $-(\text{CH}_2)_q\text{-(CHSO}_3\text{M)}\text{CH}_2\text{SO}_3\text{M}$, $-(\text{CH}_2)_q\text{-(CHSO}_2\text{M)}\text{CH}_2\text{SO}_3\text{M}$, $-(\text{CH}_2)_p\text{PO}_3\text{M}$, $-\text{PO}_3\text{M}$,
 5 preferably hydrogen, $-(\text{CH}_2)_q\text{SO}_3\text{M}$, $-(\text{CH}_2)_q\text{-(CHSO}_3\text{M)}\text{CH}_2\text{SO}_3\text{M}$, $-(\text{CH}_2)_q\text{-(CHSO}_2\text{M)}\text{CH}_2\text{SO}_3\text{M}$, more preferably hydrogen or $-(\text{CH}_2)_q\text{SO}_3\text{M}$.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies $-(\text{CH}_2)_p\text{CO}_2\text{M}$, and $-(\text{CH}_2)_q\text{SO}_3\text{M}$, thereby resulting in $-(\text{CH}_2)_p\text{CO}_2\text{Na}$, and $-(\text{CH}_2)_q\text{SO}_3\text{Na}$
 10 moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a $-(\text{CH}_2)_p\text{PO}_3\text{M}$ moiety substituted with
 15 sodium atoms has the formula $-(\text{CH}_2)_p\text{PO}_3\text{Na}_3$. Divalent cations such as calcium (Ca^{2+}) or magnesium (Mg^{2+}) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

20 X is a water soluble anion such as chlorine (Cl^-), bromine (Br^-) and iodine (I^-) or X can be any negatively charged radical such as sulfate (SO_4^{2-}) and methosulfate (CH_3SO_3^-).

The formula indices have the following values: p has the value from 1 to 6, q has
 25 the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; m has the value from 2 to 700, preferably from 4 to 400, n has the value from 0 to 350, preferably from 0 to 200; m + n has the value of at least 5.

Preferably x has a value lying in the range of from 1 to 20, preferably from 1 to
 30 10.

The preferred amino-functional polymers of the present invention comprise polyamine backbones wherein less than 50% of the R groups comprise "oxy" R

units, preferably less than 20% , more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

5 The most preferred amino-functional polymers which comprise no "oxy" R units comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C2-C12 alkylene, preferred is C2-C3 alkylene, most preferred is ethylene.

10

The amino-functional polymers of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone
15 having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artefact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of
20 polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A
25 polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

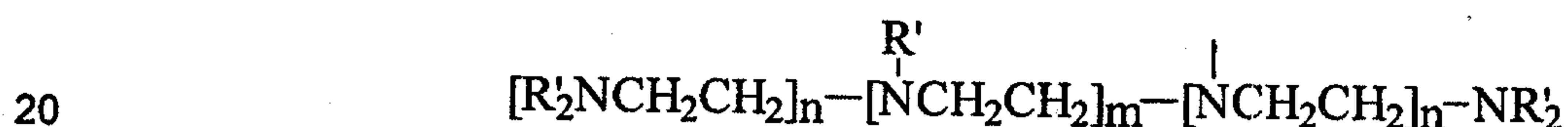
For the purposes of the present invention the term "non-homogeneous polymer
30 backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone.

35

Preferred amino-functional polymers of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneimines (PAI's), preferably polyethyleneimines (PEI's), or PEI's connected by moieties having longer R units than the parent PAI's or PEI's.

Preferred amine polymer backbones comprise R units that are C2 alkylene (ethylene) units, also known as polyethylenimines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:



wherein R', m and n are the same as defined herein above. Preferred PEI's will have a molecular weight greater than 200 daltons.

The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16,

1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

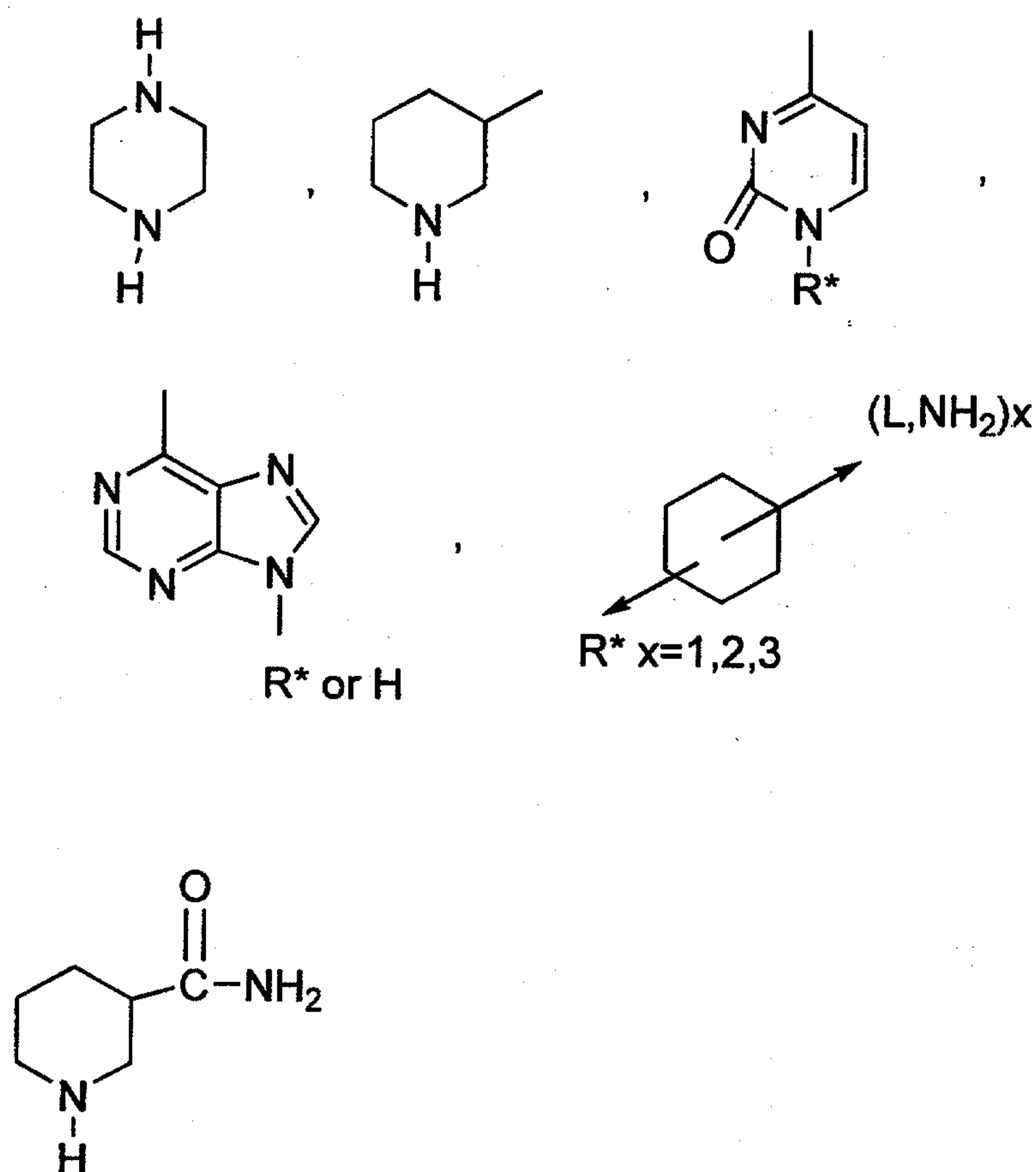
- 5 Preferred polyamines are polyethyleneimines commercially available under the tradename Lupasol like Lupasol FG, G20,wfv, PR8515, WF, FC, G20, G35, G100, HF, P, PS, SK, SNA.

Still other polyamines suitable for use in the present invention are poly[oxy(methyl-1,2-ethanediyl)], α -(2-aminomethylethyl)- ω -(2-aminomethyl-ethoxy)-; poly[oxy(methyl-1,2-ethanediyl)], α -hydro-)- ω -(2-aminomethylethoxy)-, ether with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol; commercially available under the tradename Jeffamines T-403, D-230, D-400, D-2000; 2,2',2"-triaminotriethylamine; 2,2'-diamino-diethylamine; 3,3'-diamino-dipropylamine, 1,3 bis aminoethylcyclohexane commercially available from Mitsibushi and the C12
 10 Sternamines commercially available from Clariant like the C12 Sternamin(propylenamine)_n with n=3/4, and mixtures thereof.

3.3-Substituted amines and amides

Substituted amine and amide compounds suitable for use herein have the
 20 following general formula: NH₂-L-R**, in which L is -CO- in case of an amide. Other optional linker group may be as defined under R*.

R** is as defined herein before under R* with the proviso that it contains at least 6 carbon atoms and/or N atoms and/or cyclohexyl-, piperidine, piperazine, and other heterocyclic groups like:



Optionally, H in NH can be substituted by R*.

Preferred substituted amines and amides for use herein are selected from
 5 nipecotamide, N-coco-1,3-propenediamine; N-oley-1,3-propenediamine; N-(tallow alkyl)-1,3-propenediamine; 1,4-diamino cyclohexane; 1,2-diamino-cyclohexane; 1,12-diaminododecane, and mixtures thereof.

3.4-Glucamines

10 Still a further preferred class of amine compound is the class of glucamines of general structure: NH₂-CH₂-(CH(OH))_x-CH₂OH, wherein one or several OH-function can be substituted, preferably by -OR*, and wherein x is an integer of value 3 or 4. R* can be linked to the OH groups either directly or via linker unit as mentioned herein before under L.

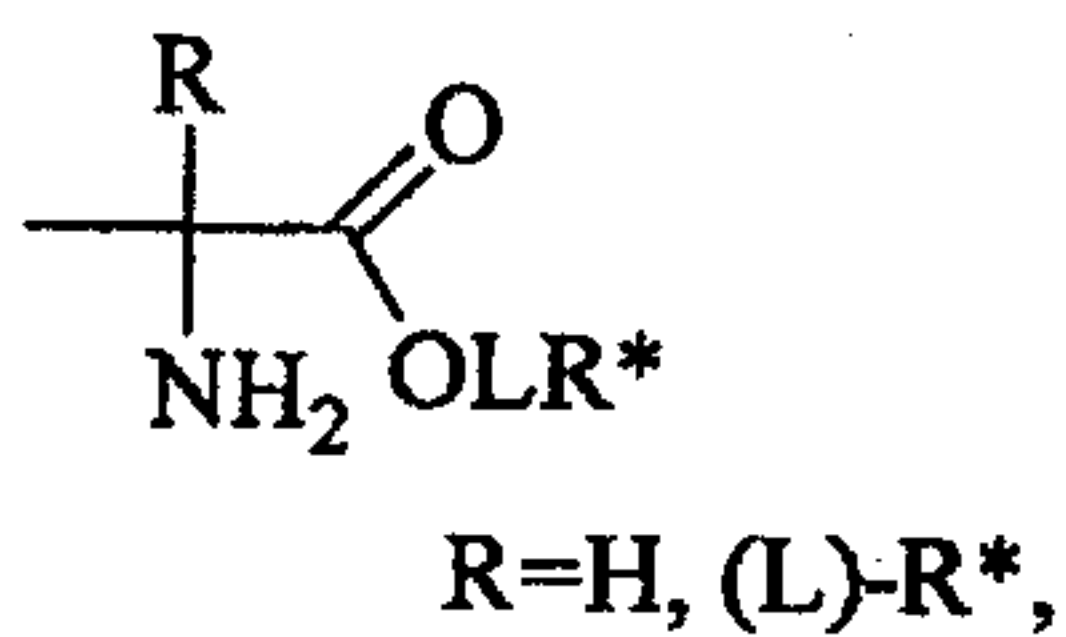
15 Preferred compound of this class are selected from 2,3,4,5,6-pentamethoxy-glucamine; 6-acetylglucamine, glucamine, and mixture thereof.

3.5-Dendrimers, chitosan saccharides amine derivatives polysaccharides

Also suitable are the dendrimers such as Starburst or Astramol sold from DSM or Aldrich and the Oligo- or Poly-saccharides derivatised amines like chitosan and/or derivatives sold by Henkel or Amerchol and like the functionalised oligosaccharides and glycans, especially the Amine & other Nitrogen containing materials sold by Carbomer Inc.

3.6-Peptidic polymer

Most preferred compounds for use in the present invention are amino acids and their derivatives, especially ester and amide derivatives. These peptidic polymers are linked to the CBD via a peptidic linkage. More preferred compounds are those providing enhanced surface substantivity due to its structural feature. Suitable amino acids have the following functionality of formula:



Suitable amino acids for use herein are selected tyrosine, tryptophane, lysine, glutamic acid, glutamine, aspartic acid, arginine, asparagine, phenylalanine, proline, glycine, serine, histidine, threonine, methionine, and mixture thereof. Homopolymers with the same amino acids or heteropolymers with different amino acids are suitable. For example, the amino acids Serine, Threonine and Tyrosine possess the reactive hydroxyl group, the Cysteine present a reactive SH group, the Asparagine and Glutamine amino acids possess a reactive amido group and the Lysine a reactive amino group. The linking will preferably be achieved on the Tyrosine, Cysteine or Lysine. Especially, the free NH₂ group from a Lysine amino acid or of the terminal amino acid within the peptidic polymer is used as attachment points for chemicals containing aldehyde, ene one, ketone, or acid or halogene moieties

Also suitable compound are the amino acid derivatives selected from tyrosine ethylate, glycine methylate, tryptophane ethylate and mixture thereof,

These peptidic polymers can be attached to the amino acid sequence comprising a cellulose binding domain, by recombinant technology. An example of the recombinant technique describing the expression of an enzyme with the CBD of

different origin is described in S. Karita et al., (1996) Journal of Fermentation and Bioengineering, Vol. 81, No. 6, pp. 553-556. The polyreactive linking region can comprise from 1 to about 100 amino acid residues, in particular of from 2 to 40 amino acid residues, e.g. from 2 to 15 amino acid residues. It is preferred to use
5 amino acids which are less favoured by the surrounding proteases. Indeed, any combination of amino acids can be selected to achieve maximal weight efficiency and protease stability.

As stated above, some chemical components are linked to these cellulose
10 binding domains, linking regions and/or polyreactive linking regions via a weak bond. Said weak bond is a bond which can be enzymatically cleaved, oxidised, cleaved by light radiation and/or hydrolysed during or after the wash/fabric care process in order to release the chemical component(s). Examples of weak bonds are Schiff-base or beta-amino-ketone linking.

15

The chemical components

The chemical component of the present invention may be encapsulated. Suitable
20 encapsulating material includes starches, poly(vinylacetate), urea/formaldehyde condensate based materials. Especially suitable encapsulating materials are water soluble capsules which consist of a matrix of polysaccharide and polyhydroxy compounds such as described in GB 1,464,616. Other suitable water soluble encapsulating materials comprise dextrans derived from
25 ungelatinized starch acid-esters of substituted dicarboxylic acids such as described in US 3,455,838. These acid-ester dextrans are, preferably, prepared from such starches as waxy maize, waxy sorghum, sago, tapioca and potato. Suitable examples of said encapsulating materials include N-Lok manufactured by National Starch. The N-Lok encapsulating material consists of a modified
30 maize starch and glucose. The starch is modified by adding monofunctional substituted groups such as octenyl succinic acid anhydride.

Perfumes

35

Most consumers have come to expect scented laundry products and to expect that fabrics which have been laundered also have a pleasing fragrance. It is also desired by consumers for laundered fabrics to maintain the pleasing fragrance over time. Perfume additives make laundry compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the amount of perfume carry-over from an aqueous laundry bath onto fabrics is often marginal and does not last long on the fabric. Fragrance materials are often very costly and their inefficient use in rinse added fabric softener compositions and ineffective delivery to fabrics from the rinse results in a very high cost to both consumers and fabric softener manufacturers. Industry, therefore, continues to seek with urgency for more efficient and effective fragrance delivery in fabric softener products, especially for improvement in the provision of long-lasting fragrance to the rinsed fabrics. Therefore, industry continues to seek improved alternatives for generating fragrances through economic and effective means.

The present invention encompasses a perfume entity comprising more than one chemical components wherein at least one component is a perfume compound, linked to an amino acid sequence comprising a cellulose binding domain. The perfume compound is linked to the CBD, linking region and/or polyreactive linking region via a weak bond. It is believed that high substantivity of the perfume will be achieved by linking perfume compounds to a CBD. A complex of several perfumes with different perfumery notes can be formed. Also encompassed in the present invention are laundry detergent and/or fabric care compositions comprising one or more of these perfume entities.

Without wishing to be bound by theory, it is believed that the slow hydrolysis of the CBD-perfume direct or indirect linking will improve the release of the perfume. Indeed, after the wash or fabric care process, the weak bond will be hydrolysed and the perfume will be released. It has been surprisingly found that such perfume entities provide pleasing, long-lasting fragrance, through economic and effective means.

For example, it is known that alcohols represent key notes in perfumery. However, many alcohols are too volatile to remain in a perceptible way on dry fabrics and/or are not sufficiently fabric substantive to deposit on fabric in an

optimum way such as in a softening through-the-wash process. The linking of these perfumery alcohols to the CBD, linking region and/or polyreactive linking region can be achieved for instance via an ester bond to a carboxylic group of the polyreactive linking region or to a molecule of succinic acid which is itself
5 linked to an hydroxy group of the polyreactive linking region.

A further example are the perfumery aldehydes known to provide a fresh note on fabrics and especially on dry fabrics. However many perfumery aldehydes do not deposit substantially enough on the fabrics and/or are too volatile. A known
10 solution to the art consists in using a second perfumery material containing an amine group to form a Schiff base. Said Schiff bases present a higher residuality on the fabrics but do not have fabric substantivity and cause a change in the aldehyde perfume character.

Such perfume entities provide high fabric substantivity which results in the
15 reduction of the perfume waste in the wash of fabric care drain and in increased perfume retention on the fabrics, i.e., increased through the wash deposition. Moreover, these perfume entities provide significant release of the perfume on laundered dry fabrics. Furthermore, the amine groups encompassed within the CBD, linking region and/or polyreactive linking region of the present invention do
20 not have any odour impact nor change the perfume character.

Generally, these perfume entities will be comprised at a level of 0% to 10%, preferably 0% to 3%, more preferably 0% to 1% by weight of the total composition.

25

Fully-formulated fragrance can be prepared using numerous known odorant ingredients of natural or synthetic origin. The range of the natural raw substances can embrace not only readily-volatile, but also moderately-volatile and slightly-volatile components and that of the synthetics can include
30 representatives from practically all classes of fragrant substances, as will be evident from the following illustrative compilation. In this list of perfume ingredients, some are commercial names conventionally known to one skilled in the art, and also includes isomers. Such isomers are also suitable for use in the present invention. A typical disclosure of suitable ketone and/or aldehydes,
35 traditionally used in perfumery, can be found in "perfume and Flavor Chemicals", Vol. I and II, S. Arctander, Allured Publishing, 1994, ISBN 0-931710-35-5.

Preferred for the purpose of the present invention are the aldehydes or ketones based products.

- Natural products such as tree moss absolute, basil oil, citrus fruit oils (such as bergamot oil, mandarin oil, etc.), mastix absolute, myrtle oil, palmarosa oil, patchouli oil, petitgrain oil Paraguay, wormwood oil;
- Alcohols such as farnesol, geraniol, linalool, nerol, phenylethyl alcohol, rhodinol, cinnamic alcohol;
- Aldehydes such as citral, Helional™, alpha-hexyl-cinnamaldehyde, hydroxycitronellal, Lilial™ (p-tert.butyl-alpha -methyldihydrocinnamaldehyde), methylnonylacetaldehyde, 1-decanal, benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde; cis/trans-3,7-dimethyl-2,6-octadien-1-al; heliotropin; 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde; 2,6-nonadienal; alpha-n-amyl cinnamic aldehyde, P.T. Bucinal, lyral, cymal, methyl nonyl acetaldehyde, hexanal, trans-2-hexenal, and mixture thereof;
- Ketones such as allylionone, alpha-ionone, beta -ionone, isoraldein (isomethyl-alpha -ionone), methylionone, Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-Ionone, Iso-E-Super, 2,4,4,7-Tetramethyloct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof;
- Esters such as allyl phenoxyacetate, benzyl salicylate, cinnamyl propionate, citronellyl acetate, citronellyl ethoxolate, decyl acetate, dimethylbenzylcarbonyl acetate, dimethylbenzylcarbonyl butyrate, ethyl acetoacetate, ethyl acetylacetate, hexenyl isobutyrate, linalyl acetate, methyl dihydrojasmonate, styrallyl acetate, vetiveryl acetate, etc.;
- Lactones such as gamma-undecalactone, various components often used in perfumery, such as musk ketone, indole, p-menthane-8-thiol-3-one, and methyl-eugenol;
- Acetals and ketals include the well-known methyl and ethyl acetals and ketals, as well as acetals or ketals based on benzaldehyde, those comprising phenylethyl moieties, or more recently developed specialties such as those described in a United States Patent entitled "Acetals and Ketals of Oxo-Tetralins and Oxo-Indanes, see U.S. Pat. No. 5,084,440, issued January 28, 1992, assigned to Givaudan Corp. ;
- Recent synthetic specialties include the enol ethers of alkyl-substituted oxo-tetralins and oxo-indanes as described in U.S. Pat. 5,332,725, July 26, 1994,

assigned to Givaudan; or Schiff Bases as described in U.S. Pat. 5,264,615, December 9, 1991, assigned to Givaudan.

5 **Hygiene agent**

Sanitisation includes all positive effects obtained by the inhibition or reduction of microbial activity on fabrics and other surfaces, such as the prevention of malodour development and bacterial/fungal growth. For example, it provides
10 prevention of malodour development on stored and weared fabrics. In particular, the composition of the invention will inhibit or at least reduce the bacterial and/or fungal development on moist fabric waiting for further laundry processing and thereby preventing the formation of malodour. The term hygiene agents herein encompasses fungicides and antimicrobials that when applied to fabric
15 respectively prevent or reduce the growth of fungi or bacteria. The sanitisation benefits of the laundry detergent and/or fabric care compositions of the present invention can be evaluated by the Minimum Inhibitory Concentration (MIC) as described in Tuber. Lung. Dis. 1994 Aug; 75(4):286-90; J. Clin. Microbiol. 1994 May; 32(5):1261-7 and J. Clin. Microbiol. 1992 Oct; 30(10):2692-7.

20 The present invention encompasses an hygiene agent entity. This hygiene agent entity comprises more than one chemical components wherein at least one component is a hygiene agent, linked to an amino acid sequence comprising a Cellulose Binding Domain. The hygiene agent will be linked to the CBD, linking
25 region and/or polyreactive linking region via weak bond in order to release the active material upon time during or after the wash or fabric care process. Such hygiene agent entity can be incorporated in a laundry detergent and/or fabric care composition of the present invention. Preferably, the hygiene agent comprises an hydroxyl, carboxyl or aldehyde reactive moiety. It has been
30 surprisingly found that such hygiene agent entities provide long lasting and efficient control of the micro-organism growth on stored and weared fabrics.

Preferred antibacterial compounds are pentadecanol, cinamaldehyde, ionone, glutaraldehyde, citronellal. Other suitable antimicrobial compounds with an
35 hydroxyl, carboxyl or aldehyde moiety are described in Parfums Cosmétiques Actualités No 125, Nov, 1995, 51-4. Other suitable antibacterial components are

the Nerodol which can for example be linked to the carboxylic groups or succinic acid linked to the alcohol group of the CBD, linking region and/or polyreactive linking region. A further example are the compounds Cipamaldehyde and/or Beta ionone which can form for example a Schiff base or β -amino ketone with the NH₂ groups of the CBD, linking region and/or polyreactive linking region.

Also suitable are the microbicidally active ingredients described in the handbook of Disinfectants and Antiseptics edited by J.M. Ascenzi and in WO97/46218 such as 2-hydroxydiphenyl ether, phenol derivatives, diphenyl compounds, benzyl alcohols, chlorhexidine, C12-14 alkylbetaines and C8-18 fatty acid amido alkylbetaines, amphoteric surfactants, trihalocarbanilides and quaternary ammonium salts. Also suitable are the cationic germicides described in EP 843 002 and in WO98/24314 and the antibacterial agents triclosan, triclocarban, DMDM hydantoin, piroctone olamine, zinc pyrithione, selenium disulfide, climnazole and 3-methyl-4-(1-methylethyl)phenol also therein described. Other examples of suitable fungicides are given in WO94/10286 (Henkel), CA943 429 (Unilever) and US3,426,024 (Henkel). Preferred antimicrobials are 2-thiocyanomethylthiobenzothiazole (Busan 30 WB ex Buckmann), butyl 4-hydroxybenzoate (Butyl Parabens ex Nipa Labs), propyl 4-hydroxybenzoate (Propyl Parabens ex Nipa Labs), Terpineol, Borneol, Fenchyl alcohol, trichlorocarbanilidem, Irgasan DP300 (2,4,4'-trichloro 2'-hydroxydiphenylether) and the higher homologues of hydroxybenzoate esters. Further examples of bactericides used in the hygiene agent entities of this invention include formaldehyde, 2-bromo-2-nitro-propane-1,3-diol sold by Inolex Chemicals, located in Philadelphia, Pennsylvania, under the trade name Bronopol[®], and a mixture of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazoline-3-one sold by Rohm and Haas Company under the trade name Kathon.

Also suitable are the agents illustrated in this compilation : 1- or 2-hexadecanol, 2-tetradecanol, 1-pentadecanol, 1-Undecanol, 2-dodecanol, 1-Tridecanol, nerolidiol, hinokitiol, tropolone, berberine, citronellic acid, Curcumin, 2-Mercaptopyridine N-oxide, Ellagic acid (dihydrate), 3-t-Butyl-5-methyl salicylic acid, 3-, 4- or 5-methyl salicylic acid, 1-nonanol, Decylalcohol, Cinamaldehyde, S- or R-Citronellal, Citronellol, Beta-ionone, Thujone, Coumarin and derivatives, Geraniol, Citral, Thymol, Iso-butyl- or Isopropyl-quinoline, 2-butyl-5-methylphenol, 2-Mercapto-3-pyrodinol, Perillyl alcohol, 6-hydroxy-1,3-benzoxathiol-2-one,

BOAT, (Iso)-Eugenol, Menth-1-en-9-ol, 2-t-Butyl-4-methylphenol, Kojic acid, Camphene, Carveol, Dihydroxycarvecol, Isojasnone, Methol, Cineol, Terpinol, Camphor, 2-t-Butyl-methyl phenol, 2-Tridecanone, Acetyl salicylic acid, Salicylaldoxime, Undecyclenic aldehyde, Nerol, 3,5,5-trimethyl-1-hexanol, Adipic
5 acid, Thiosalicylic acid, OH-Benzoic acid, 2-Methylbenzothiazole, 2-Aminobenzothiazole, Caryophyllene, Allyl-isocyanate, Carvone, Alpha-pinene, Salicylic acidfrole, Alpha-ionone, 2OH- or 3OH-Phenethyl alcohol, Trimethoxy BP, Undecylic aldehyde, Cineole, Anisaldehyde, Bornyl acetate, Salicylhydroxamic, Benzofuran Car., Syringaldehyde.

10

Preferably, the levels of hygiene agent entity should be such that they prevent bacterial and fungi growth on fabrics, rather than merely preventing growth within the laundry detergent and/or fabric care compositions per se. Generally, this hygiene agent entity will be comprised at a level of 0% to 10%, preferably
15 0.00001% to 5%, more preferably 0.01% to 1% by weight of the total composition.

Insect Control agent

20 The present invention encompasses insect control agent entities. This insect control agent entity comprises more than one chemical components wherein at least one component is an insect control agent, linked to an amino acid sequence comprising a Cellulose Binding Domain. Laundry detergent and/or fabric care compositions of the present invention can comprise such insect
25 control agent entity. It has been surprisingly found that such insect control agent entities provide long lasting insect control by the slow release of the insect control agent.

Such insect control agents are linked to the CBD, linking region and/or
30 polyreactive linking region preferably via a weak bond in order to release upon time the active material. For example, these materials can be linked to the NH₂ group present in the CBD, linking region and/or polyamino polymer via a Schiff base or Michael reaction.

35 The term insect control agent refers to both insecticides and insect repellents either individually or as mixtures. Examples of insect repellents can be found in

Kirk-Othmer Encyclopedia of Chemical technology, Fourth edition, volume 13, pages 474 to 478. Suitable insect repellents include aldehyde based compounds such as Citronellal and Rotundial, ene one based compounds such as Butopyronoxyl (Indalone TM), benzyl benzoate, bioallethrin and dimethrin, N,N-diethyl toluamide ("DEET"), N,N-diethyl benzamide, p-menthane-3,8-diol, 1S,3S,4S,6S-carene-3,4diol (Sumitomo - US5,130,136), 1-piperidinecarboxylic acid, 2-(2-hydroxyethyl)-, 1-methylpropylester, 1-(3cyclohexen-1-yl carbonyl)-2methylpiperidine, 1-(3-cyclohexen-1-yl carbonmyl) piperidine, N,N-diethyl mandelamide, isopulegol hydrate, ethyl-3(N-butyl-N-acetyl) aminopropionate, diisopropyladipate, α -biasal, psearmint oil, benzyl alcohol, N,N-diethylphenylacetamide, vitamin E, citronella oil, coconut oil, cedar oil, geraniol, lemon grass oil, thyme oil, reosemary oil, mint oil, geranium oil, eugenol, 3-acetyl-2-(2-,6-dimethyl-5-heptenyl) oxazolidine, (2-hydroxymethylcyclohexyl)acetic acid lactone and eucalyptol. Other insect control agents are based on pyrethroid insecticides, in particular 3-phenoxybenzyl-DL-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane-carboxylate (permethrin). WO98/17772 describes the insect repellent agent 3-(N-butylacetamino) ethyl propionate for use in detergents.

Preferred insect repellents are aldehyde based compounds such as Citronellal and Rotundial.

These insect control agent entities are generally comprised in the laundry detergent and/or fabric care compositions of the present invention at a level of from 0.1% to 20%, preferably 0.1% to 10%, more preferably 0.1% to 6% by weight of the composition.

Bleaching agent

The present invention encompasses a bleaching entity comprising more than one chemical components wherein at least one component is a bleaching agent, linked to an amino acid sequence comprising a cellulose binding domain. Said bleaching agent can be selected from hydrophilic bleach activator, hydrophobic bleach activator, metal catalyst and/or photoactivated bleach. It has been surprisingly found that the bleaching action with such bleaching entities results in improved stain/soil bleaching/removal and whiteness maintenance. Also

encompassed in the present invention, are laundry detergent and/or fabric care compositions comprising such a bleaching entity.

Without wishing to be bound by theory, it is believed that improved stain/soil
5 bleaching/removal and whiteness maintenance results in the generation of oxygen radical, peracetic acid or peracid perhydrolysis occurring very close the fabric. Said peracetic acid or peracid is less dilute in the wash solution and thereby improve the bleaching action on the fabric.

10 Preferably, the bleach activator is linked to the CBD via a linking region, more preferably via a polyreactive linking region. Without wishing to be bound by theory, it is believed that the presence of such linking region and/or polyreactive linking region provides some flexibility to the bleach activator that can move around the CBD and perform more efficiently on the fabric its bleaching action.

15

1) Hydrophilic bleach activator : For example, Tetra Acetyl Ethylene Diamine (TAED) is a current bleach activator used in laundry detergent and forms peracetic acid in presence of H₂O₂. It is known that the two NH₂ groups of the Ethylene Diamine are diacetylated to form TAED. Without wishing to be bound by
20 theory, it is believed that the diacetylation of the free NH₂ groups of the CBD, linking region or polyreactive linking region, forms a substantive fabric hydrophilic bleach activator. Hydrophilic bleach activator of the TAED type can be linked for example via a diacetylation reaction to any NH₂ groups of the CBD, linking region and/or polyreactive linking region of the present invention.

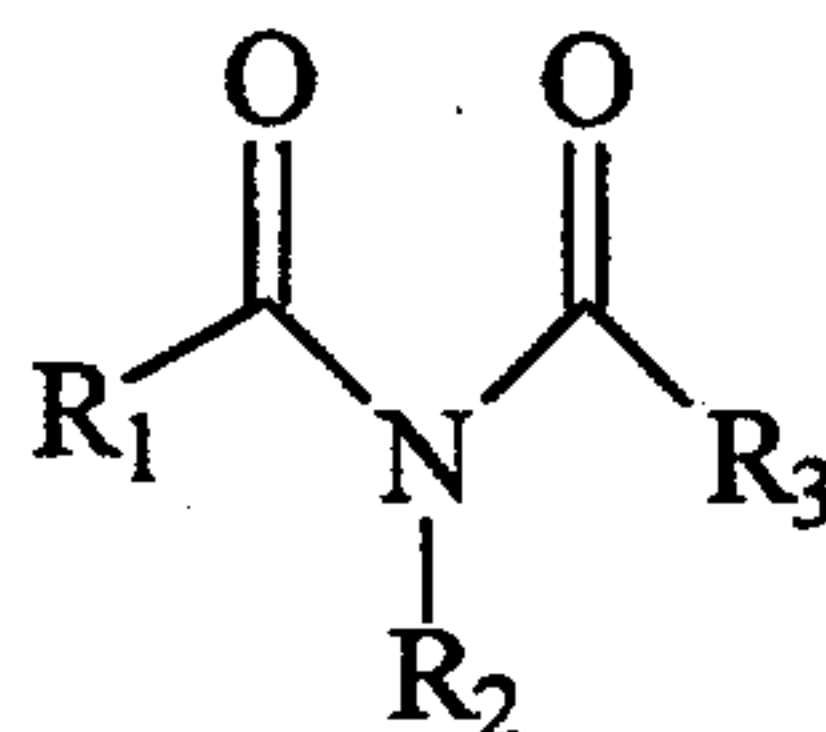
25

2) Hydrophobic bleach activators such as Nonanoyl benzene sulphonate, are current bleach activators used in laundry detergent. It has been surprisingly found that the phenolic moiety can be replaced by the one present in the tyrosine amino acid present in the CBD, linking region and/or polyreactive linking region.
30 Active hydrophobic bleach activator precursors such as nonanyl unit can be linked to the phenol group of an amino acid such as tyrosine present in the peptidic CBD, linking region and/or polyreactive linking region. Similarly, if there is no phenol entity available in the CBD, linking region and/or polyreactive linking region, a phenol unit can be linked to a group NH₂ in this CBD, linking region
35 and/or polyreactive linking region. Hydrophobic bleach activators in general can

be linked to the CBD, linking region and/or polyreactive linking region for example by a reaction on NH₂ groups.

Other examples of suitable hydrophobic bleach activators are : nonanoyloxybenzene-sulfonate (NOBS, described in US 4,412,934), 3,5,-
 5 trimethylhexanoloxybenzenesulfonate (ISONOBS, described in EP 120,591) or pentaacetylglucose (PAG) or Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid (NACA-OBS, described in WO94/28106), which are perhydrolyzed to form a peracid as the active bleaching species, leading to improved bleaching effect.

10 Also suitable bleach activators are the activators based on a caprolactam leaving group such as benzoyl caprolactam and quaternary ammonium hexanoyl caprolactam; the imides activators such as N-nonanoyl-N-methyl acetamide and unsymmetrical acyclic imide bleach activator of the following formula as disclosed in the Procter & Gamble co-pending patent applications US serial No. 60/022,786
 15 (filed July 30, 1996) and No. 60/028,122 (filed October 15, 1996) :



wherein R₁ is a C₇-C₁₃ linear or branched chain saturated or unsaturated alkyl group, R₂ is a C₁-C₈, linear or branched chain saturated or unsaturated alkyl group and R₃ is a C₁-C₄ linear or branched chain saturated or unsaturated alkyl
 20 group.. These bleach activators can for example be linked to any NH₂ groups of the polyreactive linking region.

Also suitable are the pre-formed peracid such as nonylamido peroxy adipic acid and N,N-phthaloylaminoperoxy caproic acid and the Di-acyl peroxides such as dibenzoyl peroxide.

25

3) Metal catalysts : The third type of bleach activator that can be linked to one or more CBD(s) are the below described metal catalysts. For example, these catalysts can be linked via their capping cyclo azo moieties to NH₂ groups of the CBD, linking region and/or polyreactive linking region.

30 Examples of Metal-containing catalysts for use in bleach compositions, include cobalt-containing catalysts such as Pentaamine acetate cobalt(III) salts and manganese-containing catalysts such as those described in EPA 549 271; EPA 549 272; EPA 458 397; US 5,246,621; EPA 458 398; US 5,194,416 and US

5,114,611. Bleaching composition comprising a peroxy compound, a manganese-containing bleach catalyst and a chelating agent is described in the patent application No 94870206.3.

- 5 4) Photoactivated bleach : Another group of suitable bleach activators that can be linked the CBD, linking region and/or polyreactive linking region of the present invention are the photoactivated bleaches. For example, the linking can be achieved between the NH₂ groups of and the benzyls groups of these photoactivated bleaches, activated via a preliminary bromination.
- 10 Suitable photoactivated bleaching agents are the sulfonated zinc and/or aluminum phthalocyanines. These materials can be deposited upon the substrate during the washing process. Upon irradiation with light, in the presence of oxygen, such as by hanging clothes out to dry in the daylight, the sulfonated zinc phthalocyanine is activated and, consequently, the substrate is
- 15 bleached. Preferred zinc phthalocyanine and a photoactivated bleaching process are described in U.S. Patent 4,033,718. Typically, detergent compositions will contain about 0.025% to about 1.25%, by weight, of sulfonated zinc phthalocyanine.
- 20 Generally, these bleaching entity will be comprised at a level of 0% to 20%, preferably 0% to 10%, more preferably 0% to 5% by weight of the total composition.

25 In addition to this bleaching entity the compositions of the present invention can further comprise bleaching species such as hydrogen peroxide, PB1, PB4 and percarbonate with a particle size of 400-800 microns, typically be present at levels of from about 1% to about 25%.

30 ***Fabric Softening Composition Ingredients***

The present invention encompasses a fabric softening entity. This fabric softening entity comprises more than one chemical components wherein at least one component is a softening component, linked to an amino acid sequence

35 comprising a cellulose binding domain. These fabric softening entities can be incorporated in a laundry detergent and/or fabric care composition. It has been

surprisingly found that such fabric softening entities provide, refurbish or restore tensile strength, anti-wrinkle, anti-bobbling and anti-shrinkage properties to fabrics, as well as provide static control, fabric softness, colour appearance and fabric anti-wear properties and benefits.

5

Indeed in recent years, consumer desirability for durable press fabric garments, particularly cotton fabric garments, has risen. Durable press garments include those garments which resist wrinkling of the fabric both during wear and during the laundering process. Durable press garments can greatly decrease the hand work associated with laundering by eliminating ironing sometimes necessary to prevent wrinkling of the garment. However, in most commercially available durable press fabrics, the fabric's ability to resist wrinkling is reduced over time as the garment is repeatedly worn and laundered.

10

Generally, these fabric softening entities will be comprised at a level of 0% to 50%, preferably 0% to 30, more preferably 0% to 15% by weight of the total composition.

15

One suitable softening component are dialkyl units that can be linked for example, by dialkylation of the NH₂ groups comprised in the CBD, linking region an/or polyreactive linking region. Preferably such fabric softening entities will not comprise a weak bond.

20

Dialkyl units suitable for the compositions of the present invention can be extracted from the following cationic softening surfactants currently used in the laundry detergent and/or fabric care context.

The alkyl, or alkenyl chain must contain at least 11 carbon atoms, preferably at least 16 carbon atoms. The chain may be straight or branched. Specific examples of the alkyl or alkenyl chains herein include :

25

1) N,N-di(tallowyl-oxy-ethyl);

2) N,N-di(2-tallowyloxy-2-oxo-ethyl);

3) N,N-di(2-tallowyloxyethylcarbonyloxyethyl);

4) N-(2-tallowyloxy-2-ethyl)-N-(2-tallowyloxy-2-oxo-ethyl);

5) N-(2-tallowyloxy-2-oxoethyl)-N-(tallowyl); and

6) 1,2-ditallowyloxy;

30

and mixtures of any of the above materials.

Preferred alkyl chains for the purpose of the present invention N,N-di(tallowoyl-oxy-ethyl), where the tallow chains are at least partially unsaturated.

5 Other suitable softening components include quaternary ammonium softening compounds having a solubility in water at pH2.5 and 20°C of less than 10g/l. It is particularly advantageous if the softening component is a quaternary ammonium compound in which at least one long chain alkyl group is connected to the quaternary ammonium compound via at least one ester link. Suitable cationic softener are described in US4,137,180 (Naik) and WO93/23510.

10

Also suitable as softening components are clay or silicone.

Suitable clays include a three layered smectite clay, preferably having a cationic exchange capacity as described in GB 1,400,898 and in USP 5,019,292. Especially preferred are clays which are 2:1 layer phyllosilicates possessing a
15 lattice charge efficiency in the range of 0.2 to 0.4g equivalent per half unit cell as described in EP 350 288 (Unilever).

Also encompassed in the present invention are any polymeric lubricant suitable for softening a fabric. These include silicone and in particular those described in GB1,549,180, EP 459 821 (Unilever) and EP 459 822 (Unilever).

20

Dye fixative agents

The present invention encompasses a dye fixative entity. This dye fixative entity comprises more than one chemical components wherein at least one component
25 is a dye fixative agent, linked to an amino acid sequence comprising a cellulose binding domain. Also encompassed in the present invention are laundry detergent and/or fabric care compositions comprising a dye fixative entity. It has been surprisingly found that such dye fixative entities provide improved anti-wear properties, colour appearance.

30

Indeed, coloured garments have a tendency to wear and show appearance losses. A portion of this colour appearance loss may be attributed to abrasion in the laundering process, particularly in automatic washing machines and automatic laundry dryers.

35

Dye fixing agents, or "fixatives", are well-known, commercially available materials which are designed to improve the appearance of dyed fabric by minimising the loss of dye from fabrics due to washing. Many dye fixatives are cationic, and are based on various quaternized or otherwise cationically charged organic nitrogen compounds. Fixatives are available under various trade names from several suppliers. Representative examples include: CROSCOLOR PMF (July 1981, Code No. 7894) and CROSCOLOR NOFF (January 1988, Code No. 8544) from Crosfield; INDOSOL E-50 (February 27, 1984, Ref. No. 6008.35.84; polyethyleneamine-based) from Sandoz; SANDOFIX TPS, which is also available from Sandoz and is a preferred polycationic fixative for use herein and SANDOFIX SWE (cationic resinous compound), REWIN SRF, REWIN SRF-O and REWIN DWR from CHT-Beitlich GMBH.

Other cationic dye fixing agents are described in "Aftertreatments for improving the fastness of dyes on textile fibres" by Christopher C. Cook (REV. PROG. COLORATION Vol. 12, 1982). Dye fixing agents suitable for use in the present invention are ammonium compounds such as fatty acid - diamine condensates e.g. the hydrochloride, acetate, metosulphate and benzyl hydrochloride of oleyldiethyl aminoethylamide, oylelmethyl-diethylenediaminemethsulphate, monostearyl-ethylene diaminotrimethylammonium methosulphate and oxidised products of tertiary amines; derivatives of polymeric alkyldiamines, polyamine-cyanuric chloride condensates and aminated glycerol dichlorohydrins.

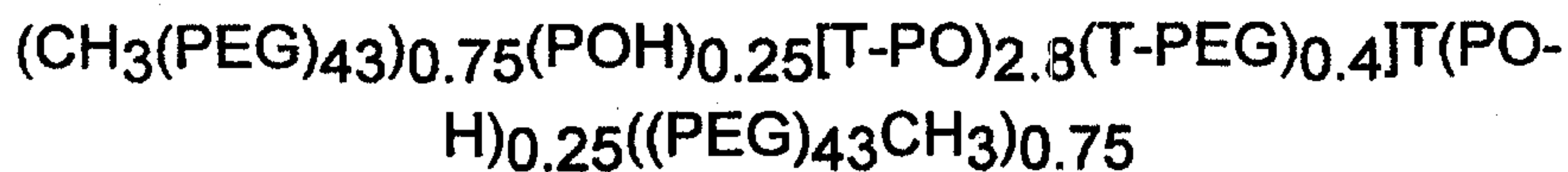
The amount of dye fixing entities to be employed in the composition of the invention is preferably from about 0.01% to about 15% by weight of the composition, more preferably from about 0.1% to about 15% by weight, most preferably from about 0.25% to about 10% by weight of the composition.

Soil release polymers

The present invention encompasses a soil release entity. This soil release entity comprises more than one chemical components wherein at least component is a soil release material, linked to an amino acid sequence comprising a cellulose binding domain. It has been surprisingly found that such modified soil release material provide better deposition of the soil release agent onto the fabric and therefore better soil release performance. Also encompassed in the present

invention are laundry detergent and/or fabric care compositions comprising a soil release entity.

The soil release material suitable in the present invention are ethylene glycols
 5 oligomers, polyethylene glycol and derivatives such as transesterified
 polyethylene glycols, and propylene polyoxy ethylene. Other suitable soil release
 agents useful in compositions of the present invention are conventionally
 copolymers or terpolymers of terephthalic acid with ethylene glycol and/or
 propylene glycol units in various arrangements. Examples of such polymers are
 10 disclosed in the commonly assigned US Patent Nos. 4116885 and 4711730 and
 European Published Patent Application No. 0 272 033. A particular preferred
 polymer in accordance with EP-A-0 272 033 has the formula



15 where PEG is $-(\text{OC}_2\text{H}_4)_n\text{O}-$, PO is $(\text{OC}_3\text{H}_6\text{O})$ and T is $(\text{pcOC}_6\text{H}_4\text{CO})$.

Also very useful are modified polyesters as random copolymers of dimethyl
 terephthalate, dimethyl sulfoisophthalate, ethylene glycol and 1-2 propane diol,
 the end groups consisting primarily of sulphobenzoate and secondarily of mono
 20 esters of ethylene glycol and/or propane-diol. The target is to obtain a polymer
 capped at both end by sulphobenzoate groups, "primarily", in the present context
 most of said copolymers herein will be end-capped by sulphobenzoate groups.
 However, some copolymers will be less than fully capped, and therefore their end
 groups may consist of monoester of ethylene glycol and/or propane 1-2 diol,
 25 thereof consist "secondarily" of such species.

The selected polyesters herein contain about 46% by weight of dimethyl
 terephthalic acid, about 16% by weight of propane -1.2 diol, about 10% by weight
 ethylene glycol about 13% by weight of dimethyl sulfobenzoic acid and about
 15% by weight of sulfoisophthalic acid, and have a molecular weight of about
 30 3.000. The polyesters and their method of preparation are described in detail in
 EPA 311 342.

Other soil release agents currently used in the detergent context are those of
 U.S. 4,968,451, November 6, 1990 to J.J. Scheibel and E.P. Gosselink: such
 35 ester oligomers can be prepared by (a) ethoxylating allyl alcohol, (b) reacting the
 product of (a) with dimethyl terephthalate ("DMT") and 1,2-propylene glycol

("PG") in a two-stage transesterification/oligomerization procedure and (c) reacting the product of (b) with sodium metabisulfite in water; the nonionic end-capped 1,2-propylene/polyoxyethylene terephthalate polyesters of U.S. 4,711,730, December 8, 1987 to Gosselink et al, for example those produced by
5 transesterification/oligomerization of poly(ethyleneglycol) methyl ether, DMT, PG and poly(ethyleneglycol) ("PEG"); the partly- and fully- anionic-end-capped oligomeric esters of U.S. 4,721,580, January 26, 1988 to Gosselink, such as oligomers from ethylene glycol ("EG"), PG, DMT and Na-3,6-dioxa-8-hydroxyoctanesulfonate; the nonionic-capped block polyester oligomeric
10 compounds of U.S. 4,702,857, October 27, 1987 to Gosselink, for example produced from DMT, Me-capped PEG and EG and/or PG, or a combination of DMT, EG and/or PG, Me-capped PEG and Na-dimethyl-5-sulfoisophthalate; and the anionic, especially sulfoaroyl, end-capped terephthalate esters of U.S. 4,877,896, October 31, 1989 to Maldonado, Gosselink et al, the latter being
15 typical of SRA's useful in both laundry and fabric conditioning products, an example being an ester composition made from m-sulfobenzoic acid monosodium salt, PG and DMT optionally but preferably further comprising added PEG, e.g., PEG 3400. Another preferred soil release agent is a sulfonated end-capped type described in US 5,415,807.

20

Brighteners

The present invention encompasses a brightener entity. This brightener entity
25 comprises more than one chemical components wherein at least one component is a brightener, linked to an amino acid sequence comprising a cellulose binding domain. It has been surprisingly found that such brightener entity provides better deposition of the brightener onto the fabric and therefore better whiteness maintenance performance. In addition, it has been found that various brighteners
30 not currently used in the detergent field could also be used in the present invention thanks to their increased fabric substantivity, in particular during a softening-through-the-wash process. Preferably, such brightener entities will not comprise a weak bond. Also encompassed are laundry detergent and/or fabric care compositions comprising a brightener entity.

35

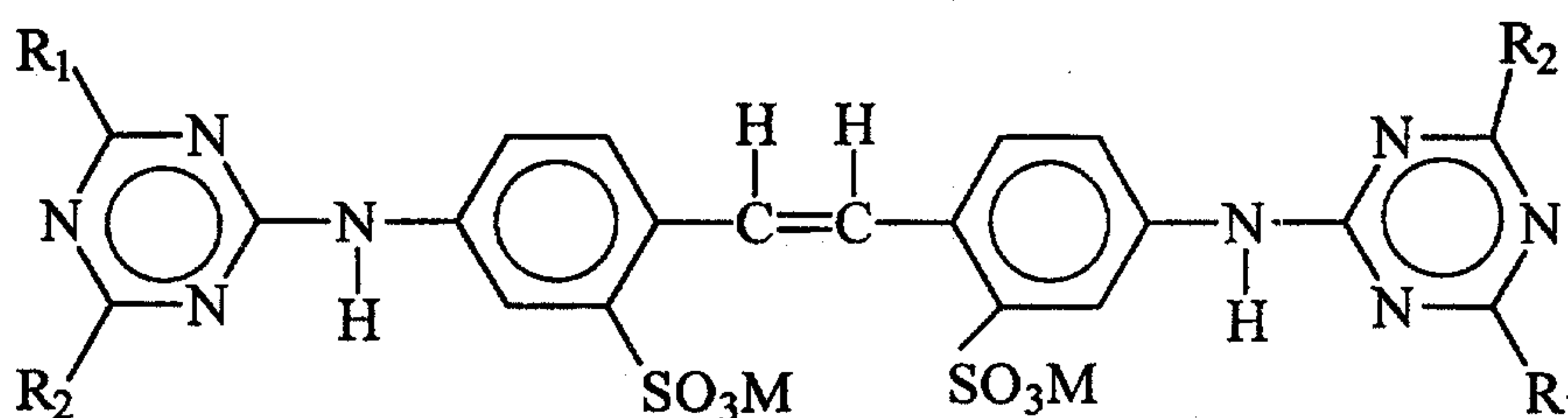
When therein included, the compositions herein may contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from about 0.001% to 3.5% by weight of such optical brighteners.

Suitable brighteners for compositions of the present invention are :

- Carbocycles types of compounds such as distyrylbenzenes, distyrylbiphenyls and divinylstilbenes,
- Triazinylaminostilbenes,
- Stilbenyl-2H-triazoles such as stilbenyl-2H-naphtol[1,2-d]triazoles and bis(1,2,3-triazol-2-yl)stilbenes,
- Benzoxazoles such as stilbenylbenzoxazoles and bis(benzoxazoles),
- Furans, Benzo[b]furnas and Benzimidazoles such as bis(benzo[b]furan-2-yl)biphenyls and cationic benzimidazoles,
- 1,3-Diphenyl-2-pyrazolines
- Coumarins
- Naphtalimides
- 1,3,5-triazin-2-yl-Derivatives.

For example, a brightener of the Coumarin type can be attached to the NH₂ group or to an amido group from the CBD, linking region or polyreactive linking region. Preferred are the bleach-stable brighteners such as 1,4-di(2-methylaminostyryl)benzene.

Other suitable brighteners that can be linked to a CBD according to the present invention are the hydrophilic optical brighteners having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino,

morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

- When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the rinse added compositions herein.

10 - When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

15 - When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Conventional detergent enzymes

25 The present invention encompasses an enzyme entity. This enzyme entity comprises more than one chemical components wherein at least one component is an enzyme which provide cleaning performance, fabric care and/or sanitisation benefits, linked to an amino acid sequence comprising a cellulose binding domain. Also encompassed are laundry detergent and/or fabric care compositions comprising an enzyme entity.

Without wishing to be bound by theory, It has been surprisingly found that said enzymes entitiy more readily attaches, affixes or otherwise comes into closer and/or more lasting contact with the fabric, thereby resulting in increased or enhanced performance of the enzyme. In particular, the laundry detergent and/or fabric care compositions of the present invention when comprising said

enzyme entities, provide improved enzymatic benefits, i.e. improved enzymatic stain removal, enhanced enzymatic fabric care and/or improved enzymatic sanitisation benefits. Said enhanced enzymatic benefits are achieved by means of a process wherein the fabric is contacted with an enzyme entity which has
5 increased affinity (relative to unmodified enzyme) for binding to a cellulosic fabric or textile.

Said enzymes include enzymes selected from cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, xylanases, lipases,
10 phospholipases, esterases, cutinases, pectinases, keratanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β -glucanases, arabinosidases, hyaluronidase, chondroitinase, laccase or mixtures thereof. A preferred combination is a cocktail of conventional applicable enzymes like protease, amylase, lipase, cutinase
15 and/or cellulase in conjunction with one or more plant cell wall degrading enzymes.

The cellulases usable in the present invention include both bacterial or fungal cellulases. Preferably, they will have a pH optimum of between 5 and 12 and a
20 specific activity above 50 CEVU/mg (Cellulose Viscosity Unit). Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, J61078384 and WO96/02653 which discloses fungal cellulase produced respectively from Humicola insolens, Trichoderma, Thielavia and Sporotrichum. EP 739 982 describes cellulases isolated from novel Bacillus species. Suitable cellulases are
25 also disclosed in GB-A-2.075.028; GB-A-2.095.275; DE-OS-2.247.832 and WO95/26398.

Examples of such cellulases are cellulases produced by a strain of Humicola insolens (Humicola grisea var. thermoidea), particularly the Humicola strain DSM 1800.

30 Other suitable cellulases are cellulases originated from Humicola insolens having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids; and a ~43kD endoglucanase derived from Humicola insolens, DSM 1800, exhibiting cellulase activity; a preferred endoglucanase component has the amino acid sequence disclosed in PCT Patent Application No. WO 91/17243.
35 Also suitable cellulases are the EGIII cellulases from Trichoderma longibrachiatum described in WO94/21801, Genencor, published September 29,

1994. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo). Carezyme and Celluzyme (Novo Nordisk A/S) are especially useful. See also WO91/17244 and
5 WO91/21801. Other suitable cellulases for fabric care and/or cleaning properties are described in WO96/34092, WO96/17994 and WO95/24471.

Said cellulases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

10 Peroxidase enzymes are used in combination with oxygen sources, e.g. percarbonate, perborate, persulfate, hydrogen peroxide, etc and with a phenolic substrate as bleach enhancing molecule. They are used for "solution bleaching", i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are
15 known in the art, and include, for example, horseradish peroxidase, ligninase and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, WO89/09813 and in European Patent application EP No. 91202882.6, filed on November 6, 1991 and EP No. 96870013.8, filed
20 February 20, 1996. Also suitable is the laccase enzyme.

Enhancers are generally comprised at a level of from 0.1% to 5% by weight of total composition. Preferred enhancers are substituted phenothiazine and phenoxazine 10-Phenothiazinepropionicacid (PPT), 10-ethylphenothiazine-4-carboxylic acid (EPC), 10-phenoxazinepropionic acid (POP) and 10-
25 methylphenoxazine (described in WO 94/12621) and substituted syringates (C3-C5 substituted alkyl syringates) and phenols. Sodium percarbonate or perborate are preferred sources of hydrogen peroxide.

Said peroxidases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent
30 composition.

Enzymatic system may be used as bleaching agents : The hydrogen peroxide may also be present by adding an enzymatic system (i.e. an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems
35 are disclosed in EP Patent Application 91202655.6 filed October 9, 1991.

Other preferred enzymes that can be included in the detergent compositions of the present invention include lipases. Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescent* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P". Other suitable commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673 from Toyo Jozo Co., Tagata, Japan; *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. Especially suitable lipases are lipases such as M1 Lipase^R and Lipomax^R (Gist-Brocades) and Lipolase^R and Lipolase Ultra^R(Novo) which have found to be very effective when used in combination with the compositions of the present invention. Also suitable are the lipolytic enzymes described in EP 258 068, WO 92/05249 and WO 95/22615 by Novo Nordisk and in WO 94/03578, WO 95/35381 and WO 96/00292 by Unilever.

Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in e.g. WO-A-88/09367 (Genencor); WO 90/09446 (Plant Genetic System) and WO 94/14963 and WO 94/14964 (Unilever).

The lipases and/or cutinases are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition.

Suitable proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis* (subtilisin BPN and BPN'). One suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold as ESPERASE[®] by Novo Industries A/S of Denmark, hereinafter "Novo". The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 to Novo. Other suitable proteases include ALCALASE[®], DURAZYM[®] and SAVINASE[®] from Novo and MAXATASE[®], MAXACAL[®], PROPERASE[®] and MAXAPEM[®] (protein

engineered Maxacal) from Gist-Brocades. Proteolytic enzymes also encompass modified bacterial serine proteases, such as those described in European Patent Application Serial Number 87 303761.8, filed April 28, 1987 (particularly pages 17, 24 and 98), and which is called herein "Protease B", and in European Patent
5 Application 199,404, Venegas, published October 29, 1986, which refers to a modified bacterial serine proteolytic enzyme which is called "Protease A" herein. Suitable is the protease called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus* in which Lysine replaced arginine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine
10 at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, corresponding to WO 91/06637, Published May 16, 1991. Genetically modified variants, particularly of Protease C, are also included herein.

A preferred protease referred to as "Protease D" is a carbonyl hydrolase variant
15 having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for a plurality of amino acid residues at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101,
20 +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in WO95/10591 and in the patent application of C. Ghosh, et al, "Bleaching Compositions Comprising Protease Enzymes" having US Serial No. 08/322,677,
25 filed October 13, 1994. Also suitable is a carbonyl hydrolase variant of the protease described in WO95/10591, having an amino acid sequence derived by replacement of a plurality of amino acid residues replaced in the precursor enzyme corresponding to position +210 in combination with one or more of the following residues : +33, +62, +67, +76, +100, +101, +103, +104, +107, +128,
30 +129, +130, +132, +135, +156, +158, +164, +166, +167, +170, +209, +215, +217, +218, and +222, where the numbered position corresponds to naturally-occurring subtilisin from *Bacillus amyloliquefaciens* or to equivalent amino acid residues in other carbonyl hydrolases or subtilisins, such as *Bacillus lentus* subtilisin (co-pending patent application US Serial No. 60/048,550, filed June 04,
35 1997).

Also suitable for the present invention are proteases described in patent applications EP 251 446 and WO 91/06637, protease BLAP® described in WO91/02792 and their variants described in WO 95/23221.

See also a high pH protease from *Bacillus* sp. NCIMB 40338 described in WO 93/18140 A to Novo. Enzymatic detergents comprising protease, one or more other enzymes, and a reversible protease inhibitor are described in WO 92/03529 A to Novo. When desired, a protease having decreased adsorption and increased hydrolysis is available as described in WO 95/07791 to Procter & Gamble. A recombinant trypsin-like protease for detergents suitable herein is described in WO 94/25583 to Novo. Other suitable proteases are described in EP 516 200 by Unilever.

The proteolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.001% to 0.2%, more preferably from 0.005% to 0.1% pure enzyme by weight of the composition.

Amylases (α and/or β) can be included for removal of carbohydrate-based stains. WO94/02597, Novo Nordisk A/S published February 03, 1994, describes cleaning compositions which incorporate mutant amylases. See also WO95/10603, Novo Nordisk A/S, published April 20, 1995. Other amylases known for use in cleaning compositions include both α - and β -amylases. α -Amylases are known in the art and include those disclosed in US Pat. no. 5,003,257; EP 252,666; WO/91/00353; FR 2,676,456; EP 285,123; EP 525,610; EP 368,341; and British Patent specification no. 1,296,839 (Novo). Other suitable amylases are stability-enhanced amylases described in WO94/18314, published August 18, 1994 and WO96/05295, Genencor, published February 22, 1996 and amylase variants having additional modification in the immediate parent available from Novo Nordisk A/S, disclosed in WO 95/10603, published April 95. Also suitable are amylases described in EP 277 216, WO95/26397 and WO96/23873 (all by Novo Nordisk).

Examples of commercial α -amylases products are Purafect Ox Am® from Genencor and Termamyl®, Ban®, Fungamyl® and Duramyl®, all available from Novo Nordisk A/S Denmark. WO95/26397 describes other suitable amylases : α -amylases characterised by having a specific activity at least 25% higher than the specific activity of Termamyl® at a temperature range of 25°C to 55°C and at a pH value in the range of 8 to 10, measured by the Phadebas® α -amylase activity

assay. Suitable are variants of the above enzymes, described in WO96/23873 (Novo Nordisk). Other amylolytic enzymes with improved properties with respect to the activity level and the combination of thermostability and a higher activity level are described in WO95/35382.

- 5 The amylolytic enzymes are incorporated in the detergent compositions of the present invention a level of from 0.0001% to 2%, preferably from 0.00018% to 0.06%, more preferably from 0.00024% to 0.048% pure enzyme by weight of the composition.
- 10 The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. Origin can further be mesophilic or extremophilic (psychrophilic, psychrotrophic, thermophilic, barophilic, alkalophilic, acidophilic, halophilic, etc.). Purified or non-purified forms of these enzymes may be used. Nowadays, it is common practice to modify wild-type enzymes via
- 15 protein / genetic engineering techniques in order to optimise their performance efficiency in the laundry detergent and/or fabric care compositions of the invention. For example, the variants may be designed such that the compatibility of the enzyme to commonly encountered ingredients of such compositions is increased. Alternatively, the variant may be designed such that the optimal pH,
- 20 bleach or chelant stability, catalytic activity and the like, of the enzyme variant is tailored to suit the particular cleaning application.

In particular, attention should be focused on amino acids sensitive to oxidation in the case of bleach stability and on surface charges for the surfactant

25 compatibility. The isoelectric point of such enzymes may be modified by the substitution of some charged amino acids, e.g. an increase in isoelectric point may help to improve compatibility with anionic surfactants. The stability of the enzymes may be further enhanced by the creation of e.g. additional salt bridges and enforcing calcium binding sites to increase chelant stability.

30

Said enzymes are normally incorporated in the detergent composition at levels from 0.0001% to 2% of pure enzyme by weight of the detergent composition. The enzymes can be added as separate single ingredients (prills, granulates, stabilized liquids, etc. containing one enzyme) or as mixtures of two or more

35 enzymes (e.g., cogramulates).

Other suitable chemical components

Other chemical components to be linked to a cellulose binding domain in accordance with the present invention are latex and resins. Latex are defined as a material suitable for improving the drape of fabric. Suitable materials include a polyvinylacetate homopolymer such as 9802 (Vinamul). Resins prevent the formation of pills on the fabrics. Suitable resins are Knittex BE from Ciba-Geigy or silicas such as Crosanol NS from Crosfield.

10

The Cellulose Binding Domain (CBD)

In the present context, the terms "Cellulose Binding Domain or CBD" are intended to indicate an amino acid sequence capable of effecting binding of the cellulase to a cellulosic substrate (e.g. as described in P. Kraulis et al., Determination of the three-dimensional structure of the C terminal domain of cellobiohydrolase I from *Trichoderma reesei*. A study using nuclear magnetic resonance and hybrid distance geometry-dynamically simulated annealing. Biochemistry 28:7241-7257, 1989). The classification and properties of cellulose binding domains are presented in P. Tomme et al., in the symposium "Enzymatic degradation of insoluble polysaccharides" (ACS Symposium Series 618, edited by J.N. Saddler and M.H. Penner, ACS, 1995).

Cellulose-binding (and other carbohydrate-binding) domains are polypeptide amino acid sequences which occur as integral parts of large polypeptides or proteins consisting of two or more polypeptide amino acid sequence regions, especially in hydrolytic enzymes (hydrolases) which typically comprise a catalytic domain containing the active site for substrate hydrolysis and a carbohydrate-binding domain for binding to the carbohydrate substrate in question. Such enzymes can comprise more than one catalytic domain and one, two or three carbohydrate-binding domains, and they may further comprise one or more polypeptide amino acid sequence regions linking the carbohydrate-binding domain(s) with the catalytic domain(s), a region of the latter type usually being denoted a "linker".

35

Examples of hydrolytic enzymes comprising a cellulose-binding domain are cellulase, xylanases, mannanases, arabinofuranosidases, acetylerases and chitinases. "Cellulose-binding domains" have also been found in algae, e.g. in the red alga *porphyra purpurea* in the form of a non-hydrolytic polysaccharide-binding protein [see P. Tomme et al., Cellulose-binding domains - Classification and Properties in Enzymatic Degradation of Insoluble Carbohydrates, John N. Saddler and Michael H. Penner (Eds.), ACS Symposium Series, No. 618 (1996)]. However, most of the known CBDs (which are classified and referred to by P. Tomme et al. (*op. cit.*) as "cellulose-binding domains") derive from cellulases and xylanases.

In the present context, the term "cellulose-binding domain" is intended to be understood in the same manner as in the latter reference (P. Tomme et al., *op. cit.*) The P. Tomme et al. reference classifies more than 120 "cellulose-binding domains" into 10 families (I-X) which may have different functions or roles in connection with the mechanism of substrate binding. However, it is to be anticipated that new family representatives and additional families will appear in the future.

In proteins/polypeptides in which CBDs occur (e.g. enzymes, typically hydrolytic enzymes such as cellulases), a CBD may be located at the N or C terminus or at an internal position. The part of a polypeptide or protein (e.g. hydrolytic enzyme) which constitutes a CBD *per se* typically consists of more than about 30 and less than about 250 amino acid residues. For example, those CBDs listed and classified in Family I in accordance with P. Tomme et al. (*op. cit.*) consist of 33-37 amino acid residues, those listed and classified in Family IIa consist of 95-108 amino acid residues, those listed and classified in Family VI consist of 85-92 amino acid residues, whilst one CBD (derived from a cellulase from *Clostridium thermocellum*) listed and classified in Family VII consists of 240 amino acid residues. Accordingly, the molecular weight of an amino acid sequence constituting a CBD *per se* will typically be in the range of from about 4kD to about 40kD, and usually below about 35kD.

Cellulose binding domains can be produced by recombinant techniques as described in H. Stålbrand et al., Applied and Environmental Microbiology, Mar.

1995, pp. 1090-1097; E. Brun et al., (1995) Eur. J. Biochem. 231, pp. 142-148; J.B. Coutinho et al., (1992) Molecular Microbiology 6(9), pp. 1243-1252

In order to isolate a cellulose binding domain of, e.g. a cellulase, several genetic engineering approaches may be used. One method uses restriction enzyme to remove a portion of the gene and then to fuse the remaining gene-vector fragment in frame to obtain a mutated gene that encodes a protein truncated for a particular gene fragment. Another method involves the use of exonucleases such as Ba131 to systematically delete nucleotides either externally from the 5' and the 3' ends of the DNA or internally from a restricted gap within the gene. These gene-deletion methods result in a mutated gene encoding a shortened gene molecule whose expression product may then be evaluated for substrate-binding (e.g. cellulose-binding) ability. Appropriate substrates for evaluating the binding ability include cellulosic materials such as Avicel™ and cotton fibres. Other methods include the use of a selective or specific protease capable of cleaving a CBD, e.g., a terminal CBD, from the remainder of the polypeptide chain of the protein in question.

Preferred CBDs for the purpose of the present invention are selected from the group consisting of : CBDs CBHII from *Trichoderma reesei*, CBD CBHI from *Trichoderma reesei* and/or CBD family 45 from *Humicola insolens*. More preferred CBD for the purpose of the present invention is the CBD originating from the fungal *Humicola Insolens* cellulase sold under the tradename "Carezyme" by Novo Nordisk A/S. Carezyme is an endoglucanase from family 45, derived from *Humicola insolens* DSM1800, having a molecular weight of about 43kDa and exhibiting cellulolytic activity.

Selected Cellulose Binding Domain (Selected CBD)

The present invention also encompasses chemical entities wherein more than one chemical components are linked to a selected cellulose binding domain. Said cellulose binding domain is selected to comprise in its amino acid sequence, at least one Lysine amino acid. The Lysine amino acid(s) and the NH₂ of the terminal amino acid will provide suitable attachment points for the chemical components.

Suitable cellulose binding domains comprising at least one Lysine amino acid from fungal origin are listed below (Please find into brackets, the gene accession code for the GENBANK database, National Center of Biotechnology Information , NIH):

- 5 CBD from *Humicola insolens* endoglucanase (A23644), CBD from the *Trichoderma longibrachiatum* EGII (X60652) for endo-1,4-beta-glucanase, CBD from the plasmid pTT11 for Endo II (A03825 mRNA), CBD from *P. janthinellum* CBHI for exo-cellobiohydrolase I (X59054), CBD from *Fusarium oxysporum* F-family cellulase (L29380), CBD from *Agaricus bisporus* cellobiohydrolase (Ce13AC) (L24520), CBD from *Humicola grisea* CBHI (D63515), CBD from *A. bisporus* (C54-carb-8) ce13a (Z34007), CBD from *Humicola grisea* CBHI (X17258), CBD from *Humicola* xylanase (AB001030), CBD from *Fusarium oxysporum* C-familiy cellulase (L29379), CBD from *Trichoderma reesei* (QM9414) endo-1,4-beta-glucanase (Z33381), CBD from *Agaricus bisporus*
- 10
- 15 cellulose-growth-specific protein (M86356), CBD from *Neurospora crassa* CBH-1 (X77778) and CBD from *Porphyra purpurea* putative polysaccharide binding domain (U08843).

- 20 Suitable cellulose binding domains comprising at least one Lysine amino acid from bacterial origin are listed below (Please find into brackets, the gene accession code for the GENBANK database, National Center of Biotechnology Information , NIH):

- CBD from *Amycolatopsis orientalis* cosmid PCZA361 (AJ223998A30), CBD from *Cellulomonas fimi* (L25809), CBD from *Streptomyces halstedii* beta-1,4-
- 25 endoglucanase (ce1A2) (U51222), CBD from *Thermonospora fusca* beta-1,4-endo-glucanase precursor (E1) (L20094), CBD from *Cellulomonas fimi* exoglucanase (Cex) (M15824), CBD from *Thermonospora fusca* beta-1,4-endo-glucanase (M73321), CBD from *Cellulomonas fimi* exo-beta-1,4-glucanase and beta-1,4-xylanase (L11080), CBD from *Cellulomonas fimi* CenB (M64644), CBD
- 30 from *Acidothermus cellulolyticus* E1 beta-1,4-endoglucanase (U33212), CBD from *Streptomyces plicatus* chitinase 63 (ChtA) (M82804), CBD from *S. lividans* for chitinase C (D12647), CBD from *Cellulomonas fimi* CenA endoglucanase (M15823), CBD from *Thermonospora fusca* beta-1,4-exocellulase (U18978), CBD from *Clostridium cellulovorans* (EngD) endoglucanase (M37434), CBD from
- 35 *Streptomyces halstedii* beta-1,4-endoxylanase (XysA) (U41627), CBD from *P. fluorescens* XynB and XynC for xylanase B and arabinofuranosidase C (X54523

or X54523A2), CBD from *Mycobacterium tuberculosis* cosmid Y39 (Z74025A32), CBD from *Thermonospora fusca* beta-1,4-endoglucanase (L01577), CBD from *P. fluorescens* xynD for esterase D (X58956), CBD from *Cellulomonas fimi* (221) ynd (X76729), CBD from *A. caulinodans* EGI (Z48958), CBD from *Fibrobacter succinognes* S85 CMC-xylanase (U94826), CBD from *Agrobacterium tumefaciens* FlaD, F1hB, FliG, FliN, FliM, MotA, FlgF, FliI (U95165 or U95165A22 or U95165A23 or U95165A24), CBD from *A. Tumefaciens* FlaA, FlaB and FlaC (X96435 or X96435A2 or X96435A3), CBD from *Shigella flexneri* FliC-SF for flagellin (D16819), CBD from *Kurthia zopfii* for chitinase (D63702),
 5 CBD from *Streptomyces halstedii* for beta-1,4-endoglucanase (ce1A2) (U51222A2), CBD from *Mycobacterium tuberculosis* cosmid SCY06H11(Z85982A24), CBD from *Sinorhizobium meliloti* FlgC, FliE, FlgG, FlgA, FlgI and FlgH (L49337A13), CBD from *Rhodobacter capsulatus* strain SB1003 (AF010496A56), CBD from *Streptomyces lividans* acetyl-xylan esterase
 10 (axeEA) and xylanase B (xlnB) (M64552 or M64552A2), CBD from *Streptomyces maltophilia* chitinase A (CHIA) (AF014950), CBD from *Thermoanaerobacterium saccharolytic* amylopullulanase(APU) (L07762), CBD from *Thermoanaerobacterium thermosulfurigenes* pullulanase (AmyB) maltose binding protein (AmyE) (M57692A2), CBD from *Clostridium thermohydrosulfuricum*
 15 amylopullulanase (apu) (M97665).

Preferred selected CBDs are selected from the group consisting of : CBDs CenC, CenA and Cex from *Cellulomonas fimi*, CBD Cellulozome from *Clostridium cellulovorans*, CBD E3 from *Thermonospora fusca*, CBD-dimer from *Clostridium stecorarium* (NCIMB11754) XynA and/or CBD from *Bacillus agaradherens* (NCIMB40482).
 25

In the instance the linking region is a peptidic polymer and/or a chemical component is an enzyme, once a nucleotide sequence encoding the substrate-binding (carbohydrate-binding) region has been identified, either as cDNA or
 30 chromosomal DNA, it may then be manipulated in a variety of ways to fuse it to a DNA sequence encoding the amino acid sequence of the polyreactive linking region and/or enzyme of interest. The DNA fragment encoding the carbohydrate-binding amino acid sequence, and the DNA encoding the amino acid of the
 35 sequence of the polyreactive linking region and/or enzyme of interest are then ligated with or without a linker. The resulting ligated DNA may then be

manipulated in a variety of ways to achieve expression. Preferred microbial expression hosts include certain *Aspergillus* species (e.g. *A. niger* or *A. oryzae*), *Bacillus* species, and organisms such as *Escherichia coli* or *Saccharomyces cerevisiae*.

5

Detergent components

10 The laundry detergent and/or fabric care compositions of the invention must contain at least one additional detergent and/or fabric care component. The precise nature of these additional components, and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

15 As already mentioned supra, all the components that may be linked to a Cellulose Binding Domain in accordance with the present invention, can also be incorporated into the laundry detergent and/or fabric care compositions of the present invention in their unmodified, conventional form.

20 The compositions of the invention may for example, be formulated as hand and machine laundry detergent compositions including laundry additive compositions and compositions suitable for use in the soaking and/or pretreatment of stained fabrics, rinse added fabric softener compositions. Pre-or post treatment of fabric include gel, spray and liquid fabric care compositions. A rinse cycle with or
25 without the presence of softening agents is also contemplated.

When formulated as compositions suitable for use in a laundry machine washing method, the compositions of the invention preferably contain both a surfactant and a builder compound and additionally one or more detergent components
30 preferably selected from organic polymeric compounds, bleaching agents, additional enzymes, suds suppressors, dispersants, lime-soap dispersants, soil suspension and anti-redeposition agents and corrosion inhibitors. Laundry compositions can also contain softening agents, as additional detergent components.

35

The compositions of the invention can also be used as detergent additive products in solid or liquid form. Such additive products are intended to supplement or boost the performance of conventional detergent compositions and can be added at any stage of the cleaning process. Therein, the levels of the ingredients can be much higher than the conventional levels.

The laundry detergent and/or fabric care compositions according to the invention can be liquid, paste, gels, bars, tablets, spray, foam, powder or granular forms. Granular compositions can also be in "compact" form, the liquid compositions can also be in a "concentrated" form. If needed the density of the laundry detergent compositions herein ranges from 400 to 1200 g/litre, preferably 500 to 950 g/litre of composition measured at 20°C.

The "compact" form of the compositions herein is best reflected by density and, in terms of composition, by the amount of inorganic filler salt; inorganic filler salts are conventional ingredients of detergent compositions in powder form; in conventional detergent compositions, the filler salts are present in substantial amounts, typically 17-35% by weight of the total composition. In the compact compositions, the filler salt is present in amounts not exceeding 15% of the total composition, preferably not exceeding 10%, most preferably not exceeding 5% by weight of the composition. The inorganic filler salts, such as meant in the present compositions are selected from the alkali and alkaline-earth-metal salts of sulphates and chlorides. A preferred filler salt is sodium sulphate.

Liquid detergent compositions according to the present invention can also be in a "concentrated form", in such case, the liquid detergent compositions according to the present invention will contain a lower amount of water, compared to conventional liquid detergents. Typically the water content of the concentrated liquid detergent is preferably less than 40%, more preferably less than 30%, most preferably less than 20% by weight of the detergent composition.

30

Surfactant system

The laundry detergent and/or fabric care compositions according to the present invention generally comprise a surfactant system wherein the surfactant can be selected from other nonionic and/or anionic and/or other cationic and/or ampholytic and/or zwitterionic and/or semi-polar surfactants.

The surfactant is typically present at a level of from 0.1% to 60% by weight. More preferred levels of incorporation are 1% to 35% by weight, most preferably from 1% to 30% by weight of laundry detergent and/or fabric care compositions in accord with the invention.

5

The surfactant is preferably formulated to be compatible with enzyme components present in the composition. In liquid or gel compositions the surfactant is most preferably formulated such that it promotes, or at least does not degrade, the stability of any enzyme in these compositions.

10

Preferred surfactant systems to be used according to the present invention comprise as a surfactant one or more of the nonionic and/or anionic surfactants described herein.

15 Polyethylene, polypropylene, and polybutylene oxide condensates of alkyl phenols are suitable for use as the nonionic surfactant of the surfactant systems of the present invention, with the polyethylene oxide condensates being preferred. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to about 14 carbon atoms,
20 preferably from about 8 to about 14 carbon atoms, in either a straight-chain or branched-chain configuration with the alkylene oxide. In a preferred embodiment, the ethylene oxide is present in an amount equal to from about 2 to about 25 moles, more preferably from about 3 to about 15 moles, of ethylene oxide per mole of alkyl phenol. Commercially available nonionic surfactants of this type
25 include IgepalTM CO-630, marketed by the GAF Corporation; and TritonTM X-45, X-114, X-100 and X-102, all marketed by the Rohm & Haas Company. These surfactants are commonly referred to as alkylphenol alkoxylates (e.g., alkyl phenol ethoxylates).

30 The condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide are suitable for use as the nonionic surfactant of the nonionic surfactant systems of the present invention. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms.
35 Preferred are the condensation products of alcohols having an alkyl group containing from about 8 to about 20 carbon atoms, more preferably from about

10 to about 18 carbon atoms, with from about 2 to about 10 moles of ethylene oxide per mole of alcohol. About 2 to about 7 moles of ethylene oxide and most preferably from 2 to 5 moles of ethylene oxide per mole of alcohol are present in said condensation products. Examples of commercially available nonionic surfactants of this type include TergitolTM 15-S-9 (the condensation product of C₁₁-C₁₅ linear alcohol with 9 moles ethylene oxide), TergitolTM 24-L-6 NMW (the condensation product of C₁₂-C₁₄ primary alcohol with 6 moles ethylene oxide with a narrow molecular weight distribution), both marketed by Union Carbide Corporation; NeodolTM 45-9 (the condensation product of C₁₄-C₁₅ linear alcohol with 9 moles of ethylene oxide), NeodolTM 23-3 (the condensation product of C₁₂-C₁₃ linear alcohol with 3.0 moles of ethylene oxide), NeodolTM 45-7 (the condensation product of C₁₄-C₁₅ linear alcohol with 7 moles of ethylene oxide), NeodolTM 45-5 (the condensation product of C₁₄-C₁₅ linear alcohol with 5 moles of ethylene oxide) marketed by Shell Chemical Company, KyroTM EOB (the condensation product of C₁₃-C₁₅ alcohol with 9 moles ethylene oxide), marketed by The Procter & Gamble Company, and Genapol LA O3O or O5O (the condensation product of C₁₂-C₁₄ alcohol with 3 or 5 moles of ethylene oxide) marketed by Hoechst. Preferred range of HLB in these products is from 8-11 and most preferred from 8-10.

20

Also useful as the nonionic surfactant of the surfactant systems of the present invention are the alkylpolysaccharides disclosed in U.S. Patent 4,565,647, Llenado, issued January 21, 1986, having a hydrophobic group containing from about 6 to about 30 carbon atoms, preferably from about 10 to about 16 carbon atoms and a polysaccharide, e.g. a polyglycoside, hydrophilic group containing from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7 saccharide units. Any reducing saccharide containing 5 or 6 carbon atoms can be used, e.g., glucose, galactose and galactosyl moieties can be substituted for the glucosyl moieties (optionally the hydrophobic group is attached at the 2-, 3-, 4-, etc. positions thus giving a glucose or galactose as opposed to a glucoside or galactoside). The intersaccharide bonds can be, e.g., between the one position of the additional saccharide units and the 2-, 3-, 4-, and/or 6- positions on the preceding saccharide units.

35 The preferred alkylpolyglycosides have the formula



wherein R^2 is selected from the group consisting of alkyl, alkylphenyl, hydroxyalkyl, hydroxyalkylphenyl, and mixtures thereof in which the alkyl groups
5 contain from about 10 to about 18, preferably from about 12 to about 14, carbon atoms; n is 2 or 3, preferably 2; t is from 0 to about 10, preferably 0; and x is from about 1.3 to about 10, preferably from about 1.3 to about 3, most preferably from about 1.3 to about 2.7. The glycosyl is preferably derived from glucose. To prepare these compounds, the alcohol or alkylpolyethoxy alcohol is formed first
10 and then reacted with glucose, or a source of glucose, to form the glucoside (attachment at the 1-position). The additional glycosyl units can then be attached between their 1-position and the preceding glycosyl units 2-, 3-, 4- and/or 6-position, preferably predominately the 2-position.

15 The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol are also suitable for use as the additional nonionic surfactant systems of the present invention. The hydrophobic portion of these compounds will preferably have a molecular weight of from about 1500 to about 1800 and will exhibit water insolubility. The addition
20 of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about 50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of
25 compounds of this type include certain of the commercially-available PlurafacTM LF404 and PluronicTM surfactants, marketed by BASF.

Also suitable for use as the nonionic surfactant of the nonionic surfactant system of the present invention, are the condensation products of ethylene oxide with
30 the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, and generally has a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from
35 about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic

surfactant include certain of the commercially available Tetronic™ compounds, marketed by BASF.

Preferred for use as the nonionic surfactant of the surfactant systems of the present invention are polyethylene oxide condensates of alkyl phenols, condensation products of primary and secondary aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide, alkylpolysaccharides, and mixtures thereof. Most preferred are C₈-C₁₄ alkyl phenol ethoxylates having from 3 to 15 ethoxy groups and C₈-C₁₈ alcohol ethoxylates (preferably C₁₀ avg.) having from 2 to 10 ethoxy groups, and mixtures thereof.

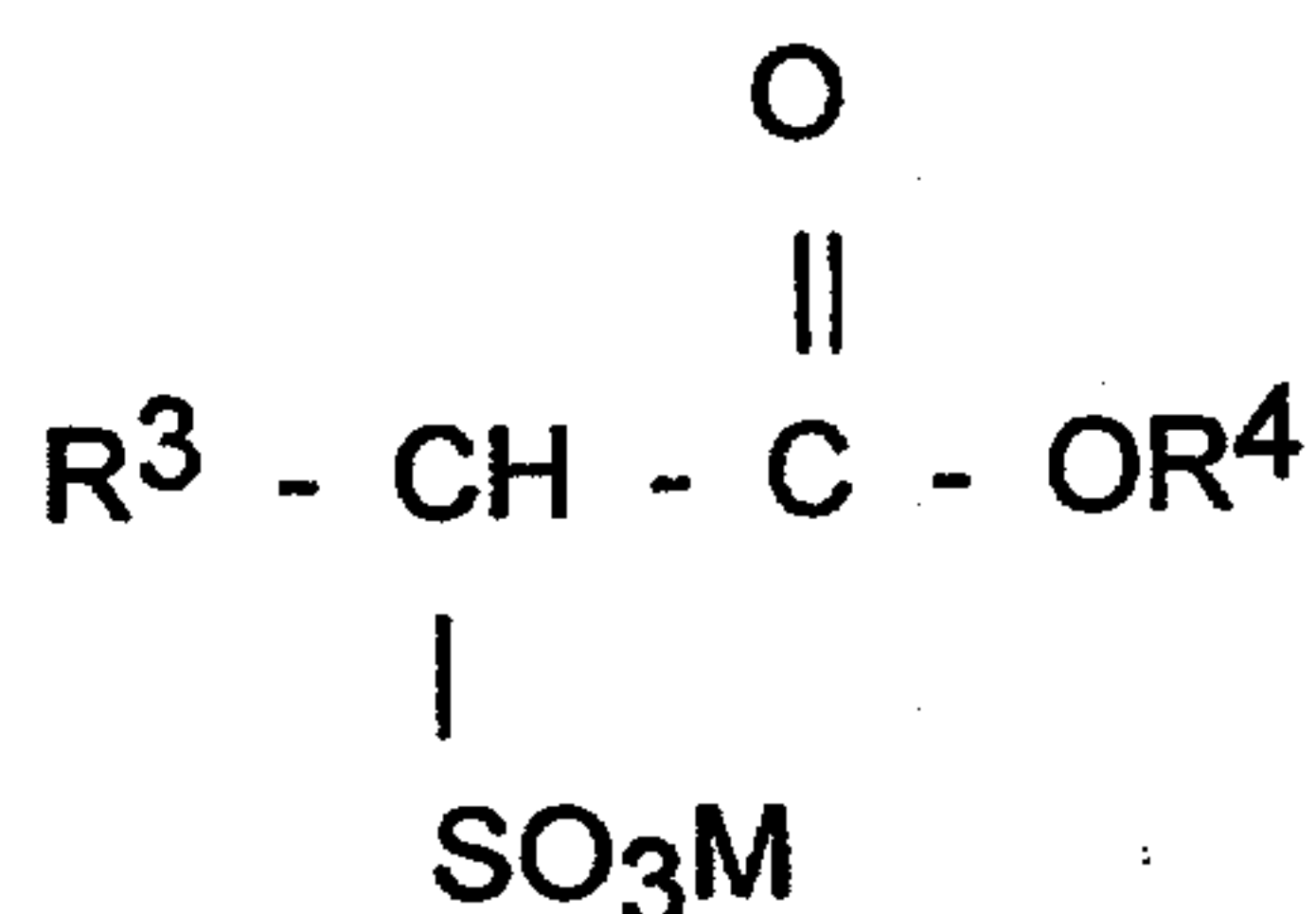
Highly preferred nonionic surfactants are polyhydroxy fatty acid amide surfactants of the formula.



wherein R¹ is H, or R¹ is C₁₋₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅₋₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof. Preferably, R¹ is methyl, R² is a straight C₁₁₋₁₅ alkyl or C₁₆₋₁₈ alkyl or alkenyl chain such as coconut alkyl or mixtures thereof, and Z is derived from a reducing sugar such as glucose, fructose, maltose, lactose, in a reductive amination reaction.

Suitable anionic surfactants to be used are linear alkyl benzene sulfonate, alkyl ester sulfonate surfactants including linear esters of C₈-C₂₀ carboxylic acids (i.e., fatty acids) which are sulfonated with gaseous SO₃ according to "The Journal of the American Oil Chemists Society", 52 (1975), pp. 323-329. Suitable starting materials would include natural fatty substances as derived from tallow, palm oil, etc.

The preferred alkyl ester sulfonate surfactant, especially for laundry applications, comprise alkyl ester sulfonate surfactants of the structural formula:



5

wherein R³ is a C₈-C₂₀ hydrocarbyl, preferably an alkyl, or combination thereof, R⁴ is a C₁-C₆ hydrocarbyl, preferably an alkyl, or combination thereof, and M is a cation which forms a water soluble salt with the alkyl ester sulfonate. Suitable salt-forming cations include metals such as sodium, potassium, and lithium, and substituted or unsubstituted ammonium cations, such as monoethanolamine, diethanolamine, and triethanolamine. Preferably, R³ is C₁₀-C₁₆ alkyl, and R⁴ is methyl, ethyl or isopropyl. Especially preferred are the methyl ester sulfonates wherein R³ is C₁₀-C₁₆ alkyl.

15

Other suitable anionic surfactants include the alkyl sulfate surfactants which are water soluble salts or acids of the formula ROSO₃M wherein R preferably is a C₁₀-C₂₄ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g. sodium, potassium, lithium), or ammonium or substituted ammonium (e.g. methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations such as tetramethylammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C₁₂-C₁₆ are preferred for lower wash temperatures (e.g. below about 50°C) and C₁₆-18 alkyl chains are preferred for higher wash temperatures (e.g. above about 50°C).

20

25

Other anionic surfactants useful for deterative purposes can also be included in the laundry detergent and/or fabric care compositions of the present invention. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C₈-C₂₂ primary or secondary alkanesulfonates, C₈-C₂₄ olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C₈-C₂₄ alkylpolyglycoethersulfates (containing up to 10 moles of

30

35

- ethylene oxide); alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinates
5 (especially saturated and unsaturated C₁₂-C₁₈ monoesters) and diesters of sulfosuccinates (especially saturated and unsaturated C₆-C₁₂ diesters), acyl sarcosinates, sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, and alkyl polyethoxy carboxylates such as those
10 of the formula RO(CH₂CH₂O)_k-CH₂COO-M⁺ wherein R is a C₈-C₂₂ alkyl, k is an integer from 1 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil.
- 15 Further examples are described in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).
- 20 When included therein, the laundry detergent compositions of the present invention typically comprise from about 1% to about 40%, preferably from about 3% to about 20% by weight of such anionic surfactants.
- Highly preferred anionic surfactants include alkyl alkoxyated sulfate surfactants
25 hereof are water soluble salts or acids of the formula RO(A)_mSO₃M wherein R is an unsubstituted C₁₀-C₂₄ alkyl or hydroxyalkyl group having a C₁₀-C₂₄ alkyl component, preferably a C₁₂-C₂₀ alkyl or hydroxyalkyl, more preferably C₁₂-C₁₈ alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and
30 about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl, trimethyl-ammonium cations and
35 quaternary ammonium cations such as tetramethyl-ammonium and dimethyl piperdinium cations and those derived from alkylamines such as ethylamine,

diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulfate (C₁₂-C₁₈E(1.0)M), C₁₂-C₁₈ alkyl polyethoxylate (2.25) sulfate (C₁₂-C₁₈E(2.25)M), C₁₂-C₁₈ alkyl polyethoxylate (3.0) sulfate (C₁₂-C₁₈E(3.0)M), and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulfate (C₁₂-C₁₈E(4.0)M), wherein M is conveniently selected from sodium and potassium.

The laundry detergent and/or fabric care compositions of the present invention may also contain cationic, ampholytic, zwitterionic, and semi-polar surfactants, as well as the nonionic and/or anionic surfactants other than those already described herein.

Cationic deterative surfactants suitable for use in the laundry detergent and/or fabric care compositions of the present invention are those having one long-chain hydrocarbyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyltrimethylammonium halogenides, and those surfactants having the formula :



20

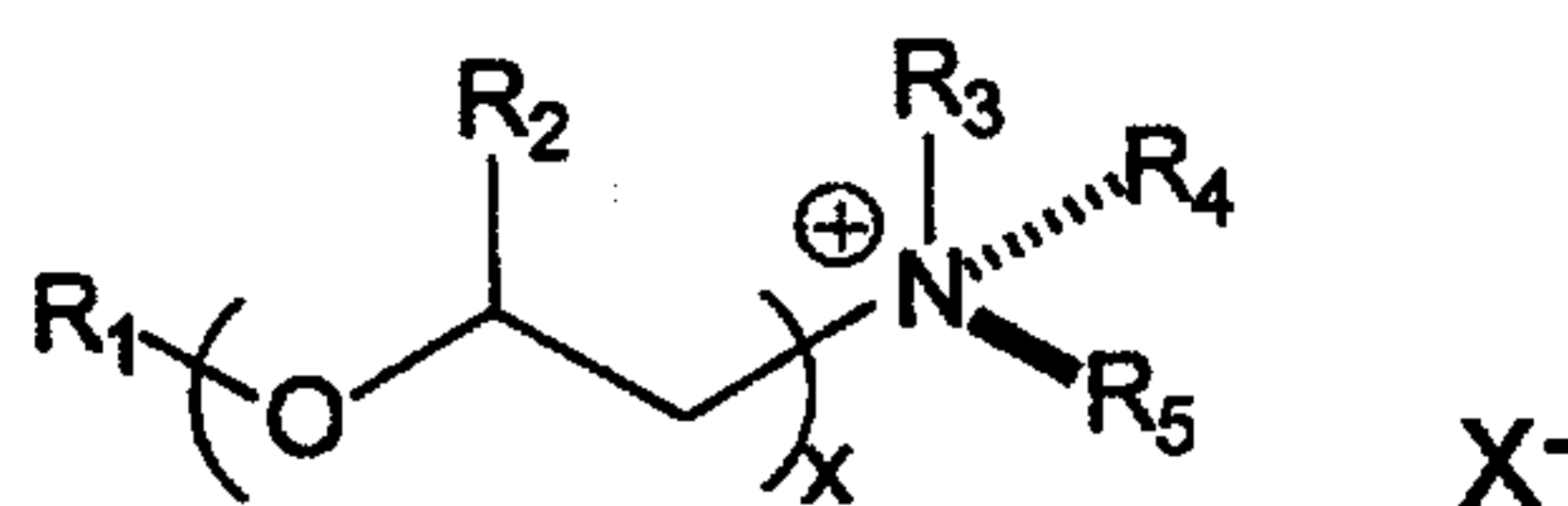
wherein R² is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R³ is selected from the group consisting of -CH₂CH₂-, -CH₂CH(CH₃)-, -CH₂CH(CH₂OH)-, -CH₂CH₂CH₂-, and mixtures thereof; each R⁴ is selected from the group consisting of C₁-C₄ alkyl, C₁-C₄ hydroxyalkyl, benzyl ring structures formed by joining the two R⁴ groups, -CH₂CHOH-CHOHCOR⁶CHOHCH₂OH wherein R⁶ is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R⁵ is the same as R⁴ or is an alkyl chain wherein the total number of carbon atoms of R² plus R⁵ is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

30

Quaternary ammonium surfactant suitable for the present invention has the formula (I):

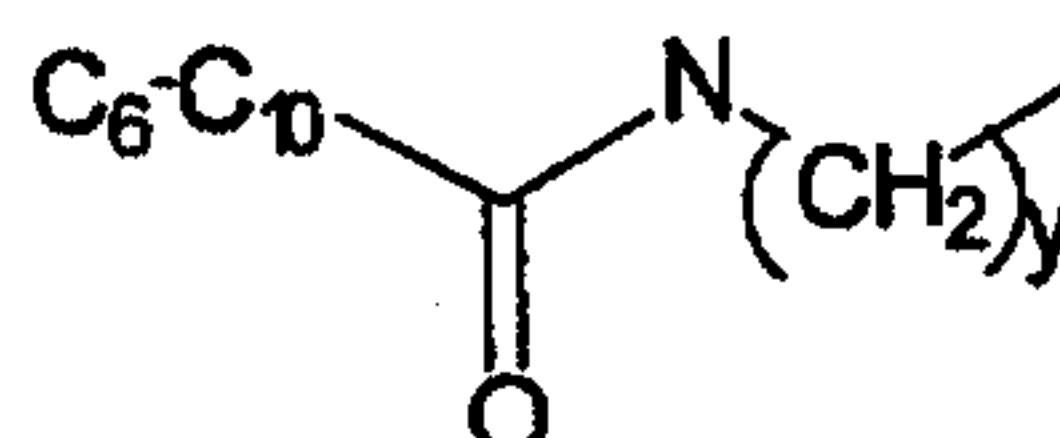
35

67



Formula I

whereby R1 is a short chainlength alkyl (C6-C10) or alkylamidoalkyl of the formula (II) :



Formula II

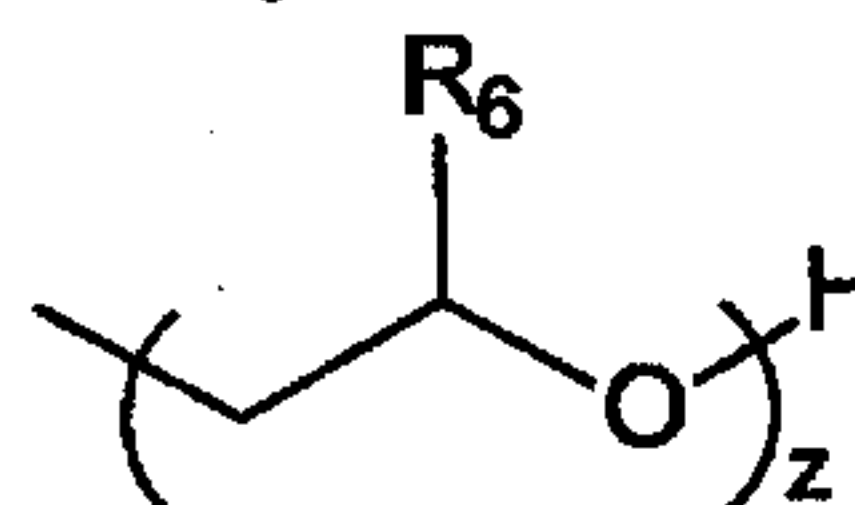
y is 2-4, preferably 3.

whereby R2 is H or a C1-C3 alkyl,

10 whereby x is 0-4, preferably 0-2, most preferably 0,

whereby R3, R4 and R5 are either the same or different and can be either a short chain alkyl (C1-C3) or alkoxylated alkyl of the formula III,

whereby X⁻ is a counterion, preferably a halide, e.g. chloride or methylsulfate.



Formula III

R6 is C₁-C₄ and z is 1 or 2.

Preferred quat ammonium surfactants are those as defined in formula I whereby

20 R₁ is C₈, C₁₀ or mixtures thereof, x=0,

R₃, R₄ = CH₃ and R₅ = CH₂CH₂OH.

Highly preferred cationic surfactants are the water-soluble quaternary ammonium compounds useful in the present composition having the formula :



25 wherein R₁ is C₈-C₁₆ alkyl, each of R₂, R₃ and R₄ is independently C₁-C₄ alkyl, C₁-C₄ hydroxy alkyl, benzyl, and -(C₂H₄)_xH where x has a value from 2 to 5, and X is an anion. Not more than one of R₂, R₃ or R₄ should be benzyl.

The preferred alkyl chain length for R₁ is C₁₂-C₁₅ particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R₂R₃ and R₄ are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions. Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are :

- coconut trimethyl ammonium chloride or bromide;
- coconut methyl dihydroxyethyl ammonium chloride or bromide;
- decyl triethyl ammonium chloride;
- decyl dimethyl hydroxyethyl ammonium chloride or bromide;
- C₁₂-15 dimethyl hydroxyethyl ammonium chloride or bromide;
- coconut dimethyl hydroxyethyl ammonium chloride or bromide;
- myristyl trimethyl ammonium methyl sulphate;
- lauryl dimethyl benzyl ammonium chloride or bromide;
- lauryl dimethyl (ethenoxy)₄ ammonium chloride or bromide;
- choline esters (compounds of formula (i) wherein R₁ is CH₂-CH₂-O-C-C₁₂-14 alkyl and R₂R₃R₄ are methyl).



Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980 and in European Patent Application EP 000,224.

When included therein, the laundry detergent and/or fabric care compositions of the present invention typically comprise from 0.2% to about 25%, preferably from about 1% to about 8% by weight of such cationic surfactants.

Ampholytic surfactants are also suitable for use in the laundry detergent and/or fabric care compositions of the present invention. These surfactants can be broadly described as aliphatic derivatives of secondary or tertiary amines, or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic radical can be straight- or branched-chain. One of the aliphatic substituents contains at least about 8 carbon atoms, typically from about 8 to

about 18 carbon atoms, and at least one contains an anionic water-solubilizing group, e.g. carboxy, sulfonate, sulfate. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, lines 18-35, for examples of ampholytic surfactants.

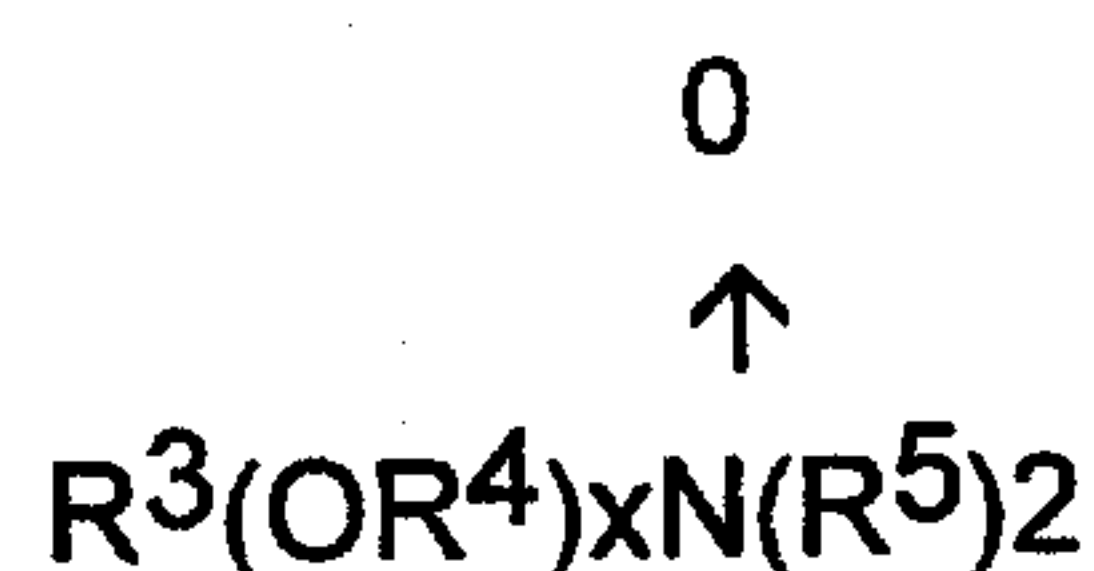
- 5 When included therein, the laundry detergent and/or fabric care compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such ampholytic surfactants.

10 Zwitterionic surfactants are also suitable for use in laundry detergent and/or fabric care compositions. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. See U.S. Patent No. 3,929,678 to Laughlin et al., issued December 30, 1975 at column 19, line 38
15 through column 22, line 48, for examples of zwitterionic surfactants.

When included therein, the laundry detergent and/or fabric care compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such zwitterionic surfactants.

- 20 Semi-polar nonionic surfactants are a special category of nonionic surfactants which include water-soluble amine oxides containing one alkyl moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl
25 moiety of from about 10 to about 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups 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 and hydroxyalkyl moieties of from about 1 to
30 about 3 carbon atoms.

Semi-polar nonionic detergent surfactants include the amine oxide surfactants having the formula



wherein R^3 is an alkyl, hydroxyalkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from about 2 to about 3 carbon atoms or mixtures thereof; x is from 0 to about 3; and each R^5 is an alkyl or hydroxyalkyl group containing from about 1 to about 3 carbon atoms or a polyethylene oxide group containing from about 1 to about 3 ethylene oxide groups. The R^5 groups can be attached to each other, e.g., through an oxygen or nitrogen atom, to form a ring structure.

These amine oxide surfactants in particular include C_{10} - C_{18} alkyl dimethyl amine oxides and C_8 - C_{12} alkoxy ethyl dihydroxy ethyl amine oxides.

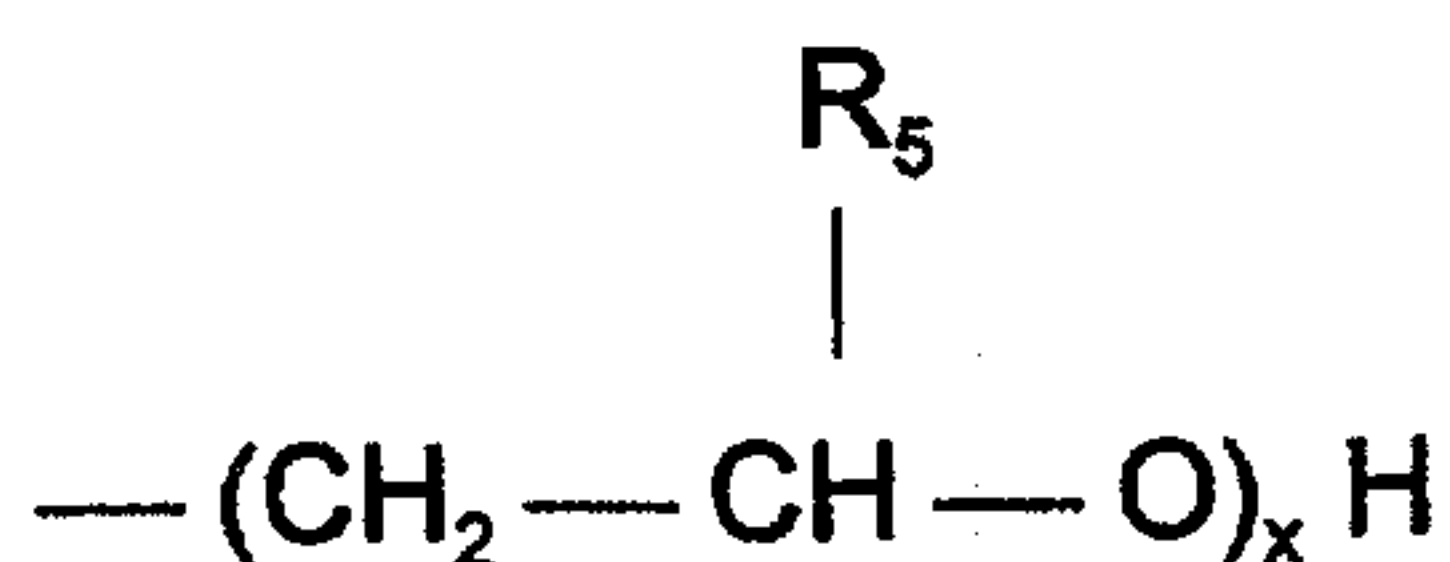
When included therein, the laundry detergent and/or fabric care compositions of the present invention typically comprise from 0.2% to about 15%, preferably from about 1% to about 10% by weight of such semi-polar nonionic surfactants.

The laundry detergent and/or fabric care composition of the present invention may further comprise a cosurfactant selected from the group of primary or tertiary amines.

Suitable primary amines for use herein include amines according to the formula R_1NH_2 wherein R_1 is a C_6 - C_{12} , preferably C_6 - C_{10} alkyl chain or $R_4X(CH_2)_n$, X is $-O-$, $-C(O)NH-$ or $-NH-$, R_4 is a C_6 - C_{12} alkyl chain n is between 1 to 5, preferably 3. R_1 alkyl chains may be straight or branched and may be interrupted with up to 12, preferably less than 5 ethylene oxide moieties.

Preferred amines according to the formula herein above are n -alkyl amines. Suitable amines for use herein may be selected from 1-hexylamine, 1-octylamine, 1-decylamine and laurylamine. Other preferred primary amines include C_8 - C_{10} oxypropylamine, octyloxypropylamine, 2-ethylhexyl-oxypropylamine, lauryl amido propylamine and amido propylamine.

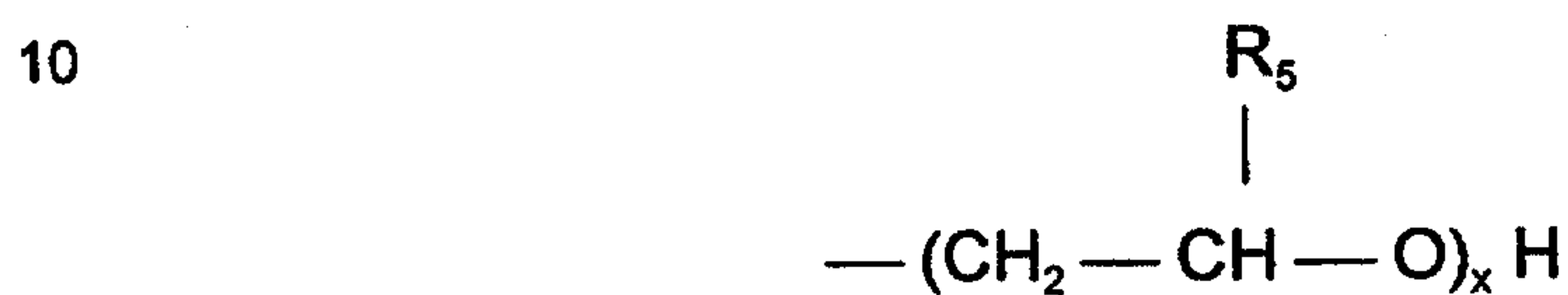
Suitable tertiary amines for use herein include tertiary amines having the formula $R_1R_2R_3N$ wherein R_1 and R_2 are C_1 - C_8 alkyl chains or



R₃ is either a C₆-C₁₂, preferably C₆-C₁₀ alkyl chain, or R₃ is R₄X(CH₂)_n, whereby X is -O-, -C(O)NH- or -NH-, R₄ is a C₄-C₁₂, n is between 1 to 5, preferably 2-3. R₅ is H or C₁-C₂ alkyl and x is between 1 to 6.

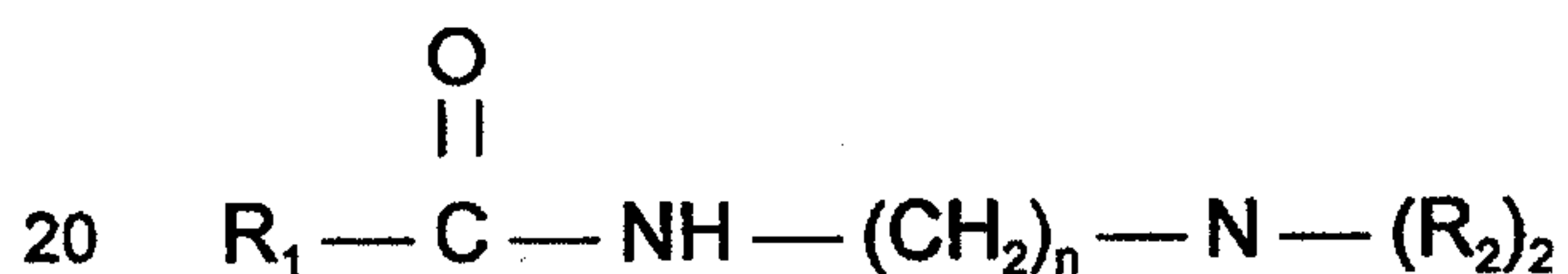
R₃ and R₄ may be linear or branched; R₃ alkyl chains may be interrupted with up to 12, preferably less than 5, ethylene oxide moieties.

Preferred tertiary amines are R₁R₂R₃N where R₁ is a C₆-C₁₂ alkyl chain, R₂ and R₃ are C₁-C₃ alkyl or



where R₅ is H or CH₃ and x = 1-2.

Also preferred are the amidoamines of the formula:



wherein R₁ is C₆-C₁₂ alkyl; n is 2-4, preferably n is 3; R₂ and R₃ is C₁-C₄

Most preferred amines of the present invention include 1-octylamine, 1-hexylamine, 1-decylamine, 1-dodecylamine, C₈-10oxypropylamine, N coco 1-3diaminopropane, coconutalkyldimethylamine, lauryldimethylamine, lauryl bis(hydroxyethyl)amine, coco bis(hydroxyethyl)amine, lauryl amine 2 moles propoxylated, octyl amine 2 moles propoxylated, lauryl amidopropyldimethylamine, C₈-10 amidopropyldimethylamine and C₁₀ amidopropyldimethylamine.

The most preferred amines for use in the compositions herein are 1-hexylamine, 1-octylamine, 1-decylamine, 1-dodecylamine. Especially desirable are n-dodecyldimethylamine and bishydroxyethylcoconutalkylamine and oleylamine 7 times ethoxylated, lauryl amido propylamine and cocoamido propylamine.

Bleaching agent

Other suitable bleaching systems that can be incorporated into the laundry detergent and/or fabric care compositions of the present invention encompass :

- 5 - One category of oxygen bleaching agent that can be used encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of meta-chloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent Application 740,446,
10 European Patent Application 0,133,354 and U.S. Patent 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxycaproic acid as described in U.S. Patent 4,634,551.
- Another category of bleaching agents that can be used encompasses the halogen bleaching agents. Examples of hypohalite bleaching agents, for
15 example, include trichloro isocyanuric acid and the sodium and potassium dichloroisocyanurates and N-chloro and N-bromo alkane sulphonamides. Such materials are normally added at 0.5-10% by weight of the finished product, preferably 1-5% by weight.
- Also suitable activators are acylated citrate esters such as disclosed in
20 Copending European Patent Application No. 91870207.7.
- Useful bleaching agents, including peroxyacids and bleaching systems comprising bleach activators and peroxygen bleaching compounds for use in detergent compositions according to the invention are described in our co-
25 pending applications USSN 08/136,626, PCT/US95/07823, WO95/27772, WO95/27773, WO95/27774 and WO95/27775.
- The hydrogen peroxide may also be present by adding an enzymatic system (i.e., an enzyme and a substrate therefore) which is capable of generating hydrogen peroxide at the beginning or during the washing and/or rinsing process. Such enzymatic systems are disclosed in EP Patent Application 91202655.6 filed
30 October 9, 1991.

Colour care and fabric care benefits

- Other suitable technologies which provide a type of colour care benefit can also
35 be included. Examples of these technologies are metallo catalysts for colour maintenance. Such metallo catalysts are described in copending European

Patent Application No. 92870181.2. Dye fixing agents, polyolefin dispersion for anti-wrinkles and improved water absorbancy, perfume and amino-functional polymer for colour care treatment and perfume substantivity are further examples of colour care / fabric care technologies and are described in the co-pending
5 Patent Application No. 96870140.9, filed November 07, 1996.

Other suitable fabric softening may be inorganic or organic in type. Inorganic softening agents are exemplified by the smectite clays disclosed in GB-A-1 400 898 and in USP 5,019,292. Organic fabric softening agents include the water
10 insoluble tertiary amines as disclosed in GB-A1 514 276 and EP-B0 011 340 and their combination with mono C12-C14 quaternary ammonium salts are disclosed in EP-B-0 026 527 and EP-B-0 026 528 and di-long-chain amides as disclosed in EP-B-0 242 919. Other useful organic ingredients of fabric softening systems include high molecular weight polyethylene oxide materials as disclosed in EP-A-
15 0 299 575 and 0 313 146.

Levels of smectite clay are normally in the range from 2% to 20%, more preferably from 5% to 15% by weight, with the material being added as a dry mixed component to the remainder of the formulation. Organic fabric softening
20 agents such as the water-insoluble tertiary amines or dilong chain amide materials are incorporated at levels of from 0.5% to 5% by weight, normally from 1% to 3% by weight whilst the high molecular weight polyethylene oxide materials and the water soluble cationic materials are added at levels of from 0.1% to 2%, normally from 0.15% to 1.5% by weight. These materials are
25 normally added to the spray dried portion of the composition, although in some instances it may be more convenient to add them as a dry mixed particulate, or spray them as molten liquid on to other solid components of the composition.

30 ***Builder system***

The laundry detergent and/or fabric care compositions according to the present invention may further comprise a builder system.

Any conventional builder system is suitable for use herein including aluminosilicate materials, silicates, polycarboxylates, alkyl- or alkenyl-succinic
35 acid and fatty acids, materials such as ethylenediamine tetraacetate, diethylene triamine pentamethyleneacetate, metal ion sequestrants such as aminopoly-

phosphonates, particularly ethylenediamine tetramethylene phosphonic acid and diethylene triamine pentamethylenephosphonic acid. Phosphate builders can also be used herein.

5 Suitable builders can be an inorganic ion exchange material, commonly an inorganic hydrated aluminosilicate material, more particularly a hydrated synthetic zeolite such as hydrated zeolite A, X, B, HS or MAP.

Another suitable inorganic builder material is layered silicate, e.g. SKS-6 (Hoechst). SKS-6 is a crystalline layered silicate consisting of sodium silicate ($\text{Na}_2\text{Si}_2\text{O}_5$).

10 Suitable polycarboxylates containing one carboxy group include lactic acid, glycolic acid and ether derivatives thereof as disclosed in Belgian Patent Nos. 831,368, 821,369 and 821,370. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycollic acid, tartaric acid, tartronic acid and fumaric
15 acid, as well as the ether carboxylates described in German Offenlegenschrift 2,446,686, and 2,446,687 and U.S. Patent No. 3,935,257 and the sulfinyl carboxylates described in Belgian Patent No. 840,623. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the
20 carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates
25 disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates. Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British
30 Patent No. 1,082,179, while polycarboxylates containing phosphone substituents are disclosed in British Patent No. 1,439,000.

Alicyclic and heterocyclic polycarboxylates include cyclopentane-cis,cis,cis-tetracarboxylates, cyclopentadienide pentacarboxylates, 2,3,4,5-tetrahydro-furan - cis, cis, cis-tetracarboxylates, 2,5-tetrahydro-furan -cis - dicarboxylates, 2,2,5,5-tetrahydrofuran - tetracarboxylates, 1,2,3,4,5,6-hexane -hexacarboxylates and
35 and carboxymethyl derivatives of polyhydric alcohols such as sorbitol, mannitol

and xylitol. Aromatic poly-carboxylates include mellitic acid, pyromellitic acid and the phthalic acid derivatives disclosed in British Patent No. 1,425,343.

Of the above, the preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

5 Preferred builder systems for use in the present compositions include a mixture of a water-insoluble aluminosilicate builder such as zeolite A or of a layered silicate (SKS-6), and a water-soluble carboxylate chelating agent such as citric acid. Preferred builder systems include a mixture of a water-insoluble aluminosilicate builder such as zeolite A, and a watersoluble carboxylate
10 chelating agent such as citric acid. Preferred builder systems for use in liquid detergent compositions of the present invention are soaps and polycarboxylates. Other builder materials that can form part of the builder system for use in granular compositions include inorganic materials such as alkali metal carbonates, bicarbonates, silicates, and organic materials such as the organic
15 phosphonates, amino polyalkylene phosphonates and amino polycarboxylates. Other suitable water-soluble organic salts are the homo- or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts
20 are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 20,000 to 70,000, especially about 40,000.

Detergency builder salts are normally included in amounts of from 5% to 80% by weight of the composition preferably from 10% to 70% and most usually from
25 30% to 60% by weight.

Chelating Agents

The laundry detergent and/or fabric care compositions herein may also optionally
30 contain one or more iron and/or manganese chelating agents. Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their
35 exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraaminehexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein. Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates to not contain alkyl or alkenyl groups with more than about 6 carbon atoms. Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene. A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins. The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and the like. If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the detergent compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

25

Suds suppressor

Another optional ingredient is a suds suppressor, exemplified by silicones, and silica-silicone mixtures. Silicones can be generally represented by alkylated polysiloxane materials while silica is normally used in finely divided forms exemplified by silica aerogels and xerogels and hydrophobic silicas of various types. These materials can be incorporated as particulates in which the suds suppressor is advantageously releasably incorporated in a water-soluble or water-dispersible, substantially non-surface-active detergent impermeable carrier. Alternatively the suds suppressor can be dissolved or dispersed in a liquid carrier and applied by spraying on to one or more of the other components.

35

A preferred silicone suds controlling agent is disclosed in Bartollota et al. U.S. Patent 3 933 672. Other particularly useful suds suppressors are the self-emulsifying silicone suds suppressors, described in German Patent Application DTOS 2 646 126 published April 28, 1977. An example of such a compound is
5 DC-544, commercially available from Dow Corning, which is a siloxane-glycol copolymer. Especially preferred suds controlling agent are the suds suppressor system comprising a mixture of silicone oils and 2-alkyl-alkanols. Suitable 2-alkyl-alkanols are 2-butyl-octanol which are commercially available under the trade name Isofol 12 R.

10 Such suds suppressor system are described in Copending European Patent application N 92870174.7 filed 10 November, 1992.

Especially preferred silicone suds controlling agents are described in Copending European Patent application N°92201649.8. Said compositions can comprise a silicone/silica mixture in combination with fumed nonporous silica such as
15 Aerosil^R.

The suds suppressors described above are normally employed at levels of from 0.001% to 2% by weight of the composition, preferably from 0.01% to 1% by weight.

20 **Others**

Other components such as soil-suspending agents, abrasives, tarnish inhibitors, and/or colouring agents may be employed.

Antiredeposition and soil suspension agents suitable herein include cellulose
25 derivatives such as methylcellulose, carboxymethylcellulose and hydroxyethylcellulose, and homo- or co-polymeric polycarboxylic acids or their salts. Polymers of this type include the polyacrylates and maleic anhydride-acrylic acid copolymers previously mentioned as builders, as well as copolymers of maleic anhydride with ethylene, methylvinyl ether or methacrylic acid, the maleic
30 anhydride constituting at least 20 mole percent of the copolymer. These materials are normally used at levels of from 0.5% to 10% by weight, more preferably from 0.75% to 8%, most preferably from 1% to 6% by weight of the composition.

35 Other useful polymeric materials are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most

preferably about 4000. These are used at levels of from 0.20% to 5% more preferably from 0.25% to 2.5% by weight. These polymers and the previously mentioned homo- or co-polymeric polycarboxylate salts are valuable for improving whiteness maintenance, fabric ash deposition, and cleaning
5 performance on clay, proteinaceous and oxidizable soils in the presence of transition metal impurities.

It is well-known in the art that free chlorine in tap water rapidly deactivates the enzymes comprised in detergent compositions. Therefore, using chlorine
10 scavenger such as perborate, ammonium sulfate, sodium sulphite or polyethyleneimine at a level above 0.1% by weight of total composition, in the formulas will provide improved through the wash stability of the detergent enzymes. Compositions comprising chlorine scavenger are described in the European patent application 92870018.6 filed January 31, 1992.

15

Alkoxylated polycarboxylates such as those prepared from polyacrylates are useful herein to provide additional grease removal performance. Such materials are described in WO 91/08281 and PCT 90/01815 at p. 4 et seq., incorporated herein by reference. Chemically, these materials comprise polyacrylates having
20 one ethoxy side-chain per every 7-8 acrylate units. The side-chains are of the formula $-(CH_2CH_2O)_m(CH_2)_nCH_3$ wherein m is 2-3 and n is 6-12. The side-chains are ester-linked to the polyacrylate "backbone" to provide a "comb" polymer type structure. The molecular weight can vary, but is typically in the range of about 2000 to about 50,000. Such alkoxylated polycarboxylates can
25 comprise from about 0.05% to about 10%, by weight, of the compositions herein.

Dispersants

The laundry detergent and/or fabric care composition of the present invention can also contain dispersants : Suitable water-soluble organic salts are the homo-
30 or co-polymeric acids or their salts, in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms.

Polymers of this type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MW 2000-5000 and their copolymers with maleic anhydride,
35 such copolymers having a molecular weight of from 1,000 to 100,000.

Especially, copolymer of acrylate and methylacrylate such as the 480N having a molecular weight of 4000, at a level from 0.5-20% by weight of composition can be added in the laundry detergent and/or fabric care compositions of the present invention.

5 The compositions of the invention may contain a lime soap peptiser compound, which has preferably a lime soap dispersing power (LSDP), as defined hereinafter of no more than 8, preferably no more than 7, most preferably no more than 6. The lime soap peptiser compound is preferably present at a level from 0% to 20% by weight.

10 A numerical measure of the effectiveness of a lime soap peptiser is given by the lime soap dispersant power (LSDP) which is determined using the lime soap dispersant test as described in an article by H.C. Borghetty and C.A. Bergman, J. Am. Oil. Chem. Soc., volume 27, pages 88-90, (1950). This lime soap dispersion test method is widely used by practitioners in this art field being referred to, for
15 example, in the following review articles; W.N. Linfield, Surfactant science Series, Volume 7, page 3; W.N. Linfield, Tenside surf. det., volume 27, pages 159-163, (1990); and M.K. Nagarajan, W.F. Masler, Cosmetics and Toiletries, volume 104, pages 71-73, (1989). The LSDP is the % weight ratio of dispersing agent to
20 sodium oleate required to disperse the lime soap deposits formed by 0.025g of sodium oleate in 30ml of water of 333ppm CaCO_3 (Ca:Mg=3:2) equivalent hardness.

Surfactants having good lime soap peptiser capability will include certain amine oxides, betaines, sulfobetaines, alkyl ethoxysulfates and ethoxylated alcohols.

Exemplary surfactants having a LSDP of no more than 8 for use in accord with
25 the present invention include C_{16} - C_{18} dimethyl amine oxide, C_{12} - C_{18} alkyl ethoxysulfates with an average degree of ethoxylation of from 1-5, particularly C_{12} - C_{15} alkyl ethoxysulfate surfactant with a degree of ethoxylation of amount 3 (LSDP=4), and the C_{14} - C_{15} ethoxylated alcohols with an average degree of ethoxylation of either 12 (LSDP=6) or 30, sold under the tradenames Lutensol
30 A012 and Lutensol A030 respectively, by BASF GmbH.

Polymeric lime soap peptisers suitable for use herein are described in the article by M.K. Nagarajan, W.F. Masler, to be found in Cosmetics and Toiletries, volume 104, pages 71-73, (1989).

Hydrophobic bleaches such as 4-[N-octanoyl-6-aminohexanoyl]benzene
35 sulfonate, 4-[N-nonanoyl-6-aminohexanoyl]benzene sulfonate, 4-[N-decanoyl-6-aminohexanoyl]benzene sulfonate and mixtures thereof; and nonanoyloxy

benzene sulfonate together with hydrophilic / hydrophobic bleach formulations can also be used as lime soap peptisers compounds.

5

Polymeric dye transfer inhibiting agents

The laundry detergent and/or fabric care compositions according to the present invention can also comprise from 0.001% to 10 %, preferably from 0.01% to 2%, more preferably from 0.05% to 1% by weight of polymeric dye transfer inhibiting agents. Said polymeric dye transfer inhibiting agents are normally incorporated into laundry detergent and/or fabric care compositions in order to inhibit the transfer of dyes from coloured fabrics onto fabrics washed therewith. These polymers have the ability to complex or adsorb the fugitive dyes washed out of dyed fabrics before the dyes have the opportunity to become attached to other articles in the wash.

15

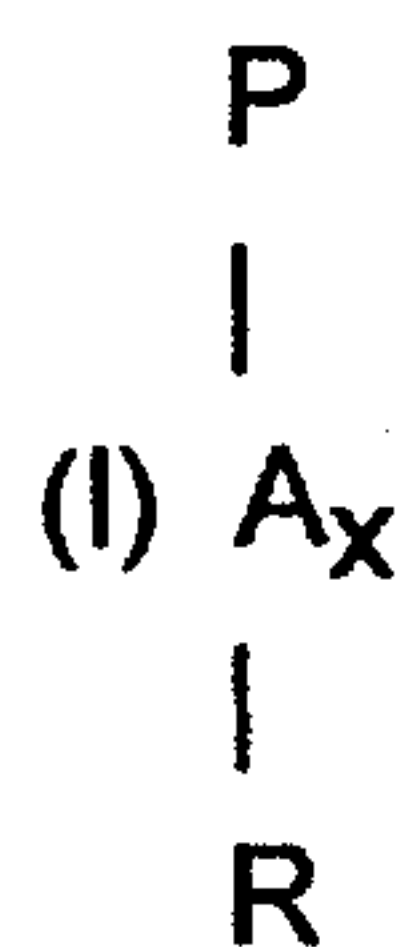
Especially suitable polymeric dye transfer inhibiting agents are polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers, polyvinylloxazolidones and polyvinylimidazoles or mixtures thereof.

20 Addition of such polymers also enhances the performance of the enzymes according to the invention.

a) Polyamine N-oxide polymers

The polyamine N-oxide polymers suitable for use contain units having the following structure formula :

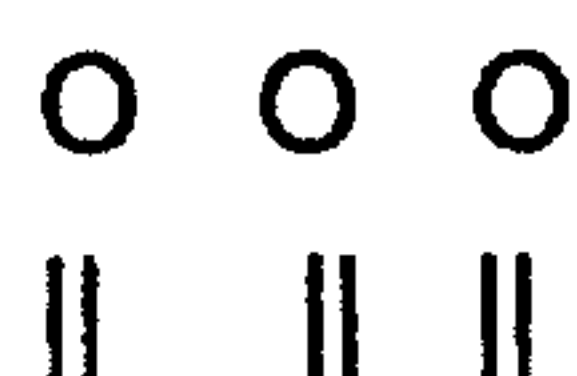
25



30

wherein P is a polymerisable unit, whereto the R-N-O group can be attached to or wherein the R-N-O group forms part of the polymerisable unit or a combination of both.

35

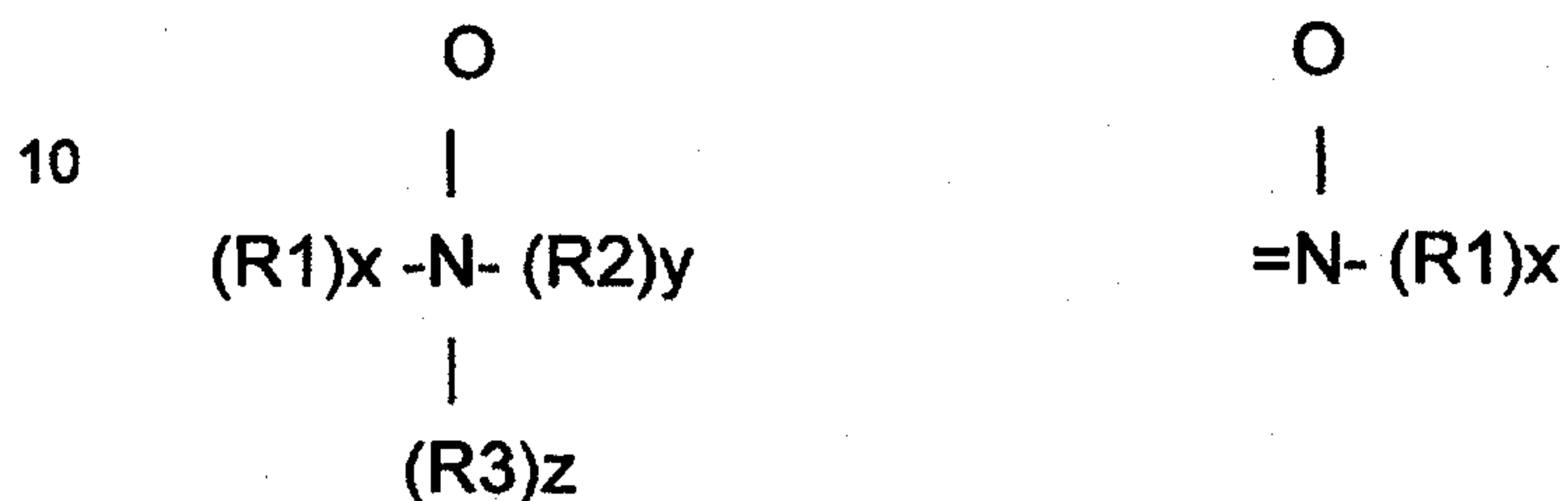


A is NC, CO, C, -O-, -S-, -N- ; x is 0 or 1;

R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

5

The N-O group can be represented by the following general structures :



15 wherein R1, R2, and R3 are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups.

20 The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups.

25 One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyrridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

30 Another class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group is attached to the R-group.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit.

Preferred class of these polyamine N-oxides are the polyamine N-oxides having the general formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group.

5 Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyrridine, pyrrole, imidazole and derivatives thereof.

Another preferred class of polyamine N-oxides are the polyamine oxides having the general formula (I) wherein R are aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is attached to said R groups.

10 Examples of these classes are polyamine oxides wherein R groups can be aromatic such as phenyl.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers,
15 polyamide, polyimides, polyacrylates and mixtures thereof.

The amine N-oxide polymers of the present invention typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1000000. However the amount of amine oxide groups present in the polyamine oxide polymer can be varied by
20 appropriate copolymerization or by appropriate degree of N-oxidation. Preferably, the ratio of amine to amine N-oxide is from 2:3 to 1:1000000. More preferably from 1:4 to 1:1000000, most preferably from 1:7 to 1:1000000. The polymers of the present invention actually encompass random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is either an
25 amine N-oxide or not. The amine oxide unit of the polyamine N-oxides has a PKa < 10, preferably PKa < 7, more preferred PKa < 6.

The polyamine oxides can be obtained in almost any degree of polymerisation. The degree of polymerisation is not critical provided the material has the desired water-solubility and dye-suspending power.

30 Typically, the average molecular weight is within the range of 500 to 1000,000; preferably from 1,000 to 50,000, more preferably from 2,000 to 30,000, most preferably from 3,000 to 20,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

The N-vinylimidazole N-vinylpyrrolidone polymers used in the present invention have an average molecular weight range from 5,000-1,000,000, preferably from 5,000-200,000.

5 Highly preferred polymers for use in detergent compositions according to the present invention comprise a polymer selected from N-vinylimidazole N-vinylpyrrolidone copolymers wherein said polymer has an average molecular weight range from 5,000 to 50,000 more preferably from 8,000 to 30,000, most preferably from 10,000 to 20,000.

10 The average molecular weight range was determined by light scattering as described in Barth H.G. and Mays J.W. Chemical Analysis Vol 113, "Modern Methods of Polymer Characterization".

Highly preferred N-vinylimidazole N-vinylpyrrolidone copolymers have an average molecular weight range from 5,000 to 50,000; more preferably from 8,000 to 30,000; most preferably from 10,000 to 20,000.

15

The N-vinylimidazole N-vinylpyrrolidone copolymers characterized by having said average molecular weight range provide excellent dye transfer inhibiting properties while not adversely affecting the cleaning performance of detergent compositions formulated therewith.

20 The N-vinylimidazole N-vinylpyrrolidone copolymer of the present invention has a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2, more preferably from 0.8 to 0.3, most preferably from 0.6 to 0.4 .

c) Polyvinylpyrrolidone

25 The laundry detergent and/or fabric care compositions of the present invention may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000. Suitable polyvinylpyrrolidones are
30 commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). Other suitable polyvinylpyrrolidones which are commercially available
35 from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12;

polyvinylpyrrolidones known to persons skilled in the detergent field (see for example EP-A-262,897 and EP-A-256,696).

d) Polyvinylloxazolidone :

- 5 The laundry detergent and/or fabric care compositions of the present invention may also utilize polyvinylloxazolidone as a polymeric dye transfer inhibiting agent. Said polyvinylloxazolidones have an average molecular weight of from about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about
10 5,000 to about 15,000.

e) Polyvinylimidazole :

- The laundry detergent and/or fabric care compositions of the present invention may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent.
15 Said polyvinylimidazoles have an average of about 2,500 to about 400,000, preferably from about 5,000 to about 200,000, more preferably from about 5,000 to about 50,000, and most preferably from about 5,000 to about 15,000.

f) Cross-linked polymers :

- 20 Cross-linked polymers are polymers whose backbone are interconnected to a certain degree; these links can be of chemical or physical nature, possibly with active groups n the backbone or on branches; cross-linked polymers have been described in the Journal of Polymer Science, volume 22, pages 1035-1039. In one embodiment, the cross-linked polymers are made in such a way that they
25 form a three-dimensional rigid structure, which can entrap dyes in the pores formed by the three-dimensional structure. In another embodiment, the cross-linked polymers entrap the dyes by swelling. Such cross-linked polymers are described in the co-pending patent application 94870213.9.

30

Method of washing

- The compositions of the invention may be used in essentially any washing,
35 cleaning and/or fabric care methods, including soaking methods, pre-treatment methods, methods with rinsing steps for which a separate rinse aid composition

may be added and post-treatment methods. The process described herein comprises contacting fabrics with a laundering solution in the usual manner and exemplified hereunder. The process of the invention is conveniently carried out in the course of the cleaning / fabric care process. The method of cleaning / fabric
 5 care is preferably carried out at 5°C to 95°C, especially between 10°C and 60°C. The pH of the treatment solution is preferably from 7 to 12.

The following examples are meant to exemplify compositions of the present invention, but are not necessarily meant to limit or otherwise define the scope of
 10 the invention. In the detergent compositions, the enzymes levels are expressed by pure enzyme by weight of the total composition and unless otherwise specified, the detergent ingredients are expressed by weight of the total compositions. The abbreviated component identifications therein have the following meanings:

15

LAS	: Sodium linear C ₁₁₋₁₃ alkyl benzene sulphonate.
TAS	: Sodium tallow alkyl sulphate.
CxyAS	: Sodium C _{1x} - C _{1y} alkyl sulfate.
CxySAS	: Sodium C _{1x} - C _{1y} secondary (2,3) alkyl sulfate.
CxyEz	: C _{1x} - C _{1y} predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide.
CxyEzS	: C _{1x} - C _{1y} sodium alkyl sulfate condensed with an average of z moles of ethylene oxide.
QAS	: R ₂ .N+(CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₁₂ -C ₁₄ .
QAS 1	: R ₂ .N+(CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = C ₈ -C ₁₁ .
APA	: C ₈₋₁₀ amido propyl dimethyl amine.
Soap	: Sodium linear alkyl carboxylate derived from a 80/20 mixture of tallow and coconut fatty acids.
STS	: Sodium toluene sulphonate.
CFAA	: C ₁₂ -C ₁₄ alkyl N-methyl glucamide.
TFAA	: C ₁₆ -C ₁₈ alkyl N-methyl glucamide.
TPKFA	: C ₁₂ -C ₁₄ topped whole cut fatty acids.
DEQA	: Di-(tallow-oxy-ethyl) dimethyl ammonium chloride.
DEQA (2)	: Di-(soft-tallowyloxyethyl) hydroxyethyl methyl ammonium methylsulfate.
DTDMAMS	: Ditallow dimethyl ammonium methylsulfate.

SDASA	: 1:2 ratio of stearyldimethyl amine:triple-pressed stearic acid.
Silicate	: Amorphous Sodium Silicate ($\text{SiO}_2\text{:Na}_2\text{O}$ ratio = 1.6-3.2).
Zeolite A	: Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 0.1 to 10 micrometers (Weight expressed on an anhydrous basis).
Na-SKS-6	: Crystalline layered silicate of formula $\delta\text{-Na}_2\text{Si}_2\text{O}_5$.
Citrate	: Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425 and 850 micrometres.
Citric	: Anhydrous citric acid.
Borate	: Sodium borate
Carbonate	: Anhydrous sodium carbonate with a particle size between 200 and 900 micrometres.
Bicarbonate	: Anhydrous sodium hydrogen carbonate with a particle size distribution between 400 and 1200 micrometres.
Sulphate	: Anhydrous sodium sulphate.
Mg Sulphate	: Anhydrous magnesium sulfate.
STPP	: Sodium tripolyphosphate.
TSP	: Tetrasodium pyrophosphate.
MA/AA	: Random copolymer of 4:1 acrylate/maleate, average molecular weight about 70,000-80,000.
MA/AA 1	: Random copolymer of 6:4 acrylate/maleate, average molecular weight about 10,000.
AA	: Sodium polyacrylate polymer of average molecular weight 4,500.
PB1	: Anhydrous sodium perborate monohydrate of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$.
PB4	: Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$.
Percarbonate	: Anhydrous sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$.
TAED	: Tetraacetythylenediamine.
NOBS	: Nonanoyloxybenzene sulfonate in the form of the sodium salt.

- NACA-OBS : (6-nonamidocaproyl) oxybenzene sulfonate.
- CBD-NACA-OBS : Reaction product of Cellulose Binding Domain from the cellulase sold under the tradename Carezyme by Novo Nordisk A/S with polytyrosine and (6-nonamidocaproyl) oxybenzene sulfonate molecules.
- DTPA : Diethylene triamine pentaacetic acid.
- HEDP : 1,1-hydroxyethane diphosphonic acid.
- DETPMP : Diethyltriamine penta (methylene) phosphonate, marketed by Monsanto under the Trade name Dequest 2060.
- EDDS : Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt
- Photoactivated Bleach : Sulfonated zinc phthalocyanine encapsulated in dextrin soluble polymer.
- Photoactivated Bleach 1 : Sulfonated alumino phthalocyanine encapsulated in dextrin soluble polymer.
- Protease : Proteolytic enzyme sold under the tradename Savinase, Alcalase, Durazym by Novo Nordisk A/S, Maxacal, Maxapem sold by Gist-Brocades and proteases described in patents WO91/06637 and/or WO95/10591 and/or EP 251 446.
- Amylase : Amylolytic enzyme sold under the tradename Purafact Ox Am^R described in WO 94/18314, WO96/05295 sold by Genencor; Termamyl[®], Fungamyl[®] and Duramyl[®], all available from Novo Nordisk A/S and those described in WO95/26397.
- Lipase : Lipolytic enzyme sold under the tradename Lipolase, Lipolase Ultra by Novo Nordisk A/S and Lipomax by Gist-Brocades.
- Cellulase : Cellulytic enzyme sold under the tradename Carezyme, Celluzyme and/or Endolase by Novo Nordisk A/S.
- CMC : Sodium carboxymethyl cellulose.
- PVP : Polyvinyl polymer, with an average molecular weight of 60,000.
- PVNO : Polyvinylpyridine-N-Oxide, with an average molecular weight of 50,000.

- PVPVI** : Copolymer of vinylimidazole and vinylpyrrolidone, with an average molecular weight of 20,000.
- Brightener 1** : Disodium 4,4'-bis(2-sulphostyryl)biphenyl.
- Brightener 2** : Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl) stilbene-2:2'-disulfonate.
- Silicone antifoam** : Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1.
- Suds Suppressor** : 12% Silicone/silica, 18% stearyl alcohol, 70% starch in granular form.
- Opacifier** : Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621.
- SRP 1** : Anionically end capped poly esters.
- SRP 2** : Diethoxylated poly (1,2 propylene terephthalate) short block polymer.
- QEA** : bis((C₂H₅O)(C₂H₄O)_n)(CH₃) -N⁺-C₆H₁₂-N⁺-(CH₃) bis((C₂H₅O)-(C₂H₄O))_n, wherein n = from 20 to 30.
- PEI** : Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen.
- SCS** : Sodium cumene sulphonate.
- HMWPEO** : High molecular weight polyethylene oxide.
- PEGx** : Polyethylene glycol, of a molecular weight of x .
- PEO** : Polyethylene oxide, with an average molecular weight of 5,000.
- TEPAE** : Tetraethylenepentaamine ethoxylate.
- CBD-Rotundial** : Reaction product of CBD Cellulozome from *Clostridium cellulovorans* , which is sold under the tradename Cellulose Binding Domain by Sigma with Rotundial molecules.
- CBD-Damascone** : Reaction product of CBD Cellulozome from *Clostridium cellulovorans* , which is sold under the tradename Cellulose Binding Domain by Sigma with polylysine and α-Damascone molecules.

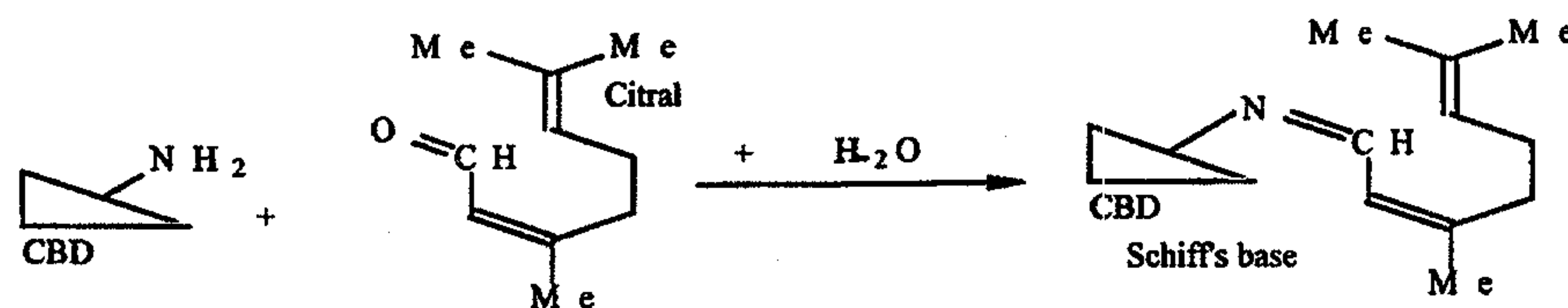
Example 1

According to the present invention, this example illustrates the coupling of a perfume citral, hygiene agent glutaraldehyde or insect control agent citronellal to a CBD.

The reaction at equal mol takes place in mild conditions (pH 6 to 9.5, from 1 to 48hours / See for example Wirth, P at al 1991 Biorg.Chem 19, 133, 1991 and Chamow SM et al Bioconjugate chem, 4, 133 1994). The chemicals such as perfume (citral), insect control agent (citronellal) and hygiene agent (glutaraldehyde) are linked to NH₂ groups of the CBD, linking region and/or polyreactive linking region via Schiff's base reaction. The reaction could also be completed in anhydrous ethanol that contain a drying agent such as Sodium Sulphate.

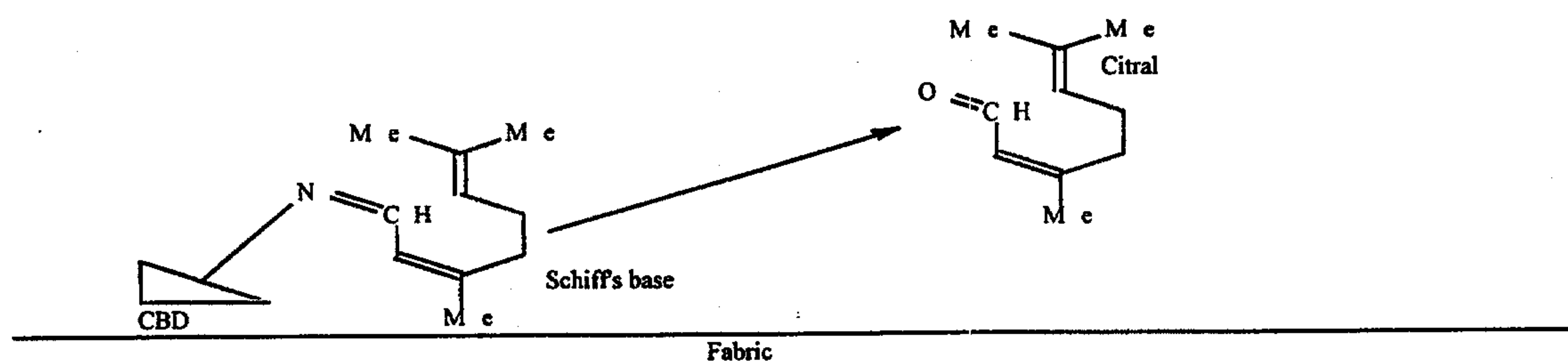
In case the CBD possesses more than one Lysine or there is a polyreactive linking region comprising more than one lysine, the reaction is identical with the appropriate number of chemicals per CBD. For example 10 equivalent of aldehyde will be added per mol of CBD from family III that contain more than 10 Lysines.

For example, the CBD having at least one Lysine, has a NH₂ reactive moiety to be linked to perfume. The CBD is non volatile and does not change the character of the aldehyde.



Improved release on dry fabrics is obtained by the slow hydrolysis of the CBD perfume linkage.

90



Example 2

5

The following high density laundry detergent compositions were prepared according to the present invention :

10

	I	II	III	IV	V	VI
LAS	8.0	8.0	8.0	2.0	6.0	6.0
TAS	-	0.5	-	0.5	1.0	0.1
C46(S)AS	2.0	2.5	-	-	-	-
C25AS	-	-	-	7.0	4.5	5.5
C68AS	2.0	5.0	7.0	-	-	-
C25E5	-	-	3.4	10.0	4.6	4.6
C25E7	3.4	3.4	1.0	-	-	-
C25E3S	-	-	-	2.0	5.0	4.5
QAS	-	0.8	-	-	-	-
QAS 1	-	-	-	0.8	0.5	1.0
Zeolite A	18.1	18.0	14.1	18.1	20.0	18.1
Citric	-	-	-	2.5	-	2.5
Carbonate	13.0	13.0	27.0	10.0	10.0	13.0
Na-SKS-6	-	-	-	10.0	-	10.0
Silicate	1.4	1.4	3.0	0.3	0.5	0.3
Citrate	-	1.0	-	3.0	-	-
Sulfate	26.1	26.1	26.1	6.0	-	-
Mg sulfate	0.3	-	-	0.2	-	0.2
MA/AA	0.3	0.3	0.3	4.0	1.0	1.0
CMC	0.2	0.2	0.2	0.2	0.4	0.4
PB4	9.0	9.0	5.0	-	-	-

	I	II	III	IV	V	VI
Percarbonate	-	-	-	-	18.0	18.0
TAED	1.5	0.4	1.5	-	3.9	4.2
NACA-OBS	-	2.0	1.0	-	-	-
DETPMP	0.25	0.25	0.25	0.25	-	-
SRP 1	-	-	-	0.2	-	0.2
EDDS	-	0.25	0.4	-	0.5	0.5
CFAA	-	1.0	-	2.0	-	-
HEDP	0.3	0.3	0.3	0.3	0.4	0.4
QEA	-	-	-	0.2	-	0.5
Protease	0.009	0.009	0.01	0.04	0.05	0.03
Amylase	0.002	0.002	0.002	0.006	0.008	0.008
Cellulase	0.0007	0.0006	0.0007	0.0008	0.0007	0.001
Lipase	0.006	-	-	0.01	0.01	0.01
Photoactivated bleach (ppm)	15	15	15	-	20	20
PVNO/PVPVI	-	-	-	0.1	-	-
Brightener 1	0.09	0.09	0.09	-	0.09	0.09
Perfume	0.3	0.3	0.3	0.4	0.4	0.4
Silicone antifoam	0.5	0.5	0.5	-	0.3	0.3
CBD-Damascone	0.2	0.02	0.01	0.1	0.5	0.01
Density in g/litre	850	850	850	850	850	850
Miscellaneous and minors	Up to 100%					

Example 3

- 5 The following granular laundry detergent compositions of particular utility under European machine wash conditions were prepared according to the present invention :

	I	II	III
LAS	5.5	7.5	7.0
TAS	1.25	1.9	0.3
C24AS/C25AS	-	2.2	2.2
C25E3S	-	0.8	1.0
C45E7	3.25	-	3.0

WO 00/18897

PCT/US98/20491

92

	I	II	III
TFAA	-	-	-
C25E5	-	5.5	-
QAS	0.8	-	-
QAS 1	-	0.7	0.7
STPP	19.7	-	-
Zeolite A	-	19.5	17.0
NaSKS-6/citric acid (79:21)	-	10.6	-
Na-SKS-6	-	-	10.0
Carbonate	6.1	21.4	18.0
Bicarbonate	-	2.0	2.0
Silicate	6.8	-	-
Citrate	-	-	-
Sulfate	39.8	-	12.0
Mg sulfate	-	-	-
MA/AA	0.5	1.6	1.0
CMC	0.2	0.4	0.4
PB4	5.0	12.7	-
Percarbonate	-	-	15.0
TAED	0.5	3.1	-
CBD-NACA-OBS	0.8	3.0	2.0
DETPMP	0.25	0.2	0.2
HEDP	-	0.3	0.3
QEA	-	-	-
Protease	0.009	0.03	0.02
Lipase	0.003	0.003	0.004
Cellulase	0.0006	0.0006	0.0007
Amylase	0.002	0.002	0.003
PVNO/PVPVI	-	-	-
PVP	0.9	1.3	0.9
SRP 1	-	-	-
Photoactivated bleach (ppm)	15	27	20
Photoactivated bleach 1 (ppm)	15	-	-
Brightener 1	0.08	0.2	0.15
Brightener 2	-	0.04	-

93

	I	II	III
Perfume	0.3	0.5	0.3
Silicone antifoam	0.5	2.4	2.0
Density in g/litre	750	750	750
Miscellaneous and minors	Up to 100%		

Example 4

5

The following detergent formulations of particular utility under European machine wash conditions were prepared according to the present invention :

	I	II	III
Blown Powder			
LAS	6.0	5.0	11.0
TAS	2.0	-	-
Zeolite A	24.0	-	-
STPP	-	27.0	24.0
Sulfate	4.0	6.0	13.0
MA/AA	1.0	4.0	6.0
Silicate	1.0	7.0	3.0
CMC	1.0	1.0	0.5
Brightener 1	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0
DETPMP	0.4	0.4	0.2
Spray On			
Brightener	0.02	-	-
C45E7	-	-	-
C45E2	2.5	2.5	2.0
C45E3	2.6	2.5	2.0
Perfume	0.5	0.3	0.5
Silicone antifoam	0.3	0.3	0.3
Dry additives			
QEA	-	-	-
EDDS	0.3	-	-
Sulfate	2.0	3.0	5.0

	I	II	III
Carbonate	6.0	13.0	15.0
Citric	2.5	-	-
QAS 1	0.5	-	-
Na-SKS-6	10.0	-	-
Percarbonate	18.5	-	-
PB4	-	18.0	10.0
TAED	2.0	2.0	-
CBD-NACA-OBS	2.0	1.0	3.0
Cellulase	0.0004	0.0006	0.0006
Protease	0.03	0.03	0.03
Lipase	0.008	0.008	0.008
Amylase	0.003	0.003	0.003
Brightener 1	0.05	-	-
Miscellaneous and minors		Up to 100%	

Example 5

5

The following granular detergent formulations were prepared according to the present invention :

	I	II	III	IV	V	VI
Blown Powder						
LAS	23.0	8.0	7.0	9.0	7.0	7.0
TAS	-	-	-	-	1.0	-
C45AS	6.0	6.0	5.0	8.0	-	-
C45AES	-	1.0	1.0	1.0	-	-
C45E35	-	-	-	-	2.0	4.0
Zeolite A	10.0	18.0	14.0	12.0	10.0	10.0
MA/AA	-	0.5	-	-	-	2.0
MA/AA 1	7.0	-	-	-	-	-
AA	-	3.0	3.0	2.0	3.0	3.0
Sulfate	5.0	6.3	14.3	11.0	15.0	19.3
Silicate	10.0	1.0	1.0	1.0	1.0	1.0

WO 00/18897

PCT/US98/20491

95

	I	II	III	IV	V	VI
Carbonate	15.0	20.0	10.0	20.7	8.0	6.0
PEG 4000	0.4	1.5	1.5	1.0	1.0	1.0
DTPA	-	0.9	0.5	-	-	0.5
Brightener 2	0.3	0.2	0.3	-	0.1	0.3
Spray On						
C45E7	-	2.0	-	-	2.0	2.0
C25E9	3.0	-	-	-	-	-
C23E9	-	-	1.5	2.0	-	2.0
Perfume	0.3	0.3	0.3	2.0	0.3	0.3
Agglomerates						
C45AS	-	5.0	5.0	2.0	-	5.0
LAS	-	2.0	2.0	-	-	2.0
Zeolite A	-	7.5	7.5	8.0	-	7.5
Carbonate	-	4.0	4.0	5.0	-	4.0
PEG 4000	-	0.5	0.5	-	-	0.5
Misc (Water etc.)	-	2.0	2.0	2.0	-	2.0
Dry additives						
QAS	-	-	-	-	1.0	-
Citric	-	-	-	-	2.0	-
PB4	-	-	-	-	12.0	1.0
PB1	4.0	1.0	3.0	2.0	-	-
Percarbonate	-	-	-	-	2.0	10.0
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.0	-	6.0	-	-	0.6
Methyl cellulose	0.2	-	-	-	-	-
Na-SKS-6	8.0	-	-	-	-	-
STS	-	-	2.0	-	1.0	-
Culmene sulfonic acid	-	1.0	-	-	-	2.0
Protease	0.02	0.02	0.02	0.01	0.02	0.02
Lipase	0.004	-	0.004	-	0.004	0.008
Amylase	0.003	-	0.002	-	0.003	-
Cellulase	0.0003	0.0005	0.0005	0.0007	0.0005	0.0008
PVPVI	-	-	-	-	0.5	0.1
PVP	-	-	-	-	0.5	-

	I	II	III	IV	V	VI
PVNO	-	-	0.5	0.3	-	-
QEA	-	-	-	-	1.0	-
SRP 1	0.2	0.5	0.3	-	0.2	-
Silicone antifoam	0.2	0.4	0.2	0.4	0.1	-
Mg sulfate	-	-	0.2	-	0.2	-
CBD-Damascone	-	0.02	0.1	-	-	-
CBD-Rotundial	1.0	0.5	0.1	0.05	0.2	5.0
Miscellaneous and minors			Up to 100%			

Example 6

- 5 The following nil bleach-containing detergent formulations of particular use in the washing of coloured clothing were prepared according to the present invention :

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	-
Sulfate	-	5.0	-
LAS	3.0	3.0	-
DETPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0
Spray-on			
CBD-Damascone	0.02	0.1	0.05
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0

WO 00/18897

PCT/US98/20491

97

	I	II	III
C25E3	2.0	2.0	2.0
Dry additives			
MA/AA	-	-	3.0
Na-SKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Transferase	0.001	1.0	0.01
Substrate	0.1	-	5.0
Protease	0.03	0.02	0.05
Lipase	0.008	0.008	0.008
Amylase	0.01	0.01	0.01
Cellulase	0.0008	0.001	0.001
Silicone antifoam	5.0	5.0	5.0
Sulfate	-	9.0	-
Density (g/litre)	700	700	700
Miscellaneous and minors		Up to 100%	

Example 7

- 5 The following detergent formulations were prepared according to the present invention:

	I	II	III	IV
Base granule				
Zeolite A	30.0	22.0	24.0	10.0
Sulfate	10.0	5.0	10.0	7.0
MA/AA	3.0	-	-	-
AA	-	1.6	2.0	-
MA/AA 1	-	12.0	-	6.0
LAS	14.0	10.0	9.0	20.0
C45AS	8.0	7.0	9.0	7.0
C45AES	-	1.0	1.0	-
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-

	I	II	III	IV
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	10.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	-	0.4	-	-
Spray On				
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-
CBD-Damascone	0.1	0.05	0.02	0.1
Dry additives				
Carbonate	5.0	10.0	18.0	8.0
PVPVI/PVNO	0.5	-	0.3	-
Pectinase	0.005	0.01	0.01	0.005
Protease	0.03	0.03	0.03	0.02
Lipase	0.008	-	-	0.008
Amylase	0.002	-	-	0.002
Cellulase	0.0002	0.0005	0.0005	0.0002
NOBS	-	4.0	-	4.5
PB1	1.0	5.0	1.5	6.0
Sulfate	4.0	5.0	-	5.0
SRP 1	-	0.4	-	-
Suds suppressor	-	0.5	0.5	-
Miscellaneous and minors		Up to 100%		

Example 8

- 5 The following granular detergent formulations were prepared according to the present invention :

	I	II	III
Blown Powder			
Zeolite A	20.0	-	15.0
STPP	-	20.0	-
Sodium sulfate	-	-	5.0

WO 00/18897

PCT/US98/20491

99

	I	II	III
Carbonate	-	-	5.0
TAS	-	-	1.0
LAS	6.0	6.0	6.0
C68AS	2.0	2.0	-
Silicate	3.0	8.0	-
MA/AA	4.0	2.0	2.0
CMC	0.6	0.6	0.2
Brightener 1	0.2	0.2	0.1
DETPMP	0.4	0.4	0.1
STS	-	-	1.0
Spray On			
C45E7	5.0	5.0	4.0
Silicone antifoam	0.3	0.3	0.1
Perfume	0.2	0.2	0.3
CBD-Rotundial	1.0	0.5	0.3
Dry additives			
QEA	-	-	1.0
Carbonate	14.0	9.0	10.0
PB1	1.5	2.0	-
PB4	18.5	13.0	13.0
TAED	2.0	2.0	2.0
QAS	-	-	1.0
Photoactivated bleach	15 ppm	15 ppm	15 ppm
Na-SKS-6	-	-	3.0
Laccase	0.02	0.06	0.003
Enhancer	1.0	0.8	0.8
Protease	0.03	0.03	0.007
Lipase	0.004	0.004	0.004
Amylase	0.006	0.006	0.003
Cellulase	0.0002	0.0002	0.0005
Sulfate	10.0	20.0	5.0
Density (g/litre)	700	700	700
Miscellaneous and minors		Up to 100%	

100

Example 9

The following detergent formulations were prepared according to the present
 5 invention:

	I	II	III
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sulfate	-	5.0	-
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DETPMP	0.4	0.2	0.4
EDDS	-	0.4	0.2
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerate			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
CBD-Damascone	0.1	0.05	0.3
Perfume	0.3	0.3	-
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
Dry Additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
PEO	-	-	0.2
Bentonite clay	-	-	10.0
Mannanase	0.005	0.002	0.0008

WO 00/18897

PCT/US98/20491

101

	I	II	III
Protease	0.03	0.03	0.03
Lipase	0.008	0.008	0.008
Cellulase	0.001	0.0007	0.001
Amylase	0.01	0.01	0.01
Silicone antifoam	5.0	5.0	5.0
Sulfate	-	3.0	-
Density (g/litre)	850	850	850
Miscellaneous and minors		Up to 100%	

Example 10

- 5 The following detergent formulations were prepared according to the present invention:

	I	II	III	IV
LAS	18.0	14.0	24.0	20.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C23E56.5	-	-	1.0	-
C45E7	-	1.0	-	-
C45E3S	1.0	2.5	1.0	-
STPP	32.0	18.0	30.0	22.0
Silicate	9.0	5.0	9.0	8.0
Carbonate	11.0	7.5	10.0	5.0
Bicarbonate	-	7.5	-	-
PB1	3.0	1.0	-	-
PB4	-	1.0	-	-
CBD-NACA-OBS	1.5	0.8	-	-
DETPMP	-	1.0	-	-
DTPA	0.5	-	0.2	0.3
SRP 1	0.3	0.2	-	0.1
MA/AA	1.0	1.5	2.0	0.5
CMC	0.8	0.4	0.4	0.2
PEI	-	-	0.4	-
Sulfate	20.0	10.0	20.0	30.0

WO 00/18897

PCT/US98/20491

102

	I	II	III	IV
Mg sulfate	0.2	-	0.4	0.9
Protease	0.03	0.03	0.02	0.02
Amylase	0.008	0.007	-	0.004
Lipase	0.004	-	0.002	-
Cellulase	0.0003	0.0001	0.0003	0.0001
Photoactivated bleach	30 ppm	20 ppm	-	10 ppm
Perfume	0.3	0.3	0.1	0.2
CBD-Damascone	-	0.1	0.05	0.2
Brightener 1/2	0.05	0.02	0.08	0.1
Miscellaneous and Minors	up to 100%			

Example 11

- 5 The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight) :

	I	II	III	IV	V
LAS	11.5	8.8	-	3.9	-
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	15.7	-
C23E9	-	2.7	1.8	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.2	-	3.1
TPKFA	1.6	-	2.0	0.5	2.0
Citric (50%)	6.5	1.2	2.5	4.4	2.5
Ca formate	0.1	0.06	0.1	-	-
Na formate	0.5	0.06	0.1	0.05	0.05
SCS	4.0	1.0	3.0	1.2	-
Borate	0.6	-	3.0	2.0	2.9
Na hydroxide	5.8	2.0	3.5	3.7	2.7
Ethanol	1.75	1.0	3.6	4.2	2.9
1,2 Propanediol	3.3	2.0	8.0	7.9	5.3
Monoethanolamine	3.0	1.5	1.3	2.5	0.8
TEPAE	1.6	-	1.3	1.2	1.2
Protease	0.03	0.01	0.03	0.02	0.02

103

	I	II	III	IV	V
Lipase	-	-	0.002	-	-
Amylase	-	-	-	0.002	-
Cellulase	0.001	0.0002	0.0002	0.0005	0.0001
SRP 1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
CBD-Damascone	0.2	0.02	0.04	0.06	0.2
Miscellaneous and water		Up to 100%			

Example 12

5

The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight) :

	I	II	III	IV
LAS	10.0	13.0	9.0	-
C25AS	4.0	1.0	2.0	10.0
C25E3S	1.0	-	-	3.0
C25E7	6.0	8.0	13.0	2.5
TFAA	-	-	-	4.5
APA	-	1.4	-	-
TPKFA	2.0	-	13.0	7.0
Citric	2.0	3.0	1.0	1.5
Dodecenyl / tetradecenyl succinic acid	12.0	10.0	-	-
Rapeseed fatty acid	4.0	2.0	1.0	-
Ethanol	4.0	4.0	7.0	2.0
1,2 Propanediol	4.0	4.0	2.0	7.0
Monoethanolamine	-	-	-	5.0
Triethanolamine	-	-	8.0	-
TEPAE	0.5	-	0.5	0.2
DETPMP	1.0	1.0	0.5	1.0
Protease	0.02	0.02	0.01	0.008

104

	I	II	III	IV
Lipase	-	0.002	-	0.002
Amylase	0.004	0.004	0.01	0.008
Cellulase	0.0005	0.0008	0.0003	0.002
SRP 2	0.3	-	0.3	0.1
Boric acid	0.1	0.2	1.0	2.0
Ca chloride	-	0.02	-	0.01
Brightener 1	-	0.4	-	-
Suds suppressor	0.1	0.3	-	0.1
Opacifier	0.5	0.4	-	0.3
CBD-Damascone	0.04	0.02	0.2	0.1
NaOH up to pH	8.0	8.0	7.6	7.7
Miscellaneous and water	Up to 100%			

Example 13

- 5 The following liquid detergent formulations were prepared according to the present invention (Levels are given in parts per weight) :

	I	II	III	IV
LAS	25.0	-	-	-
C25AS	-	13.0	18.0	15.0
C25E3S	-	2.0	2.0	4.0
C25E7	-	-	4.0	4.0
TFAA	-	6.0	8.0	8.0
APA	3.0	1.0	2.0	-
TPKFA	-	15.0	11.0	11.0
Citric	1.0	1.0	1.0	1.0
Dodecenyl / tetradecenyl succinic acid	15.0	-	-	-
Rapeseed fatty acid	1.0	-	3.5	-
Ethanol	7.0	2.0	3.0	2.0
1,2 Propanediol	6.0	8.0	10.0	13.0
Monoethanolamine	-	-	9.0	9.0
TEPAE	-	-	0.4	0.3
DETPMP	2.0	1.2	1.0	-
Protease	0.08	0.02	0.01	0.02

WO 00/18897

PCT/US98/20491

105

	I	II	III	IV
Lipase	-	-	0.003	0.003
Amylase	0.004	0.01	0.01	0.01
Cellulase	0.0003	0.0006	0.004	0.003
SRP 2	-	-	0.2	0.1
Boric acid	1.0	1.5	2.5	2.5
Bentonite clay	4.0	4.0	-	-
Brightener 1	0.1	0.2	0.3	-
Suds suppressor	0.4	-	-	-
Opacifier	0.8	0.7	-	-
CBD-Damascone	-	0.02	0.06	-
CBD-Rotundial	1.0	0.5	5.0	2.0
NaOH up to pH	8.0	7.5	8.0	8.2
Miscellaneous and water	Up to 100%			

Example 14

- 5 The following liquid detergent compositions were prepared according to the present invention (Levels are given in parts by weight) :

	I	II
LAS	27.6	18.9
C45AS	13.8	5.9
C13E8	3.0	3.1
Oleic acid	3.4	2.5
Citric	5.4	5.4
Na hydroxide	0.4	3.6
Ca Formate	0.2	0.1
Na Formate	-	0.5
Ethanol	7.0	-
Monoethanolamine	16.5	8.0
1,2 propanediol	5.9	5.5
Xylene sulfonic acid	-	2.4
TEPAE	1.5	0.8
Protease	0.05	0.02
Cellulase	0.0003	0.0006

WO 00/18897

PCT/US98/20491

106

	I	II
PEG	-	0.7
Brightener 2	0.4	0.1
CBD-Rotundial	10.0	1.0
Perfume	0.5	0.3
Miscellaneous and water	Up to 100%	

Example 15

- 5 The following granular fabric detergent compositions which provide "softening through the wash" capability were prepared according to the present invention :

	I	II
C45AS	-	10.0
LAS	7.6	-
C68AS	1.3	-
C45E7	4.0	-
C25E3	-	5.0
Coco-alkyl-dimethyl hydroxy-ethyl ammonium chloride	1.4	1.0
Citrate	5.0	3.0
Na-SKS-6	-	11.0
Zeolite A	15.0	15.0
MA/AA	4.0	4.0
DETPMP	0.4	0.4
PB1	15.0	-
Percarbonate	-	15.0
TAED	5.0	5.0
Smectite clay	10.0	10.0
HMWPEO	-	0.1
Protease	0.02	0.01
Lipase	0.02	0.01
Amylase	0.03	0.005
Cellulase	0.001	0.0009
Silicate	3.0	5.0
Carbonate	10.0	10.0

107

	I	II
Suds suppressor	1.0	4.0
CMC	0.2	0.1
CBD-Damascone	0.04	0.06
Water/minors	Up to 100%	

Example 16

5 The following rinse added fabric softener composition was prepared according to the present invention :

	I	II	III
DEQA (2)	20.0	20.0	20.0
Cellulase	0.001	0.001	0.001
HCL	0.03	0.03	0.03
Antifoam agent	0.01	0.01	0.01
Blue dye	25ppm	25ppm	25ppm
CaCl ₂	0.20	0.20	0.20
CBD-Rotundial	5.0	-	2.0
CBD-Damascone	-	0.1	0.06
Perfume	0.90	0.90	0.90
Miscellaneous and water	Up to 100%		

Example 17

10

The following fabric softener and dryer added fabric conditioner compositions were prepared according to the present invention :

	I	II	III	IV	V
DEQA	2.6	19.0	-	-	-
DEQA(2)	-	-	-	-	51.8
DTMAMS	-	-	-	26.0	-
SDASA	-	-	70.0	42.0	40.2
Stearic acid of IV=0	0.3	-	-	-	-
Neodol 45-13	-	-	13.0	-	-
Hydrochloride acid	0.02	0.02	-	-	-

	I	II	III	IV	V
Ethanol	-	-	1.0	-	-
Cellulase	0.0001	0.001	0.0005	0.005	0.0003
Perfume	1.0	1.0	0.75	1.0	1.5
Glycoperse S-20	-	-	-	-	15.4
Glycerol monostearate	-	-	-	26.0	-
Digeranyl Succinate	-	-	0.38	-	-
Silicone antifoam	0.01	0.01	-	-	-
Electrolyte	-	0.1	-	-	-
CBD-Damascone	0.06	0.1	0.2	0.04	0.3
CBD Rotundial	10.0	0.1	-	1.0	-
Clay	-	-	-	3.0	-
Dye	10ppm	25ppm	0.01	-	-
Water and minors	100%	100%	-	-	-

Example 18

5 The following laundry bar detergent compositions were prepared according to the present invention :

	I	II	III	VI	V	III	VI	V
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Na Laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Ca Carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSPP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DETPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-
Silicate	-	-	4.0	5.0	3.0	-	-	-
PVNO	0.02	0.03	-	0.01	-	0.02	-	-

WO 00/18897

PCT/US98/20491

109

	I	II	III	VI	V	III	VI	V
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
SRP 1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Amylase	-	-	0.01	-	-	-	0.002	-
Protease	-	0.004	-	0.003	0.003	-	-	0.003
Lipase	-	0.002	-	0.002	-	-	-	-
Cellulase	.0008	.0003	.0002	.0003	.0003	.0002	.0005	.0005
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
CBD-	1.0	-	0.5	0.1	0.3	-	0.02	0.04
Damascone								
CBD-Rotundial	1.0	0.5	5.0	-	0.5	0.5	-	0.04
Brightener	0.15	0.1	0.15	-	-	-	-	0.1
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0

5

10

15

CLAIMS

- 5 1. A chemical entity comprising more than one chemical components linked to an amino acid sequence comprising a cellulose binding domain.
2. A chemical entity according to claim 1 wherein all the chemical components are linked directly to said amino acid sequence comprising a cellulose binding domain.
- 10 3. A chemical entity according to claim 1 wherein at least one chemical is linked indirectly via a linking region to said an amino acid sequence comprising a cellulose binding domain.
- 15 4. A chemical entity according to claim 3 wherein at least one chemical component is linked directly to said amino acid sequence comprising a cellulose binding domain and at least one chemical component is linked indirectly via a linking region to said amino acid sequence comprising a cellulose binding domain.
- 20 5. A chemical entity according to claim 3 wherein all the chemical components are linked indirectly via a linking region to said amino acid sequence comprising a cellulose binding domain.
- 25 6. A chemical entity according to claims 3-5 wherein said linking region is a polyreactive linking region.
- 30 7. A chemical entity according to claims 1- 6, wherein said amino acid sequence comprising a cellulose binding domain comprises at least one Lysine amino acid.
- 35 8. A chemical entity according to any of the preceding claims wherein said chemical component is selected from the group consisting perfumes, hygiene agents, insect control agents, softener compounds, soil release polymers, bleaching agents, dye fixatives agents, brighteners, enzymes, latex, resins and/or mixtures thereof.

9. A chemical entity according to claim 8 wherein said chemical component is selected from perfumes, hygiene agents, insect control agents, bleaching agents and/or mixtures thereof.
- 5 10. A chemical entity according to claim 9 wherein said perfume is selected from an aldehyde based compound, preferably a citral, HelionalTM, alpha-hexyl-cinnamaldehyde, hydroxycitronellal, LilialTM (p-tert.butyl-alpha-methyldihydrocinnamaldehyde), methylnonylacetaldehyde, 1-decanal, 10 benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde; cis/trans-3,7-dimethyl-2,6-octadien-1-al; heliotropin; 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde; 2,6-nonadienal; alpha-n-amyI cinnamic aldehyde, P.T. Bucinal, lyral, cymal, methyl nonyl acetaldehyde, hexanal, 15 trans-2-hexenal; a ketone based compound, preferably a allylionone, alpha-ionone, beta-ionone, isoraldein (isomethyl-alpha-ionone), methylionone, Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-Ionone, Iso-E-Super, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone; and/or mixtures thereof.
- 20 11. A chemical entity according to claim 9 wherein said hygiene agent is selected from pentadecanol, cinamaldehyde, ionone, glutaraldehyde, citronellal and/or mixtures thereof.
- 25 12. A chemical entity according to claim 9 wherein said insect control agent is selected from an aldehyde based compound, preferably Citronellal, Rotundial and/or mixtures thereof.
- 30 13. A chemical entity according to claim 9 wherein said bleaching agent is selected from Tetra Acetyl Ethylene Diamine, Nonanoyl benzene sulphonate, Phenolsulfonate ester of N-nonanoyl-6-aminocaproic acid and/or mixtures thereof.
- 35 14. A chemical entity according to claims 1-6 wherein the amino acid sequence comprising a cellulose binding domain is selected from the group consisting of CBDs CBHII from *Trichoderma reesei*, CBDs CenC, CenA and Cex from

Cellulomonas fimi, CBD CBHI from *Trichoderma reesei*, CBD Cellulozome from *Clostridium cellulovorans*, CBD E3 from *Thermonospora fusca*, CBD-dimer from *Clostridium stecorarium* (NCIMB11754) XynA, CBD from *Bacillus agaradherens* (NCIMB40482), CBD family 45 from *Humicola insolens*, and/or mixtures thereof

15. A chemical entity according to claim 14 wherein the amino acid sequence comprising a cellulose binding domain is CBD family 45 from *Humicola insolens*.

16. A chemical entity according to claim 7 wherein said amino acid sequence comprising a cellulose binding domain comprising at least one Lysine amino acid, is selected from CBDs CenC, CenA and Cex from *Cellulomonas fimi*, CBD Cellulozome from *Clostridium cellulovorans*, CBD E3 from *Thermonospora fusca*, CBD-dimer from *Clostridium stecorarium* (NCIMB11754) XynA and/or CBD from *Bacillus agaradherens* (NCIMB40482).

17. A chemical entity according to claims 2-5 wherein the linking region is polyethylene glycol derivative.

18. A chemical entity according to claim 17 wherein said polyethylene glycol derivative is a t-BOC-NH-PEG-NH₂ polymer.

19. A chemical entity according to claim 6 wherein the polyreactive linking region is an amino-containing compound.

20. A chemical entity according to claim 19 wherein said amino-containing compound is a peptidic polymer.

21. A chemical entity according to claim 20 wherein said peptidic polymer comprises amino acids selected from tyrosine, lysine, cysteine and/or mixtures thereof.

22. A chemical entity according to any of the preceding claims wherein the linking between a chemical component and an amino acid sequence

comprising a cellulose binding domain, the linking region and/or polyreactive linking region is achieved via a weak bond.

- 5 23. A chemical entity according to claim 22 wherein said chemical component is selected from perfumes, hygiene agents, insect control agents and/or mixtures thereof.
- 10 24. A laundry detergent and/or fabric care composition comprising a chemical entity according to any of the preceding claims and another laundry detergent and/or fabric care ingredient.
- 15 25. A laundry detergent and/or fabric care composition according to claim 24 which is in the form of an additive, a pre-treatment, a post-treatment, a soaking treatment and/or a rinsing treatment composition.
- 20 26. A fabric care composition according to claims 24-25 comprising a cationic surfactant comprising two long alkyl chain lengths.
- 25 27. A method of treating a fabric with a chemical entity according to claims 1-23 or with a laundry detergent and/or fabric care composition according to claims 24-26 for fabric care, including anti-wrinkle, anti-bobbling and anti-shrinkage properties to fabrics, for static control, fabric softness, fabric freshness, colour appearance and fabric anti-wear properties and benefits.
- 30 28. A method of cleaning a fabric with a chemical entity according to claims 1-23 or with a laundry detergent and/or fabric care composition according to claims 24-26 for fabric cleaning and/or fabric stain removal and/or fabric whiteness maintenance and/or fabric dye transfer inhibition.
- 35 29. A method of treating a fabric with a chemical entity according to claims 1-23 or with a laundry detergent and/or fabric care composition according to claims 24-26 for sanitisation and/or insect control.