Title: LAUNDRY DETERGENT COMPOSITION

Abstract: The present invention relates to a laundry detergent composition comprising a polyesteramide polymer. The composition exhibits enhanced detergency, especially in relation to particulate stains and oily stains. The invention further relates to a method of improving stain removal of stained fabrics and to the use of a polyesteramide polymer to provide improved detergency of a laundry detergent surfactant system.
LAUNDRY DETERGENT COMPOSITION

Technical Field of the Invention

The present invention relates to a laundry detergent composition comprising a polyesteramide, said detergent composition exhibits improved detergency.

Background of the Invention

Polymers can be added to laundry compositions for various reasons, typically to improve the efficacy of the composition in some way. Two examples of polymer classes are: soil release polymers that adhere to the fabric, thereby making subsequent staining easier to remove; or anti-redeposition polymers which keep soil in suspension during the wash, thereby stopping redeposition of the soil onto the fabric.

Branched polymers, such as dendrimers and so called hyper-branched polymers are known. Dendrimers tend to be structurally and molecularly uniform; whilst hyperbranched polymers can sometimes have a degree of non-uniformity about their structure and functionality. Polyesteramides are polymers that can be used in dendrimer or hyperbranched architectures, either as uniform or non-uniform structures.


WO 99/16810 (DSM) relates to a linear or branched polymer containing ester groups and at least one amide group in the backbone, having hydroxyalkylamide end groups and having a weight average molecular mass of greater than 800g/mol. These polymers can be used in thermosetting powder-paint compositions.

EP 1 306 401 (DSM) relates to a method to produce a modified hyperbranched polyesteramide. These polymers find application as a rheology modifier in gas-oil, or as an anti-freeze agent or to catch metals and soot in diesel.

Dendritic polymers, such as hyperbranched polyesteramides, are incorporated along with quaternary ammonium compounds in compositions to provide antimicrobial activity according to US 2003/01 14342 (Lonza Inc.).
US 2006/0188537 (Lamba-Kohli) also relates to anti-microbial activity. In this application, the dendritic polymer is functionalised with silane and quaternary ammonium groups.

US 2004/0016060 (BASF) relates to a process for wrinkle proofing cellulosic textiles by treating them with a finish comprising one or more highly branched polymers. Preferred polymers are based on highly branched polyurethanes.

WO 2007/134614 (Henkel) relates to the prevention of transfer of colours during the laundering process.

WO 2007/098889 (DSM) relates to polymers for use in body care or household products, for example shampoos.

US 2007/0274942 (Rhodia) relates to the use of polymers to provide advantageous properties to surfaces, especially to hair or skin.

US 2005/0130862 (Rhodia) relates to the use of linear sulfonated copolymers as soil-release polymers for detergent compositions.

US 4,165,334 (Procter & Gamble) relates to the use of cationic surfactants for removal of clay.

A problem that exists is to improve the detergency effect, especially the primary detergency effect of laundry detergent compositions on textile stains, for example particulate stains.

We have surprisingly found that this problem can be overcome by incorporating polyesteramide polymers in laundry detergent compositions.

**Summary of the Invention**
A first aspect of the present invention provides a laundry detergent composition comprising:

a) detergente surfactant;

b) polyesteramide comprising at least one ester linkage and at least two amide linkages;

wherein the polyesteramide has a structure according to formula (I):
wherein each \( Z \) is independently either a terminal group selected from \( \text{OH}, \text{COOH}, \) fatty acid ester, acetate, benzoate, tertiary amine, \( \text{O(C1-C24 alkyl)} \);

or is a unit of formula (II):

\[
\begin{array}{c}
\text{O} \\
\text{A} \\
\text{N} \\
\text{Z}
\end{array}
\]

with the proviso that at least one \( Z \) group of formula (I) is a unit of formula (II);

wherein for both formula (I) and (II):

- \( A \) is a linking group, independently selected from: \( \text{CrC}_2 \text{alkyl}; \text{cycloalkyl or aryl}; \) optionally substituted by one or more \( \text{CrC}_2 \text{alkyl}, \text{cycloalkyl or aryl moieties}; \) preferably \( A \) is: \( \text{C}_2\text{H}_4; \text{CHRXH}_2, \text{CH}_2\text{CHR}^*, \text{CHRXHR}^*; \) wherein each \( R^* \) is independently a \( \text{CrC}_2 \text{straight chain or branched alkyl or alkenyl group}; \) or \( A \) can also be two adjacent carbon atoms of a cyclohexane or benzene ring, said rings may also be substituted with one or more \( R^* \) groups as defined above;

- \( X \) is a linker, which can independently be any of the same groups as stated for \( A \), but is preferably \( \text{CrC}_2 \text{alkyl}, \text{optionally alkyl or alkenyl substituted}; \) and each \( Y \), which may be present or alternatively absent, is independently a linking group as stated for \( A \); or an alkylene oxide chain containing from 1 to 50 units; and

- optionally carriers and adjuncts to 100 wt. %.

Another aspect of the current invention provides the use of a polyesteramide comprising at least one ester linkage and at least two amide linkages, as defined under b in the composition according to the first aspect of the invention, to provide increased detergency to a laundry detergent composition comprising detersive surfactant.
A further aspect of the present invention relates to a method for improving the stain removal from a textile substrate, comprising the following steps:

a) provision of a wash liquor comprising the laundry detergent composition of the first aspect of the invention dissolved or dispersed within an aqueous medium; and,

b) contacting one or more stained textile substrates with said wash liquor during one or more steps of a laundry process.

The aqueous medium of the wash liquor is preferably water, but may comprise one or more solvents suitable for use for domestic laundry purposes. Preferably the improved stain removal occurs during the main wash of the laundry process, i.e. preferably the laundry detergent composition of the invention is a main wash product.

The invention is particularly suitable for use on particulate stains; such as clay, or oily stains.

The incorporation of the polyesteramide polymers in laundry detergent compositions according to the invention provide one or more of the following advantages: improved detergency of the surfactant system, especially in relation to primary detergency; improved detergency with respect to different types of stains, for example particulate soil stains.

Primary detergency is herein described as the detergency effect on a stain in the primary or first wash. The fabric is stained and subsequently treated with the laundry detergent composition of the invention. The detergency effect (measured as stain removal) of the laundry composition on the stain is termed as primary detergency. This is a separate process to so-called soil release using a polymer, which is treatment of fabric with a polymer (through a wash or other such treatment), with subsequent staining of the fabric, the soil release polymer having the effect of the easier removal of the stain.

The inclusion of the polyesteramide shows an improvement to the primary detergency of a detersive surfactant system. It may also exhibit soil release/anti-redeposition benefits in addition to this primary detergency benefit; however it is not required to exhibit these as such.
The polyesteramide polymer may be incorporated within the laundry detergent compositions in any suitable fashion within the knowledge of a person of ordinary skill in the art.

**Detailed Description of the Invention**

All percentages quoted herein are defined as percentages by weight unless otherwise stated. All weight percentages are stated herein as weight percent on total formulation unless otherwise stated.

The textile/fabric substrates used can be any typical textile/fabric substrate, such as cotton (woven, knitted and denim), polyester (woven, knitted and microfibre), nylon, silk, polycotton (polyester/cotton blends), polyester elastine, cotton elastine, viscose rayon, acrylic or wool.

Particularly suitable textile/fabric substrates are cotton, polycotton and polyester substrates.

**Polyesteramide**

The polyesteramide is herein described as a polymer comprising at least one ester linkage and at least two amide linkages. Preferably the polyesteramide comprises at least two amide linkages and at least two ester linkages, more preferably at least two amide linkages and at least four ester linkages. Highly preferred polyesteramide embodiments comprise at least six amide linkages and at least four ester linkages.

The polyesteramide may be a single polyesteramide polymer, or a mixture of different polyesteramide polymers.

The polyesteramide may have a molecularly or functionally symmetrical structure (i.e. similar to a dendrimer structure for example), or it may be molecularly or functionally non-uniform (i.e. having unsymmetrical branching or having different functional groups attached).

Preferably the polyesteramide comprises one or more poly(alkylene) oxide chains, said chains comprising from 1 to 50 repeat units, more preferably from 4 to 50 repeat units.

Preferably, said poly(alkylene) oxide chain comprises poly(ethylene) oxide units,
poly(propylene) oxide units or mixtures thereof, said mixtures being preferably arranged in block fashion.

Preferably, the polyesteramide does not contain any silane functionality.

The polyesteramide has a structure according to formula (I):

wherein \( A \) is a linking group, alternatively called a bridging group, and is independently a \( C_2 \) alkyl, cycloalkyl or aryl, optionally substituted by one or more \( C_2-C_4 \) alkyl, cycloalkyl or aryl moieties, preferably \( A \) is: \( C_2H_4 \), \( CHRXH_2 \), \( CH_2CHR^* \), \( CHRXHR^* \), wherein each \( R^* \) is independently a \( C_2-C_4 \) straight chain or branched alkyl or alkenyl group; or \( A \) can also be two adjacent carbon atoms of a cyclohexane or benzene ring, said rings may also be substituted with one or more \( R^* \) groups as defined above;

each \( X \) is a linker, which can independently be any of the same groups as stated for \( A \), but is preferably \( C_2-C_4 \) alkyl optionally alkyl or alkenyl substituted, more preferably \( C_2-C_4 \) alkyl substituted with \( C_2 \) alkyl, even more preferably \( CH_2CHMe \), i.e. an isopropyl linker, preferably linking to the nitrogen atom via the \( CH_2 \) group;

each \( Y \), which may be present or alternatively absent, is independently: a linking group as stated for \( A \); or is an alkylene oxide chain containing from 1 to 50 units, preferably a poly(alkylene) oxide chain, comprising from 4 to 50 units, which may comprise a single alkylene oxide repeat unit, or alternatively comprise a mixture of alkylene oxide repeat units said chains preferably comprising poly(ethylene)oxide, poly(propylene)oxide or mixtures thereof. If the poly(alkylene) oxide chain is a mixture of different alkylene oxides, then preferably they are arranged in block fashion, i.e. comprising each alkylene oxide in blocks of two or more repeat units;

each \( Z \) is independently either: a terminal group selected from \( OH, COOH \), fatty acid ester, acetate, benzoate, tertiary amine, \( O(C1-C24 \) alkyl) or zwitterionic groups such as amine oxides or betaines; or is a unit of formula (II):
With the proviso that at least one Z group of formula (I) is a unit of formula (II); and A, X, Y and Z of formula (II) are the same groups as stated in formula (I).

Highly preferred polyesteramide structures are hyperbranched structures available as Hybrane (Trademark) from DSM. An example of which is Hybrane (Trademark) S1200, which is commercially available from DSM, Geleen, The Netherlands. Discussions of possible Hybrane (Trademark) structures, along with starting materials and methods for production and derivatisation can be found in for example, EP 1 306 401, WO 99/16810 and Froehling, J Polym Sci Part A: Polym Chem, 2004, 42, 3110 (all DSM).

The Hybrane (Trademark) polyesteramides have the basic structure in formula (III), and can be functionalised accordingly. The structures in formula (III) comprise at least six amide linkages and at least four ester linkages.

W depicts a bridging group between the carbonyl groups of two carbon atoms, said W can independently be: C\(_2\)H\(_4\), CHRXH\(_2\), CH\(_2\)CHR', CHRXHR', wherein each R' is independently a C\(_1\)-C\(_4\) straight chain or branched alkyl or alkenyl group; or W can also be two adjacent carbon atoms of a cyclohexane or benzene ring, said rings may also be substituted with one or more R' groups as defined above;
Ri is independently chosen from:

a) terminal groups, for example a tertiary amine terminal group such as \((C_1^t\text{C}_6)N(R'R'')_2\), in which R' and R'' may be the same or different \(\text{CrC}_6\) alkyl groups; hydroxy groups linked to the nitrogen via a \(\text{CrC}_6\) alkyl group, such as \((\text{CrC}_6)\text{OH}\), (these alkyl groups may optionally be \(\text{CrC}_6\) branched); \(\text{CrC}_6\) alkoxy terminated variants of the aforementioned hydroxy group which may additionally comprise a poly(alkylene) oxide chain; or ester terminated variants of the aforementioned hydroxy groups, for example acetate, benzoate or fatty acid ester variants;

b) propagating groups, for example, additional ester/amide groups, which continue the branches polyesteramide, said propagating group Ri having the following structure:

\[
\begin{array}{c}
\text{O} \\
\text{R}_2 \\
\text{O} \\
\text{N} \\
\text{R}_1' \\
\text{R}_1 \\
\end{array}
\]

\(R_2\) is attached to the nitrogen atom of (III) and is \(C_1^t\text{C}_{24}\) alkyl or alkenyl, optionally substituted with one or more \(\text{CrC}_{24}\) alkyl or alkenyl groups, \(W\) is as above for formula (III), and each \(R_1'\) is independently the same groups as described for \(R_1\) of formula (III).

The two carbon atom W bridging group between the carbonyl groups of the ester/amide moieties can be altered depending on the anhydride used to form the polyesteramide. Mixtures of two or more different anhydrides can be used, giving rise to polyesteramides with differing bridging groups.

In a preferred embodiment of formula (III), \(R_1\) is independently: \(\text{CH}_2\text{C}(\text{Me})\text{OH}\), \((\text{C}_1^t\text{C}_6)\text{NMe}_2\), a fatty acid ester with formula \(\text{CH}_2\text{C}(\text{Me})\text{O}(\text{COC}_5\text{C}_3\text{alkyl or alkenyl}), \) or \(\text{CH}_2\text{C}(\text{Me})\text{O}(\text{C}_0\text{C}_6\text{alkyl})\cdot\text{PAO-O(C}_7\text{C}_6\text{alkyl}), \) preferably Me, wherein PAO is stated herein as 'poly(alkylene) oxide' comprising from 1 to 50 repeat units, and is preferably PEO (poly(ethylene) oxide), PPO (poly(propylene) oxide), or a mixture of PEO and PPO arranged in block fashion, with 2 or more units present in each block.

Preferred Hybran (Trademark) structures of formula (III) according to the current invention comprise at least one poly(alkylene) oxide chain, (preferably comprising poly(ethylene) oxide units, poly(propylene) oxide units, or a mixture thereof arranged in blocks of 2 or more units), comprising 4 to 50 repeat units.
The weight average molecular weight of the polyesteramide is preferably 800 Daltons or greater. More preferably, the polyesteramide has a molecular weight between 800 and 60000 Daltons, even more preferably between 1000 and 20000 Daltons.

The polyesteramide is preferably present in the laundry composition at a level of from 0.1 to 20 wt.% by on total composition. More preferably, the polyesteramide is present at a level of from 0.1 to 15 wt.%, even more preferably from 0.5 to 10 wt.% on total composition.

Preferably, the ratio of polyesteramide to total amount of detersive surfactant present in the laundry composition is from 1:50 to 2:1, more preferably from 1:25 to 1:1, most preferably from 1:20 to 1:1.

**Detersive Surfactant**

The laundry detergent compositions of the invention comprise detersive surfactant. Where the polyesteramide comprised within the laundry detergent composition exhibits surfactant like, or detersive surfactant like properties, the laundry detergent composition comprises a detersive surfactant in addition to any detersive surfactant properties of the polyesteramide.

By a detersive surfactant, as incorporated in the laundry detergent composition of the invention, we mean that the surfactant, or at least one surfactant of any surfactant mixture, provides a detersive, i.e. cleaning effect to textile fabrics treated as part of a laundering process. Other surfactants, which may or may not be detersive surfactants can be used as part of the composition.

The detersive surfactant can be a single surfactant or a mixture of two or more surfactants. In general any surfactant may be used, including anionic, non-ionic, and cationic surfactants. Preferably the detersive surfactant comprises anionic surfactant, non-ionic surfactant or a mixture of the two. More preferably the detersive surfactant is a mixture of anionic and non-ionic surfactant.

The detersive surfactant is present by weight in the laundry detergent compositions at a level of from 1 to 95 wt.%, preferably from 1.5 to 60 wt.%, more preferably from 2 to 40 wt.%, most preferably from 2.5 to 35 wt%. Additional surfactants can also be incorporated.
in the laundry compositions of the invention; these may be detersive or non-detersive surfactants.

If present, anionic surfactant is present at a level of from 0.1 to 95 wt.%, preferably from 1 to 50 wt.%, more preferably from 1.5 to 25 wt.% based on total weight of the laundry composition. Nonionic surfactant, if present is incorporated at a level of from 0.1 to 95 wt.%, preferably from 1 to 50 wt.%, more preferably from 1.5 to 25 wt.% based on total weight of the laundry composition. If a detersive surfactant mixture is used that incorporates both anionic and nonionic surfactant, then preferably the ratio of anionic surfactant to nonionic surfactant is from 10:1 to 1:10.


Non-ionic Surfactant

For the purposes of this disclosure, "non-ionic surfactant" shall be defined as amphiphilic molecules with a molecular weight of less than about 10,000, unless otherwise noted, which are substantially free of any functional groups that exhibit a net charge at the normal wash pH of 6-11.

Any type of non-ionic surfactant may be used, although preferred materials are further discussed below. Highly preferred are fatty acid alkoxylates, especially ethoxylates, having an alkyl chain of from C₈-C₃₅, preferably C₈-C₃₀, more preferably C₁₀-C₁₄, especially C₁₀-C₁₈ carbon atoms, for example, Neodols from Shell (Houston, Tex.); ethylene oxide/propylene oxide block polymers which may have molecular weight from 1,000 to 30,000, for example, Pluronic (Trademark) from BASF (Mount Olive, NJ.); and alkylphenol ethoxylates, for example Triton X-100, available from Dow Chemical (Midland, Mich.).

Other non-ionic surfactants should also be considered within the scope of this invention. These include condensates of alkanolamines with fatty acids, such as cocamide DEA, polyol-fatty acid esters, such as the Span series available from Uniqema (Wilmington,
Del.), ethoxylated polyol-fatty acid esters, such as the Tween series available from Uniqema (Wilmington, Del.), Alkylpolyglucosides, such as the APG line available from Cognis (Gulph Mills, Pa.) and n-alkylpyrrolidones, such as the Surfadone series of products marketed by ISP (Wayne, NJ). Furthermore, non-ionic surfactants not specifically mentioned above, but within the definition, may also be used.

Preferred anionic surfactants are outlined below.

**Anionic surfactants**

"Anionic surfactants" are defined herein as amphiphilic molecules comprising one or more functional groups that exhibit a net anionic charge when in aqueous solution at the normal wash pH of between 6 and 11.

Preferred anionic surfactants are the alkali metal salts of organic sulphur reaction products having in their molecular structure an alkyl radical containing from about 6 to 24 carbon atoms and a radical selected from the group consisting of sulphonic and sulphuric acid ester radicals.

Although any anionic surfactant hereinafter described can be used, such as alkyl ether sulphates, soaps, fatty acid ester sulphonates, alkyl benzene sulphonates, sulphosuccinate esters, primary alkyl sulphates, olefin sulphonates, paraffin sulphonates and organic phosphate; preferred anionic surfactants are the alkali and alkaline earth metal salts of fatty acid carboxylates, fatty alcohol sulphates, preferably primary alkyl sulfates, more preferably they are ethoxylated, for example alkyl ether sulfates; and alkylebenzene sulfonates or mixtures thereof.

Alternative or complimentary surfactants may also be present, for example cationic surfactants.

**Amphoteric or zwitterionic surfactant**

The composition according to the invention preferably comprises an amphoteric or zwitterionic surfactant. Amphoteric surfactants are molecules that contain both acidic and basic groups and will exist as zwitterions at the normal wash pH of between 6 and 11.

Preferably an amphoteric or zwitterionic surfactant is present at a level of from 0.1 to 20 wt%, more preferably from 0.25 to 15 wt%, even more preferably from 0.5 to 10 wt%.
Suitable zwitterionic surfactants are exemplified as those which can be broadly described as derivatives of aliphatic quaternary ammonium, sulfonium and phosphonium compounds with one long chain group having about 8 to about 18 carbon atoms and at least one water solubilizing radical selected from the group consisting of sulfate, sulfonate, carboxylate, phosphate or phosphonate. A general formula for these compounds is:

$$R_1(R_2)_xY^xR_3Z^-$$

wherein $R_1$ contains an alkyl, alkenyl or hydroxyalkyl group with 8 to 18 carbon atoms, from 0 to 10 ethylene-oxy groups or from 0 to 2 glyceryl units; $Y$ is a nitrogen, sulfur or phosphorous atom; $R_2$ is an alkyl or hydroxyalkyl group with 1 to 3 carbon atoms; $x$ is 1 when $Y$ is a sulfur atom and 2 when $Y$ is a nitrogen or phosphorous atom; $R_3$ is an alkyl or hydroxyalkyl group with 1 to 5 carbon atoms and $Z$ is radical selected from the group consisting of sulfate, sulfonate, carboxylate, phosphate or phosphonate.

Preferred amphoteric or zwitterionic surfactants for incorporation in the composition according to the present invention are betaine surfactants. Examples of these are mentioned in the following list.

The sulfatobetaines, such as:
3-(dodecyldimethylammonium)-1-propane sulfate, and
2-(cocodimethylammonium)-1-ethane sulfate.

The sulfobetaines, such as:
3-(dodecyldimethyl-ammonium)-2-hydroxy-1-propane sulfonate,
3-(tetradecyl-dimethylammonium)-1-propane sulfonate,
3-(Ci$_2$-Ci$_4$ alkyl-amidopropyldimethylammonium)-2-hydroxy-1-propane sulfonate, and
3-(cocodimethylammonium)-1-propane sulfonate.

The carboxybetaines, such as
(dodecyldimethylammonium) acetate (also known as lauryl betaine),
(tetradecyldimethylammonium) acetate (also known as myristyl betaine),
(cocodimethylammonium) acetate (also known as coconut betaine),
(oleyldimethylammonium) acetate (also known as oleyl betaine),
(dodecyloxymethyltrimethylammonium) acetate, and
(cocoamido-propyldimethylammonium) acetate (also known as cocoamido-propyl betaine or CAPB).

The sulfoniumbetaines, such as:
(dodecyldimethylsulfonium) acetate, and
3-(cocodimethyl-sulfonium)-1-propane sulfonate.
The phosphonium betaines, such as:
4-(trimethylphosphonium)-1-hexadecane sulfonate,
3-(dodecyldimethylphosphonium)-1-propanesulfonate, and
2-(dodecyldimethylphosphonium)-1-ethane sulfate.

The compositions according to the present invention preferably comprise carboxybetaines or sulphobetaines as amphoteric or zwitterionic surfactants, or mixtures thereof. Especially preferred is lauryl betaine.

Product Form
A product according to the invention may take any suitable form, such as a solid, liquid or paste composition. Preferably the product is in a liquid form, which may be a concentrated liquid.

Optional Ingredients
In addition to the essential components detailed in the claims, the formulation may include one or more optional ingredients. While it is not necessary for these elements to be present in order to practice this invention, the use of such materials is often very helpful in rendering the formulation acceptable for consumer use.

Examples of optional components include, but are not limited to: additional surfactants, including nonionic and anionic surfactants, cationic surfactants; hydro tropes, fluorescent whitening agents, photobleaches, fibre lubricants, reducing agents, enzymes, enzyme stabilising agents (such as borates and polyols), powder finishing agents, defoamers, builders (such as alkali and alkaline earth metal carbonates, phosphates, zeolites and organic builders such as citrates, succinates, sulphamates and malonates), bleaches, bleach catalysts, soil release agents, antiredeposition agents, dye transfer inhibitors, buffers, colorants, fragrances, pro-fragrances, rheology modifiers, anti-ashing polymers, preservatives, insect repellents, soil repellents, water-resistance agents, suspending agents, aesthetic agents, structuring agents, sanitisers, solvents, including aqueous and non-aqueous solvents, fabric finishing agents, dye fixatives, wrinkle-reducing agents, fabric conditioning agents and deodorizers.

The invention will now be illustrated by the following non-limiting examples.
EXAMPLES

Measurement of Soil Release Index (SRI)

SRI is a measure of how much of a stain on textile is removed during a washing process. The intensity of any stain can be measured by means of a reflectometer in terms of the difference between the stain and clean cloth giving $\Delta E^*$ for each stain. It is defined as $\Delta E^*$ and is calculated as:

$$ \Delta E^* = \sqrt{(L_{\text{stain-before}}^* - L_{\text{clean-cloth}}^*)^2 + (a_{\text{stain-before}}^* - a_{\text{clean-cloth}}^*)^2 + (b_{\text{stain-before}}^* - b_{\text{clean-cloth}}^*)^2} $$

$L^*$, $a^*$, and $b^*$ are the coordinates of the CIE 1976 ($L^*, a^*, b^*$) colour space, determined using a standard reflectometer. $\Delta E^*$ can be measured before and after the stain is washed, to give $\Delta E_{bw}^*$ (before wash) and $\Delta E_{aw}^*$ (after wash). SRI is then defined as:

$$ \text{SRI} = 100 - \frac{\Delta E_{aw}^*}{\Delta E_{bw}^*} $$

A SRI of 100 means complete removal of a stain.

Detergency Measure ($\Delta \Delta E$)

The change in intensity of any stain brought about by washing in a detergent formulation can be measured using the $\Delta \Delta E$ value. $\Delta \Delta E$ is a measure of how much of the original stain is removed and is defined as:

$$ \Delta \Delta E = \Delta E_{bw}^* - \Delta E_{aw}^* $$

A larger positive $\Delta \Delta E$ value shows better stain removal.

Standard wash protocol, called the Linitest Protocol, using a Linitest washing machine:

1. Measurement of the colour of the stain on the textile cloth.
2. Fill up the containers in the Linitest with required stock solution as well as demineralised water to make up the relevant washing liquor.
3. Load the stains swatches as well as ballast into the containers.
4. Put the lids on the containers after 50 ball bearings are added and start the wash (30 min at 30°C).
5. After the wash, get rid of the washing liquor and squeeze the excess liquor out of the fabrics.
6. Add 200ml of 6°FH (French hardness) water into the containers and close the lids.
7. Start the machine for 3 min.
8. Repeat the above steps 5-7.
9. Wring the cloths and transfer the washed stains swatch onto the drying rack.
10. Cloths will be drying overnight in the dark, followed by colour measurement of the stain.

Standard wash protocol, called the Tergotometer Protocol, using a Tergotometer washing machine
1. Measure colour of the stains on the textile cloth.
2. Switch on Tergotometer and set to temperature of 25°C
3. Add demineralised water and electrolyte to each pot, leave to heat to 25°C.
4. Add formulation to each pot and then agitate at 100rpm for 1 minute.
5. Add the stain swatches and ballast into each pot.
6. Start the wash, agitate at 100 rpm and leave for 12 minutes.
7. Rinse with demineralised water for 2 minutes.
8. Repeat rinse.
9. Dry overnight in the dark.
10. Measure colour of the stains on the textile cloth.

Example 1  Garden soil removal from polyester (measured in limitest protocol)
A wash liquor was formulated, containing as surfactants the compounds indicated in table 1 at the indicated concentrations. Additionally the wash liquor contained other standard compounds of a laundry detergent (e.g. builder). Some typical formulations of detergent compositions according to the present invention are given in tables 9 and 10.
Table 1  Concentrations of surfactants in wash liquor, formulations 1 and 2

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Formulation 1 (comparative)</th>
<th>Formulation 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary alcohol sulfate (anionic surfactant)</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>Alcohol ethoxylate</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>S1200</td>
<td>0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

S1200 is a Hybrane (Trademark) product, and is a dendrimeric polyesteramide polymer commercially available from DSM, Geleen, The Netherlands.

The following results were obtained for the detergency measure.

Table 2  Garden soil removal from polyester (measured in linitest protocol), formulations 1 and 2.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>SRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>88.6</td>
</tr>
<tr>
<td>2</td>
<td>90.7</td>
</tr>
</tbody>
</table>

Example 2  Red gravel removal from polyester (measured in linitest protocol)

A wash liquor was formulated, containing as surfactants the compounds indicated in table 3 at the indicated concentrations. Additionally, the wash liquor contained other standard compounds of a laundry detergent (e.g. builder). Some typical formulations of detergent compositions according to the present invention are given in tables 9 and 10.

Table 3  Concentrations of surfactants in wash liquor, formulations 3 and 4

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Formulation 3 (comparative)</th>
<th>Formulation 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary alcohol sulfate (anionic surfactant)</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>Alcohol ethoxylate</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>S1200</td>
<td>0</td>
<td>0.1</td>
</tr>
</tbody>
</table>
S1200 is a Hybrane (Trademark) product, and is a dendrimeric polyesteramide polymer commercially available from DSM, Geleen, The Netherlands.

The following results were obtained for the detergency measure.

### Table 4  Red gravel removal from polyester (measured in linitest protocol).

<table>
<thead>
<tr>
<th>Formulation</th>
<th>SRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>87.6</td>
</tr>
<tr>
<td>4</td>
<td>91.6</td>
</tr>
</tbody>
</table>

Example 3  Red clay stain removal from polyester

A wash liquor was formulated, containing as surfactants the compounds indicated in table 5 at the indicated concentrations. Additionally the wash liquor contained other standard compounds of a laundry detergent (e.g. builder). Some typical formulations of detergent compositions according to the present invention are given in tables 9 and 10.

### Table 5 Concentrations of surfactants in wash liquor, formulations 5 and 6.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Formulation 5 (comparative)</th>
<th>Formulation 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary alcohol sulfate</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Alcohol ethoxylate (C₁₂ 7EO)</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Lauryl betaine</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Polyesteramide S1200</td>
<td>0</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Polyesteramide S1200 is a Hybrane (trademark) product, and is a dendrimeric polyesteramide polymer commercially available from DSM (Geleen, The Netherlands).

The following results were obtained for the removal of red clay stains from polyester cloth, as measured in the Linitest protocol.
Table 6  Stain removal index for red clay stains on polyester (Linitest protocol).

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<tr>
<th>Formulation</th>
<th>SRI</th>
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<tr>
<td>5</td>
<td>89.6</td>
</tr>
<tr>
<td>6</td>
<td>93.4</td>
</tr>
</tbody>
</table>

**Example 4**  Grass *stain* removal *from cotton*

A wash liquor was formulated, containing as surfactants the compounds indicated in Table 7 at the indicated concentrations. Additionally the wash liquor contained other standard compounds of a laundry detergent (e.g. builder). Some typical formulations of detergent compositions according to the present invention are given in Tables 9 and 10.

The following results were obtained for the removal of grass stains from cotton cloth, as measured in the Tergotometer Protocol.

Table 7  Concentrations of surfactants in wash liquor, formulations 3 and 4.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Formulation 7 (comparative)</th>
<th>Formulation 8 in wash concentration (g/L)</th>
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<tr>
<td>Primary alcohol sulfate</td>
<td>0.31</td>
<td>0.31</td>
</tr>
<tr>
<td>Alcohol ethoxylate (C_{12} 7EO)</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Lauryl betaine</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Polyesteramide S1200</td>
<td>0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Polyesteramide S1200 is a Hybrane (trademark) product, and is a dendrimeric polyesteramide polymer commercially available from DSM (Geleen, The Netherlands).

The following results were obtained for the detergency measure.

Table 8  Grass removal from cotton (measured in Tergotometer protocol).

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<tr>
<th>Formulation</th>
<th>Detergency measure ΔΔE</th>
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<tr>
<td>7</td>
<td>21.3</td>
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<tr>
<td>8</td>
<td>23.9</td>
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</tbody>
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Table 9  Typical product formulations according to the invention.

<table>
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<tr>
<th>Ingredient</th>
<th>Powder Formulation (concentration in final product [weight %])</th>
<th>Liquid Detergent Formulation (concentration in final product [weight %])</th>
<th>Concentrated Liquid Detergent (concentration in final product [weight %])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear alkyl benzene sulfonate</td>
<td>10</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Anionic surfactant</td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Alcohol ethoxylate</td>
<td>5</td>
<td>6</td>
<td>15</td>
</tr>
<tr>
<td>Zeolite builder</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Enzymes</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Whitening agent</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Bleach</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bleach activator</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyesteramide</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Sodium citrate</td>
<td></td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Sodium chloride</td>
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<td>2</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Dispersant</td>
<td>1</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Water, perfume, foam control &amp; other minors</td>
<td>balance (no water)</td>
<td>balance</td>
<td>balance</td>
</tr>
</tbody>
</table>
Table 10  Typical product formulations according to the invention.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Powder Formulation (concentration in final product [weight %])</th>
<th>Liquid Detergent Formulation (concentration in final product [weight %])</th>
<th>Concentrated Liquid Detergent (concentration in final product [weight %])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear alkyl benzene sulfonate</td>
<td>10</td>
<td>12</td>
<td>24</td>
</tr>
<tr>
<td>Alcohol ethoxylate</td>
<td>5</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>Amphoteric or zwitterionic surfactant</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Zeolite builder</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium carbonate</td>
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<td></td>
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</tr>
<tr>
<td>Enzymes</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Whitening agent</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Bleach</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Bleach activator</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyesteramide</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Sodium citrate</td>
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<td></td>
<td>5</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>2</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>1</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Dispersent</td>
<td>1</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Water, perfume, foam control &amp; other minors</td>
<td>balance (no water)</td>
<td>balance</td>
<td>balance</td>
</tr>
</tbody>
</table>
1. A laundry detergent composition comprising:
   a) detersive surfactant;
   b) polyesteramide comprising at least one ester linkage and at least two amide
      linkages;
      wherein the polyesteramide has a structure according to formula (I):

      \[
      \begin{array}{c}
      Z \quad Y \quad X \quad O \quad A \quad O \quad N \quad Y \quad Z \\
      Y \quad Z \quad O \quad A \quad N \quad X \quad Y \quad Z \\
      Z \quad X \quad Y \quad A \quad N \quad X \quad Y \quad Z \\
      \end{array}
      \]

      (I)

      wherein each Z is independently either a terminal group selected from OH, COOH,
      fatty acid ester, acetate, benzoate, tertiary amine, O(C1-C24 alkyl);
      or is a unit of formula (II):

      \[
      \begin{array}{c}
      O \quad A \quad Y \quad Z \\
      O \quad A \quad X \quad Y \quad Z \\
      \end{array}
      \]

      (II)

      with the proviso that at least one Z group of formula (I) is a unit of formula (II);
      wherein for both formula (I) and (II):
      A is a linking group, independently selected from: C₁-C₂₄ alkyl; cycloalkyl or aryl;
      optionally substituted by one or more CrC₂₄ alkyl, cycloalkyl or aryl moieties;
      preferably A is: C₂H₄, CHRX₂, CH₂CHR³, CHRXHR⁴; wherein each R³ is
      independently a CrC₂₄ straight chain or branched alkyl or alkenyl group; or A can
      also be two adjacent carbon atoms of a cyclohexane or benzene ring, said rings
      may also be substituted with one or more R³' groups as defined above;
      X is a linker, which can independently be any of the same groups as stated for A, but
      is preferably CrC₂₄ alkyl, optionally alkyl or alkenyl substituted;
      and each Y, which may be present or alternatively absent, is independently a linking
      group as stated for A; or an alkylene oxide chain containing from 1 to 50 units, and,
c) optionally carriers and adjuncts to 100 wt.%.

2. A composition according to claim 1, further comprising an amphoteric or zwitterionic surfactant.

3. A composition according to claim 1 or 2, wherein the ratio of polyesteramide to detersive surfactant is from 1:50 to 2:1, preferably from 1:25 to 1:1, more preferably from 1:20 to 1:1.

4. A composition according to any of claims 1 to 3 wherein the polyesteramide comprises one or more poly(alkylene)oxide chains containing from 1 to 50 repeat units, said chains preferably comprising poly(ethylene)oxide, poly(propylene)oxide or mixtures thereof.

5. A composition according to claim 4 wherein the poly(ethylene)oxide and poly(propylene)oxide units are arranged in block fashion.

6. A composition according to any one of claims 1 to 5, wherein the polyesteramide comprises at least two amide linkages and at least two ester linkages.

7. A composition according to claim 6, wherein the polyesteramide comprises at least four ester linkages.

8. A composition according to claim 6 or 7, wherein the polyesteramide comprises at least six amide linkages and at least four ester linkages.

9. A composition according to any one of claims 1 to 8, wherein the polyesteramide has a number average molecular weight of from 800 to 20,000 Daltons.

10. A composition according to any one of claims 1 to 9, wherein the detersive surfactant is an anionic surfactant, nonionic surfactant, or a mixture thereof.

11. A composition according to any one of claims 2 to 10, wherein the amphoteric or zwitterionic surfactant is a betaine surfactant.
12. A composition according to any one of claims 2 to 11, wherein the amphoteric or zwitterionic surfactant is a carboxybetaine or sulphobetaine surfactant or a mixture thereof.

13. A composition according to any one of claims 2 to 12, wherein the concentration of amphoteric or zwitterionic surfactant is from 0.1 to 20 wt%.

14. Use of a polyesteramide comprising at least one ester linkage and at least two amide linkages wherein the polyesteramide has a structure according to formula (I):

\[
[Z \quad X \quad Y \quad N \quad O \quad A \quad N \quad O \quad X \quad Y \quad Z]
\]

wherein each Z is independently either a terminal group selected from OH, COOH, fatty acid ester, acetate, benzoate, tertiary amine, O(C1-C24 alkyl); or is a unit of formula (II):

\[
[O \quad A \quad N \quad X \quad Y \quad Z]
\]

with the proviso that at least one Z group of formula (I) is a unit of formula (II); wherein for both formula (I) and (II):

A is a linking group, independently selected from: CrC\textsubscript{24} alkyl; cycloalkyl or aryl; optionally substituted by one or more CrC\textsubscript{24} alkyl, cycloalkyl or aryl moieties; preferably A is: C\textsubscript{2}H\textsubscript{4}; CH\textsubscript{2}CHR\textsuperscript{1}; CH\textsubscript{2}CHR\textsuperscript{1}'; CHXHR\textsuperscript{2}; CHXRHR\textsuperscript{2}'; wherein each R\textsuperscript{1} is independently a CrC\textsubscript{24} straight chain or branched alkyl or alkenyl group; or A can also be two adjacent carbon atoms of a cyclohexane or benzene ring, said rings may also be substituted with one or more R\textsuperscript{2} groups as defined above;

X is a linker, which can independently be any of the same groups as stated for A,
but is preferably CrC₄ alkyl, optionally alkyl or alkenyl substituted; and each Y, which may be present or alternatively absent, is independently a linking group as stated for A; or an alkyene oxide chain containing from 1 to 50 units; to provide improved detergency to a laundry detergent composition comprising detersive surfactant.

15. A method for improving the stain removal from a textile substrate, comprising the following steps:

10 a) provision of a wash liquor comprising the laundry detergent composition according to any one of claims 1 to 13 or dispersed within an aqueous medium; and,

b) contacting one or more stained textile substrates with said wash liquor during one or more steps of a laundry process.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

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

INV. C11D3/37

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim</th>
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Further documents are listed in the continuation of Box C

See patent family annex

* Special categories of cited documents

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'E' earlier document but published on or after the international filing date
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"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"A" document member of the same patent family

Date of the actual completion of the international search: 3 February 2009

Date of mailing of the international search report: 12/02/2009

Name and mailing address of the ISA/
European Patent Office
P B 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040,
Fax (+31-70) 340-3016

Authorized officer

Pfannenstein, Heide
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<td>MUSCAT D ET AL: &quot;HYPERBRANCHED POLYESTERAMIDES - NEW DENDRITIC POLYMERS&quot;</td>
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<td>TOPICS IN CURRENT CHEMISTRY, SPRINGER, BERLIN, DE, vol. 212, 1 January 2001 (2001-01-01), pages 41-80, XP001068479</td>
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<td>US 4 165 334 A (GOSSELINK EUGENE P ET AL) 21 August 1979 (1979-08-21) cited in the application column 12 - column 14; claims</td>
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Form PCT/isa/pmt patent family member(s)