Abstract:

An aqueous concentrated liquid laundry detergent comprising: (a) at least 8 wt%, preferably at most 40 wt%, anionic non-soap surfactant; (b) at most 30 wt% of nonionic surfactant; (c) at most 10 wt% of surfactant other than (a) and (b); (d) at least 0.1 wt%, preferably at most 10 wt%, alkyl hydroxamate; and (e) at least 2 wt%, preferably at most 20 wt%, nonionic ethoxylated polyethylene imine with an average of between 7 and 40 ethoxy units per substitution site on each nitrogen.

Title: AQUEOUS CONCENTRATED LAUNDRY DETERGENT COMPOSITIONS

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AQUEOUS CONCENTRATED LAUNDRY DETERGENT COMPOSITIONS

Technical Field

This invention relates to aqueous concentrated laundry detergent compositions and their use at low dosage, and hence low in wash surfactant concentrations, for cleaning of red clay from polyester fabrics under hard water washing conditions.

Background

EP 388 389 A2 (Monsanto) discloses bleach free under-built liquid detergent compositions containing hydroxamic acids and their derivatives which assist in the removal of bleachable wine stains from fabrics during laundering.

Hydroxamates as in Formula I are disclosed, wherein R\(^1\) represents an optionally substituted straight- or branched chain C\(^5\)-C\(^{21}\) alkyl or C\(^5\)-C\(^{21}\) alkenyl group or an optionally-substituted phenyl group. One of the examples shows an improved bleaching performance when a hydroxamate is used in a detergent composition in hard water (20\(^{\circ}\) German hardness (DH), which is about 143 milligram calcium per litre). The examples use C\(^{12}\) linear, C\(^{12}\) branched, C\(^{13}\) branched and C\(^{18}\) hydroxamates in detergent formulations comprising mixtures of anionic surfactant and nonionic surfactant. In examples I, II and IV there is an excess of nonionic surfactant of at least 1.25 to 1 and in example III there is 100% anionic surfactant.
WO201 0/069957 (Unilever) discloses the use of hydroxamate in conjunction with a specific anionic and nonionic surfactant system to improve the cleaning performance of both powder and liquid compositions on certain stains, notably red clay. Various formulation possibilities are discussed. The examples all use high in-wash surfactant levels. Washing is done under both soft (6°FH) and hard (26°FH) water conditions. A builder (1 wt% sodium citrate) is added for washing in hard water. The ratio of surfactant to hydroxamate claimed is from 5:1 to 15:1.

WO201 1/15 170 (Unilever) discloses that the beneficial effect described in WO201 0/069957 can also be obtained when using similar laundry detergent formulations that containing less than 0.5 wt% hydroxamic acid, or its corresponding hydroxamate. The weight ratio of the defined surfactant system to the hydroxamate is correspondingly extended up to 16 000:1, the preferred ratio being from 10:1 to 400:1.

No suggestion is made to use ethoxylated polyethylene imine polymer (EPEI) in any of the preceding documents concerned with hydroxamates.

EPEI is known from many publications as a polymer that can be added to detergent compositions along with the usual surfactants to improve stain removal: both oily stains and particulate stains. EPEI is available in the original nonionic form based on PEI of various molecular weights (typically 200 to 2000) and degrees of branching and various further modifications have been proposed. For example the EPEI may be cationic (quaternised) and possibly sulphated. It may have nitrogen oxide groups added to make amine oxides and the alkoxyl groups may comprise a mixture of ethylene oxide and other alkylene oxides, for example propylene oxide or butylene oxide. These may be arranged in blocks.

US 5 834 412 is primarily concerned with soil release polymers. However, at column 37 lines 22 to 43 it makes a summary of various EPEIs known as clay soil removal/anti redeposition agents. Included in the list are cationic and amine oxide...
materials. No preference is given to nonionic EPEIs and no EPEI is used in any exemplary formulations.

EP 2 1 3 5 9 3 4 A 1 (Unilever) discloses a synergistic clay soil removal benefit when nonionic EPEI is used in combination with a specific type of first wash lipase (Lipex). The clay is not necessarily red clay (i.e. clay with high iron content). Paragraph 12 of this publication contains an obvious error. In defining what is meant by primary detergency it makes use of a definition transferred from a different application and refers in error to a composition in which "the hydroxamate is used as cosurfactant according to the invention". Firstly, hydroxamate is a properly categorised as a sequestrant, not as a cosurfactant, secondly hydroxamate is totally absent from the invention described and claimed in EP 2 1 3 5 9 3 4. Similar obvious errors are found in paragraphs 59 and 60 of this publication. Since each time it is mentioned the hydroxamate is qualified as being used "as cosurfactant according to the invention" and the invention in EP 2 1 3 5 9 3 4 is clearly nothing of the sort, the skilled person should disregard this disclosure as being an obvious error. The examples in this patent publication were carried out in hard water (26°FH) and 1.71 wt% of citric acid builder was included in the compositions. At the low in wash surfactant levels exemplified increasing the level of EPEI reduced efficacy on yellow clay.

WO2009/1 5 3 1 8 4 (Unilever) describes a method of laundering fabrics that uses very low levels of in wash surfactant (that may be an anionic surfactant). Wash performance is boosted by inclusion of high levels of specific polymers and enzymes. A preferred enzyme is lipase, most preferably Lipex. Preferred polymers are a combination of EPEI and a polyester soil release polymer. The surfactant system preferably includes SLES and most preferably also carbobetaine. A sequestrant is included in the exemplified compositions: De quest 2066. This is Di ethylenetriamine penta(methylene phosphonic acid). No mention is made of hydroxamate.
It is desirable to provide new detergent compositions comprising surfactants and hydroxamate and having excellent performance when used at low in-wash surfactant levels as discussed in WO2009/153184, particularly when the composition does not also comprise a lipase enzyme and most particularly when used under hard water conditions for the removal of red clay stains from polyester.

Unless otherwise stated wt% refers to the total weight percentage in the liquid as dry weight.

Summary of the Invention

According to the present invention there is provided an aqueous concentrated liquid laundry detergent comprising:

(a) at least 8 wt%, preferably at most 40 wt%, anionic non-soap surfactant,

(b) at most 30 wt% of nonionic surfactant,

(c) at most 10 wt% of surfactant other than (a) and (b)

(d) at least 0.1 wt%, preferably at most 10 wt%, alkyl hydroxamate; and

(e) at least 2 wt%, preferably at most 20 wt%, nonionic ethoxylated polyethylene imine with an average of between 7 and 40 ethoxy units per substitution site on each nitrogen.

Polyethylene imines comprise amino moieties where one two or three hydrogens on a nitrogen have been replaced. In this specification a substitution site means a residual hydrogen on the nitrogen. For example if the nitrogen is a terminal one
having two hydrogens then it has two substitution sites and replacing each hydrogen with a 20EO group means that there are 20 ethoxy units on each substitution site on the nitrogen and the average substitution is also 20.

5 Preferably the amount of (a) is greater than or equal to the amount of (b), more preferably the amount of (b) is at least 3 wt%. When the composition comprises less than 3 wt% of nonionic (b) the preferred anionic surfactants (a) comprise a mixture of LAS and AES.

10 Because both alkyl hydroxamate and EPEI are known to improve the removal of clay from fabric, particularly polyester it might be considered to be obvious to create a composition comprising both of these technologies together with a surfactant system. However, it is known that EPEI does not provide a good effect at high water hardness. Thus although we did not expect to see a benefit we were surprised that addition of EPEI to the hydroxamate containing compositions taught as having a benefit for the removal of red clay from polyester, for example in WO201/0/69957 gave a worse result than the original composition without any EPEI included when tested under hard water wash conditions. The surprising conclusion from this was that the finding from WO201/0/69957 that addition of hydroxamate to an already good cleaning system gave a boost did not seem to hold true for the systems comprising EPEI if used in hard water. Given that the hydroxamate provides the red clay removal by cooperation with the surfactant system it was even more surprising that the improved red clay removal with hydroxamate was found again if the EPEI and hydroxamate containing composition was formulated and used to provide low in wash surfactant levels in line with the teaching in WO2009/1 531 84. To obtain the required level of EPEI whilst keeping the in-wash surfactant level low means that the ratio of total surfactant to EPEI in the composition (which is the same as in the wash liquor) is lower than that taught by most of the prior art concerned with inclusion of EPEI.

30 Thus preferred compositions according to the invention have a weight ratio of non-
soap surfactant [(a)+(b)+(c) - soap] to EPEI of from 2:1 to 7:1, preferably from 3:1 to 6:1, even about 5:1.

Preferred detersive surfactant (c) is soap, amphoteric surfactants, for example betaine and mixtures thereof. Component (c) also includes any amine oxide surfactant present in the composition. Soap levels in the composition are preferably less than 3 wt%.

Because the compositions of the invention are concentrated compositions designed for dilution by a factor of at least 500 when forming a wash liquor, the amount of alkyl hydroxamate in the compositions is large as a weight percentage of the composition.

The preferred weight ratio of alkyl hydroxamate (d) to total detersive surfactant system (a), (b) and (c) for optimum particulate red clay soil removal lies in the range 1:4 to 1:8000. More preferred is 1:7 to 1:40. An even more preferred range of ratios being 1:10 to 1:30 parts by weight. The amount of alkyl hydroxamate (d) is preferably at least 0.5, more preferably at least 1.0 wt%.

The compositions may comprise polyester based soil release polymers that are particularly effective with the EPEI and hydroxamate combination at low surfactant levels. Lipase is generally incompatible with such ester containing materials. It is therefore preferred that lipase is absent from the compositions.

Desirably the composition further comprises at least 0.4 wt% perfume, preferably at least 0.5 wt%. When present, the perfume is selected from free oil perfume encapsulated perfume and mixtures thereof. Preferably it comprises mixtures of these types of perfume.
According to a second aspect of the invention there is provided a method of washing polyester fabrics comprising the steps of combining 15 to 25 ml of the composition according to the invention with water having a hardness of at least 20°FH to form a wash liquor having a non-soap surfactant concentration of less than 0.5 g/L and washing the polyester with the wash liquor. The invention further comprises the use of a composition according to the invention in a washing process carried out in water of hardness of at least 20°FH to remove red clay from polyester.

Detailed Description of the Invention

To form the wash liquor for use in the method according to the second aspect of the invention a concentrated laundry liquid with lower surfactant than is normal for such a concentrated composition is used, as described in WO2009/153184. Thus, in one embodiment, a low volume of less than 25 ml and preferably around 20 ml, of the concentrated liquid composition of the invention is dosed to a wash load and diluted with water to form the wash liquor for use in the washing method according to the second aspect of the invention. Although the exact dilution will vary from load to load and from one washing machine to another it is expected that suitable compositions for use in the process according to the invention may comprise the ingredients described below at the levels detailed below.

The Detergent Liquid

The compositions comprise surfactant. The non-soap detertive surfactant makes up at least 10 wt% of the liquid composition, preferably it makes up from 12 to 60 wt%. The compositions for use according to the invention most preferably have total active detertive surfactant levels of at least 15 wt%.
In the method the compositions are used in small doses that require them to be diluted in at least 500 times their own volume of water to form a main-wash liquor comprising at most 0.5 g/l surfactant. They may be concentrated compositions designed for front-loading automatic washing machines, hand-washing or top-loading automatic washing machines. In hand-washing less water may be used and in top-loading automatic washing machines a higher amount of water would normally be used than for a front-loading automatic machine. The dose of detergent liquid is adjusted accordingly to give similar wash liquor concentrations.

Water
The compositions are aqueous. The amount of water is at least 5 wt%, preferably at least 25 wt%.

Alky Hydroxamate
Whenever either the term 'hydroxamic acid' or 'hydroxamate' is used, this encompasses both hydroxamic acid and the corresponding hydroxamate (salt of hydroxamic acid), unless indicated otherwise.

Hydroxamic acids are a class of chemical compounds in which a hydroxylamine is inserted into a carboxylic acid. The general structure of a hydroxamic acid is the following:

\[
\begin{align*}
\text{O} & \\
\text{R}^1 & \\
\text{C} & \\
\text{N} & \\
\text{OH} & \\
\text{H} & 
\end{align*}
\]

(Formula I)

In which \( R^1 \) is an organic residue, for example alkyl or alkylene groups. The hydroxamic acid may be present as its corresponding alkali metal salt, or hydroxamate. The preferred salt is the potassium salt.
The hydroxamates may conveniently be formed from the corresponding hydroxamic acid by substitution of the acid hydrogen atom by a cation as shown in Formula II.

\[
\begin{align*}
\text{R}^1 & \text{C} \equiv \text{N} \text{OH} \quad \text{L}^{-} \quad \text{R}^1 \text{C} \equiv \text{N} \text{O}^{-} L^{-} \\
\text{(Formula II)}
\end{align*}
\]

In Formula II, \(L^+\) is a monovalent cation for example the alkali metals (e.g. potassium, sodium), or ammonium or a substituted ammonium.

In the present invention the alkyi hydroxamic acid or its corresponding alkyi hydroxamate has the structure shown in Formula I:

\[
\begin{align*}
\text{R}^1 & \text{C} \equiv \text{N} \text{OH} \\
\text{(Formula I)}
\end{align*}
\]

wherein \(R^1\) is:

- a straight or branched \(C_4 - C_{20}\) alkyi, or
- a straight or branched substituted \(C_4 - C_{20}\) alkyi, or
- a straight or branched \(C_4 - C_{20}\) alkenyl, or
- a straight or branched substituted \(C_4 - C_{20}\) alkenyl, and

the types of substitution include one or more of \(\text{NH}_2\), \(\text{OH}\), \(\text{S}\), \(-\text{O}^-\), \(\text{COOH}\), and
References to a number of carbon atoms include mixed chain length materials provided that some of the hydroxamate material falls within the ranges specified and the ratios and amounts are determined by excluding any material falling outside of the specified range.

The preferred alkyl hydroxamates are those where \( R^1 \) is Cs to \( C_{14} \) alkyl, preferably normal alkyl, most preferably saturated.

The alkyl hydroxamate containing compositions according to the invention are particularly suitable for use on red clay and especially suited to the removal of red clay stains from polyester under hard water washing conditions and with low levels of detersive surfactant in the wash water.

The general structure of a hydroxamic acid in the context of the present invention has been indicated in Formula 1, and \( R^1 \) is as defined therein. Preferably, \( R^1 \) is chosen from the group consisting of \( C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{11}, C_{12} \) and \( C_{14} \) normal alkyl group, most preferably \( R^1 \) is at least a Cs-i_4 normal alkyl group. When the Cs material is used this is called octyl hydroxamic acid. The potassium salt is particularly useful.

\[ \text{Octanohydroxamic acid K salt} \]
However, other hydroxamic acids, whilst less preferred, are suitable for use in the present invention. Such suitable compounds include, but are not limited to, the following compounds:

- Lysine Hydroxamate
- Methionine Hydroxamate
- Norvaline Hydroxamate

Such hydroxamic acids are commercially available.

The alkyl hydroxamate is thought to act by binding to metal ions that are present in the soil on the fabric. This binding action, which is, in effect, the known sequestrant property of the hydroxamate is not, in itself, of any use to remove the soil from the fabric. The key is the "tail" of the hydroxamate i.e. the group R. The tail is selected to have an affinity for the surfactant system. This means that the soil removal ability of an already optimised surfactant system is further enhanced by the use of the hydroxamate as it, in effect, labels the difficult to remove particulate material (clay) as "soil" for removal by the surfactant system acting on the hydroxamate molecules now fixed to the particulates via their binding to the metal ions embedded in the clay type particulates. The non-soap detergent surfactants will adhere to the hydroxamate, leading overall to more surfactants interacting with the fabric, leading to better soil release. Therewith the alkyl
hydroxamate acts as a linker molecule facilitating the removal and suspension of the particulate soil from the fabric into a wash liquor and thus boosting the primary detergency.

5 Alkyl hydroxamates have a higher affinity for transition metals, like iron, than for alkaline earth metals, for example calcium and magnesium, therefore the hydroxamate primarily acts to improve the removal of soil on fabric, especially particulate soils, and not additionally as a builder for calcium and magnesium.

10 A preferred alkyl hydroxamate is the 80% solids coco hydroxamic acid available under the trade name RK853 from Axis House. The corresponding alkyl hydroxamate Potassium salt is available from Axis House under the trade name RK852. Axis house also supply the coco hydroxamic acid as a 50% solids material under the trade name RK858. The 50% coco hydroxamate potassium salt is available as RK857. Another preferred material is RK842, an Alkyl hydroxamic acid made from Palm Kernel Oil, from Axis House. Alkyl hydroxamates do not generate any residues.

Surfactants

20 Surfactants assist in removing soil from the textile materials and also assist in maintaining removed soil in solution or suspension in the wash liquor. Anionic or blends of anionic and nonionic surfactants are a preferred feature of the present invention. The amount of anionic non-soap surfactant is at least 8 wt%.

25 Anionic Surfactants
Prefered anionic surfactants are alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates (LAS) having an alkyl chain length of Cs-Cl₂. The counter ion for the anionic surfactants is generally an alkali metal, typically sodium, although other counter-ions for example MEA, TEA or ammonium can be used. Preferred linear alkyl benzene sulphonate surfactants are Detal LAS with
an alkyl chain length of from 8 to 15, more preferably 12 to 14. LAS can be at least partially replaced by methyl ester sulphonate (MES), or, less preferably, partially replaced by up to 20 wt % Primary alcohol sulphate (PAS).

It is desirable that, in addition to LAS, component (a) of the composition further comprises an alkyl polyethoxylate sulphate (AES) anionic surfactant of Formula 3:

\[
RO(C_2H_4O)_xSO_3M^+ 
\]  
(Formula III)

where \( R \) is an alkyl chain having from 10 to 22 carbon atoms, saturated or unsaturated, \( M \) is a cation which makes the compound water-soluble, especially an alkali metal, ammonium or substituted ammonium cation, and \( x \) averages from 1 to 15.

Preferably \( R \) is an alkyl chain having from 12 to 16 carbon atoms, \( M \) is Sodium and \( x \) averages from 1 to 3, preferably \( x \) is 3. This is the anionic surfactant sodium lauryl ether sulphate (SLES). The predominantly \( C_{12-15} \) lauryl alkyl group has been ethoxylated, in the case of SLES(3EO), with an average of 3 moles of ethylene oxide per mole: i.e. \( x \) is 3. Preferably, the anionic surfactant system comprises SLES, together with optional soap and mixtures thereof. Soap is not included in the calculation of amount of non-soap surfactant. A LAS/AES surfactant blend has a superior foam profile to a LAS / Nonionic surfactant blend and is therefore preferred for hand-wash formulations requiring high levels of foam. AES may be used at levels of up to 30%. Preferably the composition comprises at least 2 wt% SLES.

Although less preferred, some alkyl sulphate surfactant (PAS) may be used, especially the non-ethoxylated \( C_{12-15} \) primary and secondary alkyl sulphates. A particularly preferred material, commercially available from Cognis, is Sulphopon 1214G. PAS is preferably used in admixture with LAS and most preferably in
admixture with LAS and SLES. A preferred SLES/AO/LAS/PAS liquid has a
detersive surfactant system comprising 60 parts SLES, 20 parts amine oxide, 10
parts LAS and 10 parts PAS.

5 Nonionic Surfactants
Nonionic surfactants include primary and secondary alcohol ethoxylates,
especially C8-C20 aliphatic alcohol ethoxylated with an average of from 1 to 20
moles of ethylene oxide per mole of alcohol, and more especially the C10-C15
primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to
10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic
surfactants include alkyl polyglycosides, glycerol monoethers and polyhydroxy
amides (glucamides). Mixtures of nonionic surfactant may be used. When
included therein the composition contains from 0.2 wt% to 30 wt%, preferably 1
wt% to 20 wt%, more preferably 5 to 15 wt% of a non-ionic surfactant, for example
alcohol ethoxylate, nonylphenol ethoxylate, alkylpolyglycoside,
alkyldimethylamineoxide, ethoxylated fatty acid monoethanolamide, fatty acid
monoethanolamide, polyhydroxy alkyl fatty acid amide, or N-acyl N-alkyl
derivatives of glucosamine ("glucamides").

20 Nonionic surfactants that may be used include the primary and secondary alcohol
ethoxylates, especially the C8-C20 aliphatic alcohols ethoxylated with an average
of from 1 to 35 moles of ethylene oxide per mole of alcohol, and more especially
the C10-C15 primary and secondary aliphatic alcohols ethoxylated with an average
of from 1 to 10 moles of ethylene oxide per mole of alcohol.

25 Amine Oxide Surfactants
The composition may comprise up to 10 wt% of amine oxide (AO) of the formula
(IV):

30 $R^1 N(O)(CH_2 R^2)_2$ (Formula IV)
In which $R^1$ is a long chain moiety and each $CH_2R^2$ is a short chain moiety. $R^2$ is preferably selected from hydrogen, methyl and $-CH_2OH$. In general $R^1$ is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, $R^1$ is a primary alkyl moiety. $R^1$ is a hydrocarbyl moiety having chain length of from about 8 to about 18.

In preferred amine oxides $R^1$ is Cs-Cs alkyl, and $R^2$ is H. These amine oxides are illustrated by C12-14 alkyl dimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide.

A preferred amine oxide material is Lauryl dimethylamine oxide, also known as dodecyl dimethylamine oxide or DDAO. Such an amine oxide material is commercially available from Huntsman under the trade name Empigen® OB.

Amine oxides suitable for use herein are also available from Akzo Chemie and Ethyl Corp. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers.

Whereas in certain of the preferred embodiments $R^2$ is H, it is possible for $R^2$ to be a moiety larger than H. Specifically, $R^2$ may be $CH_2OH$, for example: hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearyl bis(2-hydroxyethyl)amine oxide and oleyl bis(2-hydroxyethyl)amine oxide.

Preferred amine oxides have the Formula (V):

$$O^- \cdot N^+\left(Me\right)_2R^1$$  \hspace{1cm} (Formula V)

where $R^1$ is C12-16 alkyl, preferably C12-14 alkyl and Me is a methyl group. A preferred surfactant system for use in high suds (foam) applications comprises SLES and AO.
Zwitterionic Surfactants
Nonionic-free systems with up to 95 wt% of the surfactant system LAS can be made provided that some zwitterionic surfactant, for example carbobetaine, is present. A preferred zwitterionic material is a betaine available from Huntsman under the name Empigen® BB. Betaines further improve particulate soil detergency in the compositions of the invention.

Cationic Surfactants
Cationic surfactants are preferably substantially absent.

Soaps
The compositions may comprise soap which can act as a builder and/or as an antifoam. The amount of non-soap anionic surfactant must exceed the amount of soap. The amount of soap must be less than or equal to 15 wt% of the total liquid composition, preferably it is less than 3 wt%. The fatty acid used preferably contains from about 16 to about 22 carbon atoms, preferably in a straight chain configuration. The anionic contribution from soap may be from 0 to 30 wt% of the total anionic. Use of more than 10 wt% soap is not preferred. Saturated fatty acids are preferred.

Polymers

EPEI
The composition comprises an ethoxylated polyethyleneimine polymer (EPEI) for cleaning. The EPEI is nonionic. That means it does not have any quaternary nitrogens, or nitrogen oxides or any ionic species other than possible pH effected protonation of nitrogens.
Polyethylene imines (PEIs, especially modified PEIs) are materials composed of ethylene imine units -CH2CH2NH- and, where branched, the hydrogen on the nitrogen is replaced by another chain of ethylene imine units. These polyethyleneimines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst for example carbon dioxide, sodium bisulphite, sulphuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, and the like. Specific methods for preparing these polyamine backbones are disclosed in U.S. Pat. No. 2,182,306, Ulrich et al., issued Dec. 5, 1939; U.S. Pat. No. 3,033,746, Mayle et al., issued May 8, 1962; U.S. Pat. No. 2,208,095, Esselmann et al., issued Jul. 16, 1940; U.S. Pat. No. 2,806,839, Crowther, issued Sep. 17, 1957; and U.S. Pat. No. 2,553,696, Wilson, issued May 21, 1951.

The EPEI comprises a polyethyleneimine backbone wherein the modification of the polyethyleneimine backbone is intended to leave the polymer without quaternisation. Such nonionic EPEI may be represented as PEI(X)YEO where X represents the molecular weight of the unmodified PEI and Y represents the average moles of ethoxylation per nitrogen atom in the polyethyleneimine backbone. This is the same as the average per substitution site if the number of nitrogens with no hydrogen is balanced by the number with two hydrogens in the unethoxylated PEI. The ethoxylation number Y may range from 7 to 40 ethoxy moieties per modification, preferably it is in the range of 16 to 26, most preferably 18 to 22. X is selected to be from about 300 to about 10000 weight average molecular weight and is preferably about 600.

The ethoxylated polyethyleneimine polymer (EPEI) is preferably present in the composition at a level of between 2 and 20 wt%, more preferably at a level of less than 9.5 wt%, most preferably from 3 to 9 wt% and with a ratio of non-soap surfactant to EPEI of from 2:1 to 7:1, preferably from 3:1 to 6:1, even about 5:1.
Soil Release Polymer
The composition may optionally further comprise at least 0.5 wt% of a polymeric soil release agent for oily soil removal from polyester.

Soil release polymers improve the main wash performance of the compositions when used in the low in wash surfactant process of the second aspect of the present invention.

One preferred class of soil release polymer is the fabric-substantive polymers comprising at least one of (i) saccharide or (ii) dicarboxylic acid and polyol monomer units. Typically these polymers have soil release properties and, while they can have a primary detergency effect, they generally assist in subsequent cleaning. Preferably these polymers are present at a level of at least 2% wt, more preferably at least 3 wt% of the composition.

The soil release polymer will preferably comprise up to 10 wt%, of the detergent composition, more preferably up to 9 wt%, preferably they are used at greater than 2 wt% and more preferably greater than 3 wt% in the composition.

Generally the soil release polymers for polyester will comprise polymers of aromatic dicarboxylic acids and alkylene glycols (including polymers containing polyalkylene glycols).

The polymeric soil release agents useful herein include those soil release agents having:

(a) one or more nonionic hydrophilic components consisting essentially of:
(i) polyoxyethylene segments with a degree of polymerization of at least 2, or

(ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophilic segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or

(iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophilic component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fibre surfaces upon deposit of the soil release agent on such surface, said hydrophilic segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or

(b) one or more hydrophobic components comprising:

(i) \( \text{C}_3 \) oxyalkylene terephthalate segments, wherein, if said hydrophobic components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate: \( \text{C}_3 \) oxyalkylene terephthalate units is about 2:1 or lower,

(ii) \( \text{C}_4 \cdot \text{C}_6 \) alkyylene or oxy \( \text{C}_4 \cdot \text{C}_6 \) alkylene segments, or mixtures therein,

(iii) poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2, or
(iv) C\textsubscript{i} - C\textsubscript{4} alkyl ether or C\textsubscript{4} hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C\textsubscript{i} - C\textsubscript{4} alkyl ether or C\textsubscript{4} hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C\textsubscript{i} - C\textsubscript{4} alkyl ether and/or C\textsubscript{4} hydroxyalkyl ether units to deposit upon conventional polyester synthetic fibre surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fibre surface, to increase fibre surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100.

Soil release agents characterized by polyvinyl ester) hydrophobic segments include graft copolymers of polyvinyl ester), e.g., C\textsubscript{i} - C\textsubscript{6} vinyl esters, preferably polyvinyl acetate) grafted onto polyalkylene oxide backbones, for example polyethylene oxide backbones. See European Patent Application 0219 048, published Apr. 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Pat. No. 3,959,230 to Hays, issued May 25, 1976 and U.S. Pat. No. 3,893,929 to Basadur issued Jul. 8, 1975.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10 to 15 wt% of ethylene terephthalate units.
together with 90 to 80 wt% weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300 to 5000. Examples of this polymer include ZELCON 5126 (from DuPont) and MILEASE T (from ICI). See also U.S. Pat. No. 4,702,857, issued Oct. 27, 1987 to Gosselink.

The most preferred soil release polymers are the water soluble/miscible or dispersible polyesters for example those supplied under the Texcare brand by Clariant, especially Texcare® SRN170, and heavily branched polyesters for example those available from Sasol and described in US 7119056. Combinations of soil release polymers may be used.

Other polymers
In addition to the essential nonionic EPEI and optional polyester soil release polymer(s) the compositions may further comprise one or more further polymers selected from the group comprising dye transfer inhibition polymers, anti redeposition polymers and cotton soil release polymers based on modified cellulosic materials. EPEI that is not of the essential nonionic type may provide one or more of these polymer functions.

Enzymes
It is preferable that at least one or more enzymes, preferably more than one, may be present in the compositions for cleaning boost.

Protease
Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or a trypsin-like protease. Preferred commercially available protease enzymes include Alcalase™, Savinase™, Primase™, Duralase™, Dyrazym™, Esperase™, Everlase™, Polarzyme™, and
Kannase™, (Novozymes A/S), Maxatase™, Maxacal™, Maxapem™, Properase™, Purafect™, Purafect OxP™, FN2™, and FN3™ (Genencor International Inc.).

5 Amylase
Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from Bacillus, e.g. a special strain of B. licheniformis, described in more detail in GB 1,296,839, or the Bacillus sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

15 Pectate Lyase
Pectate lyases (also called polygalacturonate lyases): Examples of pectate lyases include pectate lyases that have been cloned from different bacterial genera for example Erwinia, Pseudomonas, Klebsiella and Xanthomonas, as well as from Bacillus subtilis (Nasser et al. (1993) FEBS Letts. 335:319-326) and Bacillus sp. YA-14 (Kim et al. (1994) Biosci. Biotech. Biochem. 58:947-949).


Examples of commercially available alkaline pectate lyases include BIOPREP™ and SCOURZYMÉ™ L from Novozymes A/S, Denmark.

**Mannanase**

Bacillus sp., and Humicola insolens disclosed in WO 99/64619. Especially contemplated are the Bacillus sp. mannanases concerned in the Examples in WO 99/64619.

Examples of commercially available mannanases include Mannaway™ available from Novozymes A/S Denmark.

**Cellulase**
Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera Bacillus, Pseudomonas, Humicola, Fusarium, Thielavia, Acremonium, e.g. the fungal cellulases produced from Humicola insolens, Thielavia terrestris, Myceliophthora thermophila, and Fusarium oxysporum disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307. Commercially available cellulases include Celluzyme™, Carezyme™, Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation).

**Peroxidase/oxidase**
Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from Coprinus, e.g. from C. cinereus, and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257. Commercially available peroxidases include Guardzyme™ and Novozym™ 51004 (Novozymes A/S).

**Cutinase**
The method of the invention may be carried out in the presence of cutinase. classified in EC 3.1.1.74. The cutinase used according to the invention may be of
any origin. Preferably cutinases are of microbial origin, in particular of bacterial, of fungal or of yeast origin.

Enzymes and any perfume/fragrance or pro-fragrance present may show some interaction and should be chosen such that this interaction is not negative. Some negative interactions may be avoided by encapsulation of one or other of enzyme and pro-fragrance and/or other segregation within the product.

Enzyme Stabilizers

Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol for example propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative for example 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

Further Optional Ingredients

The compositions of the invention may contain one or more other ingredients. Such ingredients include viscosity modifiers, foam boosting agents, preservatives (e.g. bactericides), pH buffering agents, polyelectrolytes, anti-shrinking agents, anti-wrinkle agents, anti-oxidants, sunscreens, anti-corrosion agents, drape imparting agents, anti-static agents and ironing aids. The compositions may further comprise, colorants, pearlisers and/or opacifiers, and shading dye.

Fluorescent Agents

It may be advantageous to include fluorescer in the compositions. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.5 wt %.
Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN.

Preferred fluorescers are: sodium 2 (4-styryl-3-sulfophenyl)-2H-napthol[1,2-d]triazole, disodium 4,4'-bis{[(4-anilino-6-(N-methyl-N-2-hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfostyryl)biphenyl.

Bleach Catalysts

Detergent compositions according to the invention may comprise a weight efficient bleach system. Such bleach systems typically do not utilise the conventional peracid or bleach activator with perborate/percarbonate "oxygen" bleach systems, but rely instead on a bleach catalyst used at a low level as the main bleach component.

The present invention may be used in a formulation that is used to bleach via air, or an air bleach catalyst system. Suitable complexes and organic molecule (ligand) precursors for forming complexes are available to the skilled worker, for example, from: WO 98/39098; WO 98/39406, WO 97/48787, WO 00/29537; WO 00/52124, and WO00/60045. An example of a preferred catalyst is a transition metal complex of MeN₄Py ligand (N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane). Suitable bispidon catalyst materials and their action are described in WO02/48301.

When present, the bleach catalyst is typically incorporated at a level of about 0.0001 to about 10 wt%, preferably about 0.001 to about 5 wt%.
Photobleach

Photobleaches may also be employed. In the context of the present invention a "photobleach" is any chemical species that forms a reactive bleaching species on exposure to sunlight, and preferably is not permanently consumed in the reaction.

Preferred photo-bleaches include singlet oxygen photo-bleaches and radical photo-bleaches. Suitable singlet oxygen photo-bleaches may be selected from, water soluble phthalocyanine compounds, particularly metallated phthalocyanine compounds where the metal is Zn or Al-Z1 where Z1 is a halide, sulphate, nitrate, carboxylate, alkanolate or hydroxyl ion. Preferably the phthalocyanin has 1-4 SO3X groups covalently bonded to it where X is an alkali metal or ammonium ion. Such compounds are described in WO2005/014769 (Ciba).

Perfume

The compositions preferably comprise from 0.001 to 5 wt % perfume. Given that

the composition of the present invention is designed to be used at very low levels of product dosage, it is advantageous to ensure that perfume is employed efficiently.

A particularly preferred way of ensuring that perfume is employed efficiently is to use an encapsulated perfume. Use of a perfume that is encapsulated reduces the amount of perfume vapour that is produced by the composition before it is diluted. This is important when the perfume concentration is increased to allow the amount of perfume per wash to be kept at a reasonably high level.

It is even more preferable that the perfume is not only encapsulated but also that

the perfume encapsulate is provided with a deposition aid to increase the efficiency of perfume deposition and retention on fabrics. The deposition aid is preferably attached to the encapsulate by means of a covalent bond, entanglement or strong adsorption, preferably by a covalent bond or

entanglement.
Shading dyes
Shading dye can be used to improve the performance of the compositions used in the method of the present invention. The deposition of shading dye onto fabric is improved when they are used in compositions of the invention and according to the process of the invention. Preferred dyes are violet or blue. It is believed that the deposition on fabrics of a low level of a dye of these shades, masks yellowing of fabrics. A further advantage of shading dyes is that they can be used to mask any yellow tint in the composition itself.

Suitable and preferred classes of dyes are disclosed in WO2009/153184 and elsewhere.

Builders and sequestrants
Sequestrants other than the alkyl hydroxamate may be present at low levels in the compositions. Because the hydroxamate technology is affected by competing sequestrants, for maximum performance of the hydroxamate any phosphonate or similar sequestrants that may complex with iron are preferably absent or used at a low level of up to 1 wt%, preferably less than 0.5 wt%. Most preferably they are absent. Citric acid and citrate builders are also preferably absent. When used a preferred sequestrant is HEDP (1-Hydroxyethylidene -1,1,1-diphosphonic acid), for example sold as Dequest® 2010. Also suitable, but less preferred as it gives inferior cleaning results, is Dequest® 2066 (Diethylenetriamine penta(methylene phosphonic acid or Heptasodium DTPMP).

Hydrotropes
The compositions preferably comprise one or more hydrotropes; although the minimum amount consistent with the need for concentration should be used. Suitable hydrotropes include MPG (monopropylene glycol). This and/or other conventionally employed hydrotropes may be used in the composition at levels of from 2 to 25 wt%. In the context of this invention a hydrotrope is a solvent that is
neither water nor conventional surfactant that aids the solubilisation of the surfactants and other components in the aqueous liquid to render it isotropic. In addition to MPG, among suitable hydrotropes there may be mentioned as preferred: glycerol, sodium cumene sulphonate, ethanol, other glycols, e.g. dipropylene glycol, diethers and urea.

Buffers
The presence of some buffer is preferred for pH control; preferred buffers are monoethanolamine (MEA), and triethanolamine (TEA). If present, they are preferably used in the composition at levels of from 5 to 15 wt%.

External Structurants
The compositions may have their rheology modified by use of a material or materials that form a structuring network within the composition. Suitable structurants include hydrogenated castor oil, microfibrous cellulose and natural based structurants, for example citrus pulp fibre. Citrus pulp fibre is preferred especially if cellulase or pectate lyase enzyme is included in the composition.

Visual Cues
The compositions may comprise visual cues of solid material that is not dissolved in the composition. Preferably they are used in combination with an external structurant to ensure that they remain in suspension. Preferred visual cues are lamellar cues formed from polymer film and possibly comprising functional ingredients that may not be as stable if exposed to the alkaline liquid. Enzymes and bleach catalysts are examples of such ingredients. Also perfume, particularly microencapsulated perfume.

Packaging and dosing
The liquids may be packaged as unit doses. To allow greater flexibility in dosing the liquids may alternatively be supplied in multiuse plastics packs with a top or
bottom closure. A dosing system may be supplied with the pack either as a part of the cap or as an integrated system.

**Method of use**

Following the teaching in WO2009/153184 the liquids according to the invention may be formulated to allow them to be dosed to a typical front loading automatic washing machine at a dosage level of 20 ml. The low in wash surfactant level being compensated by the presence of enzymes, soil release polymer and EPEI together with further optional high efficacy cleaning ingredients, for example enzymes. However, the invention is also suitable for the more conventional dosage levels of about 35 ml. To obtain suitable concentrated liquids of this greater dose volume it is necessary is to add further water and preferably additional perfume to the 20 ml composition before it is packaged.

The invention will now be further described with reference to the following non-limiting examples.

**EXAMPLES**

In the examples the following materials are used:

- **LAS acid**: is C-12-14 linear alkylbenzene sulphonic acid.
- **Fatty acid**: is saturated lauric fatty acid Prifac® 5908 ex Croda.
- **SLES 3EO**: is sodium lauryl ether sulphate with 3 moles EO.
- **SLES 1EO**: is sodium lauryl ether sulphate with 1 mole EO.
- **Empigen® BB**: is an alkyl betaine ex Huntsman (Coco dimethyl carbobetaine).
- **N1 7EO**: is C12-15 alcohol ethoxylate 7EO non ionic
- **Neodol® 25-7**: (ex Shell Chemicals).
MPG is mono propylene glycol.
TEA is triethanolamine.
NaOH is sodium hydroxide (from 47% solution).
EPEI is Sokalan HP20 - ethoxylated polyethylene imine cleaning polymer: PEI(600) 20EO ex BASF.
SRP is soil release polymer (Texcare® SRN1 70 ex Clariant).
Dequest® 2066 is Diethylenetriamine penta(methylene phosphonic acid (or Heptasodium DTPMP) ex Thermphos.
Perfume is free oil perfume.
HXA is Coco hydroxamic Acid: Axis House RK 853.
HXA K+ is Coco hydroxamate K+ salt: Axis House RK 852.

15 Stain Release Index (SRI)

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 shown below

$$\Delta E^* = \sqrt{(L^*_{\text{stain-before}} - L^*_{\text{clean-cloth}})^2 + (a^*_{\text{stain-before}} - a^*_{\text{clean-cloth}})^2 + (b^*_{\text{stain-before}} - b^*_{\text{clean-cloth}})^2}$$

This can be measured before and after the stain is washed, to give $AE^*_{bw}$ and $AE^*_{aw}$

SRI is a measure of how much of the stain is removed and is calculated by the expression:

$$\text{SRI} = 100 - AE^*_{aw}$$

A SRI of 100 means complete stain removal.
Comparative examples at high in-wash non-soap surfactant levels
Composition A, similar to hydroxamate containing compositions taught in WO201 0/069957 was prepared as shown in table 1. Variants on this composition without any hydroxamate but with EPEI included instead (Composition B) and using a combination of hydroxamate and EPEI (Composition C) were also prepared.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>PPG</td>
<td>9.00</td>
<td>9.00</td>
<td>9.00</td>
</tr>
<tr>
<td>NaOH</td>
<td>4.73</td>
<td>4.73</td>
<td>4.73</td>
</tr>
<tr>
<td>TEA</td>
<td>3.24</td>
<td>3.24</td>
<td>3.24</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>0.98</td>
<td>0.98</td>
<td>0.98</td>
</tr>
<tr>
<td>LAS</td>
<td>27.60</td>
<td>27.60</td>
<td>27.60</td>
</tr>
<tr>
<td>NI</td>
<td>12.50</td>
<td>12.50</td>
<td>12.50</td>
</tr>
<tr>
<td>Soap</td>
<td>4.78</td>
<td>4.78</td>
<td>4.78</td>
</tr>
<tr>
<td>Potassium Octyl Hydroxamate</td>
<td>5.00</td>
<td>-</td>
<td>2.50</td>
</tr>
<tr>
<td>EPEI</td>
<td>-</td>
<td>5.00</td>
<td>2.50</td>
</tr>
<tr>
<td>Water</td>
<td>Balance</td>
<td>Balance</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The three compositions A, B and C were used to wash polyester fabrics stained with red clay using a Linitest equipment. The Linitest pots were filled with 26°FH water (2:1 Ca^{2+}:Mg^{2+}) and then 2.6 g/L formulations coactive such that the final wash liquor volume was 100 ml. This equates to a non-soap in-wash surfactant level of just over 1 g/L. To each Linitest pot were added two knitted polyester cloths stained with Georgia clay, a red clay, together with six ballast cloths (four cotton and two knitted polyester) to obtain liquor to cloth ratios of 8:1. Finally, fifty metal ball bearings were added before closing the Linitest pots and washing the cloths for 30 minutes at 40°C and 100 rpm. After the wash was completed, the ball bearings were removed. The cloths were then squeezed to remove excess wash liquor and rinsed twice within the Linitest pot for 3 minutes (at 100 rpm) in
two portions of 200 ml 6°FH water. The cloths were wrung out and allowed to dry on racks at room temperature.

Table 2 gives the Soil release index for each composition (a comparative composition with neither hydroxamate nor EPEI gives an SRI of 79.4 under these conditions.

Table 2

<table>
<thead>
<tr>
<th>Composition</th>
<th>SRi&lt;sub&gt;aw&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>89.1</td>
</tr>
<tr>
<td>B</td>
<td>79.6</td>
</tr>
<tr>
<td>C</td>
<td>84.17</td>
</tr>
</tbody>
</table>

From this it can be concluded that at high in wash surfactant levels under hard water washing conditions composition B having only EPEI is not much better than a composition without any EPEI. As expected, Composition C based on the teaching in WO2010/069957 and WO2011/151170, shows a significant improvement in red clay removal. Significantly and rather surprisingly under these wash conditions the combination of EPEI and hydroxamate has no positive effect and indeed provides poorer soil removal than the hydroxamate used alone. The ratio of non-soap surfactant to EPEI in these examples is at least 8:1 and is thus in line with the ratio found in a non-concentrated laundry liquid.
Example 1 and Comparative examples D, E and F

Table 3 - Compositions tested

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>LAS Acid</td>
<td>13.23</td>
<td>13.23</td>
<td>13.23</td>
<td>13.23</td>
</tr>
<tr>
<td>NI 7EO</td>
<td>3.31</td>
<td>3.31</td>
<td>3.31</td>
<td>3.31</td>
</tr>
<tr>
<td>SLES 1EO</td>
<td>16.54</td>
<td>16.54</td>
<td>16.54</td>
<td>16.54</td>
</tr>
<tr>
<td>MPG</td>
<td>9.00</td>
<td>9.00</td>
<td>9.00</td>
<td>9.00</td>
</tr>
<tr>
<td>NaOH</td>
<td>1.81</td>
<td>1.81</td>
<td>1.81</td>
<td>1.81</td>
</tr>
<tr>
<td>TEA</td>
<td>4.08</td>
<td>4.08</td>
<td>4.08</td>
<td>4.08</td>
</tr>
<tr>
<td>Citric Acid</td>
<td>1.25</td>
<td>1.25</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>Fluorescer</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>EPEI</td>
<td>-</td>
<td>-</td>
<td>9.00</td>
<td>9.00</td>
</tr>
<tr>
<td>HXA</td>
<td>-</td>
<td>2.20</td>
<td>-</td>
<td>2.20</td>
</tr>
<tr>
<td>Protease enzyme</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>Water</td>
<td>48.58</td>
<td>46.38</td>
<td>39.58</td>
<td>37.38</td>
</tr>
</tbody>
</table>

The compositions in Table 3 were used to wash red mud on knitted polyester in a Tergotometer using the wash protocol described below. In all cases the formulation dose was 0.78 g/L giving an in-wash non-soap surfactant level of 0.26 g/L.

Tergotometer Wash Protocol

Measure "before" wash stains. Switch on Tergotometer and set to temperature of 30°C. Add water of 26°FH, leave to heat to 30°C for 10 minutes. Add formulation to each pot and then agitate at 100 rpm for 1 minute. Add the stain swatches and ballast into each pot. Start the wash, agitate at 100 rpm and leave for 12 minutes.
Rinse with fresh water for 2 minutes. Repeat rinse. Dry overnight in the dark. Measure "after" wash stains.

Wash liquor compositions are given in Table 4.

**Table 4 - Wash Liquors**

<table>
<thead>
<tr>
<th></th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>In wash concentration (g/L)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LAS Acid</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>NI 7EO</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>SLES 1EO</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>EPEI</td>
<td>0.00</td>
<td>0.00</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td>HXA</td>
<td>0.00</td>
<td>0.018</td>
<td>0.00</td>
<td>0.018</td>
</tr>
</tbody>
</table>

The results of these wash test examples are given in Table 5.

**Table 5 - SRI**

<table>
<thead>
<tr>
<th>Composition</th>
<th>SRI Red Mud* on knitted polyester</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>74.4</td>
</tr>
<tr>
<td>E</td>
<td>77.0</td>
</tr>
<tr>
<td>F</td>
<td>71.1</td>
</tr>
<tr>
<td>1</td>
<td>84.2</td>
</tr>
</tbody>
</table>

*Red Mud is Indian red clay
It can be seen that there is a consistent improvement in stain removal between Base Composition D and Composition 1 comprising both EPEI and hydroxamate.

5 Examples 2 and 3 and Comparative examples G, H, J and K

G - 5X base (surfactant only)
H - 5X base + EPEI
J - 5X base + Coco Hydroxamic acid
K - 5X base + Coco Hydroxamate K+ salt
2 - 5X base + Coco Hydroxamic acid / EPEI
3 - 5X base + Coco Hydroxamate K+ salt / EPEI

5X means that the composition is designed to dose to European front loading washing machines at a standard dose of 20 ml which is approximately 20% of the normal dose of a dilute liquid and less than the current "concentrated" 3X formulations that are dosed from 30-40 ml per wash.

Table 6 - Compositions

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>G</th>
<th>H</th>
<th>J</th>
<th>K</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solids (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LAS acid</td>
<td>8.49</td>
<td>8.49</td>
<td>8.49</td>
<td>8.49</td>
<td>8.49</td>
<td>8.49</td>
</tr>
<tr>
<td>Fatty acid</td>
<td>1.50</td>
<td>1.50</td>
<td>1.50</td>
<td>1.50</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>Ni 7EO</td>
<td>12.74</td>
<td>12.74</td>
<td>12.74</td>
<td>12.74</td>
<td>12.74</td>
<td>12.74</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>TEA</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
<td>3.50</td>
</tr>
<tr>
<td>MPG</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
<td>20.00</td>
</tr>
<tr>
<td>EPEI</td>
<td>-</td>
<td>5.46</td>
<td>-</td>
<td>-</td>
<td>5.46</td>
<td>5.46</td>
</tr>
<tr>
<td>HXA</td>
<td>-</td>
<td>-</td>
<td>1.63</td>
<td>-</td>
<td>1.63</td>
<td>-</td>
</tr>
<tr>
<td>HXA K+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.63</td>
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<td>Perfume</td>
<td>2.43</td>
<td>2.43</td>
<td>2.43</td>
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<td>Water and minors</td>
<td>to 100.00</td>
<td>to 100.00</td>
<td>to 100.00</td>
<td>to 100.00</td>
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</table>
Base 5X Composition G was used at 1.41 g/L. Thus the non-soap surfactant level in wash was about 0.4 g/L. When additional ingredients were added to the composition the water balance was reduced to keep the dose of surfactant to the wash constant. The undiluted compositions had a pH of about 6.5.

The in-wash levels of the additional ingredients were:

- EPEI: 77 ppm
- HXA: 23 ppm
- HXA K+: 23 ppm

Knitted polyester stained with Indian red clay was washed using the previously described Tergotometer wash protocol, using 26°FH water as before but at the lower wash temperature of 25°C for 20 minutes, followed by a 1 minute rinse. The liquor to cloth ratio was 25:1. Table 7 gives the results. It is clearly seen that under hard water, low surfactant, wash conditions the combination of EPEI and hydroxamate in Examples 2 and 3 is statistically superior to the other compositions and that under these conditions the composition with hydroxamate only gives inferior results to the composition with EPEI only. The ratio of non-soap surfactant to EPEI in these compositions is the shorter ratio found in the concentrated liquids according to WO2009/153184 and is about 5 to 1. The apparent benefit of combining EPEI and hydroxamate under low surfactant conditions was not obvious given the lack of benefit in the more conventional higher in wash surfactant compositions and the know cooperation between surfactant and EPEI on the one hand and surfactant and hydroxamate on the other hand.
### Table 7 - SRI

<table>
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<tr>
<th>Example</th>
<th>SRI Least Sq Mean</th>
<th>Significance to Base G</th>
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<tr>
<td>G</td>
<td>67.00</td>
<td>=</td>
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<tr>
<td>H</td>
<td>70.12</td>
<td>=</td>
</tr>
<tr>
<td>J</td>
<td>69.95</td>
<td>=</td>
</tr>
<tr>
<td>K</td>
<td>69.98</td>
<td>=</td>
</tr>
<tr>
<td>2</td>
<td>74.24</td>
<td>+</td>
</tr>
<tr>
<td>3</td>
<td>73.93</td>
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CLAIMS

1. An aqueous concentrated liquid laundry detergent comprising:
   (a) at least 8 wt%, preferably at most 40 wt%, anionic non-soap surfactant;
   (b) at most 30 wt% of nonionic surfactant;
   (c) at most 10 wt% of surfactant other than (a) and (b)
   (d) at least 0.1 wt%, preferably at most 10 wt%, alkyi hydroxamate; and
   (e) at least 2 wt%, preferably at most 20 wt%, nonionic ethoxylated polyethylene imine with an average of between 7 and 40 ethoxy units per substitution site on each nitrogen.

2. A composition according to claim 1 wherein the weight ratio of non-soap surfactant to EPEI is from 2:1 to 7:1, preferably from 3:1 to 6:1.

3. A composition according to claim 2 in which the amount of (a) is greater than or equal to the amount of (b).

4. A composition according to claim 3 in which the amount of (b) is at least 3 wt%.

5. A composition according to claim 3 which comprises less than 3 wt% of nonionic (b) and wherein the anionic non-soap surfactant (a) comprises a mixture of linear alkyi benzene sulphonate (LAS) and alkyi ethoxy sulphate (AES).
6. A composition according to any preceding claim which comprises at least 0.4 wt% perfume.

7. A composition according to any preceding claim comprising at least 1 wt% alkyl hydroxamate (d).

8. A composition according to claim 6 in which the further detersive surfactant (c) comprises soap.

9. A composition according to claim 8 in which the level of soap in the composition is less than 3 wt%.

10. A composition according to any preceding claim in which the ratio of hydroxamate to total detersive surfactant system (surfactant) lies in the range 1:4 to 1:8000, preferably 1:7 to 1:40, more preferably 1:10 to 1:30 parts by weight.

11. A method of washing polyester fabrics comprising the steps of combining 15 to 25 ml of a composition according to any one of claims 1 to 10 with water having a hardness of greater than 20°FH to form a wash liquor having a non-soap surfactant concentration of less than 0.5 g/L and washing the polyester with the wash liquor.

12. Use of a composition according to any one of claims 1 to 10 in a washing process carried out in water with a hardness of at least 20°FH to remove red clay from polyester.
### B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C11D

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

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

EPO-Internal, WPI Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>A</td>
<td>WO 2010/069957 Al (UNI LEVER) 24 June 2010 (2010-06-24) cited in the application on page 1, lines 7-13; claims</td>
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<tr>
<td>A</td>
<td>US 5 834 412 A (ROHRBAUGH ROBERT H ET AL) 10 November 1998 (1998-11-10) cited in the application on column 37, line 22 - line 48; claims</td>
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<td>A</td>
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* Further documents are listed in the continuation of Box C. ** See patent family annex.

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  - "O" document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the international search: 23 July 2012

Date of mailing of the international search report: 31/07/2012

Name and mailing address of the ISA/Authorized officer

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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