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(54) **Laundry detergent compositions**

(57) The present invention relates to the cleaning of fabrics with liquid compositions comprising an enzyme, a surfactant and a solvent system comprising a hydrophilic solvent and a hydrophobic solvent at a weight ratio of said hydrophilic solvent to said hydrophobic solvent of 10:1 to 2:1. These compositions deliver improved stain removal on a variety of stains including bleachable stains, greasy stains, enzymatic stains and/or mud/clay stains.

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**Description**

Technical Field

5 The present invention relates to liquid compositions and processes for laundering fabrics therewith.

Background of the invention

10 A great variety of liquid laundering compositions have been described in the art, such as liquid compositions comprising enzymes and surfactants which deliver most of the cleaning performance. However, a problem associated with such common liquid cleaning compositions, when used in a laundry application to treat different kinds of fabrics, including cotton and synthetic fabrics such as polyesters, polyamides and the like, is that they do not deliver an effective performance satisfactorily meeting consumer's needs, on all types of stains including greasy stains, enzymatic stains, mud/clay stains, bleachable stains and the like.

15 It is thus an object of the present invention to provide overall improved stain removal performance on a wide range of stains.

It has now been found that this object can be met by cleaning fabrics with a liquid composition comprising from 0.0001% to 5% by weight of the total composition of an enzyme, a surfactant and a solvent system comprising a hydrophobic solvent, i.e., a solvent having a hydrophilic index of less than 15, and a hydrophilic solvent, i.e., a solvent having 20 a hydrophilic index of more than 15, at a weight ratio of said hydrophilic solvent to said hydrophobic solvent of 10:1 to 2:1.

The hydrophilic index is defined by the following equation:

$$25 \frac{\text{molecular weight of the hydrophilic part of the solvent}}{\text{total molecular weight of the solvent}} * 100.$$

Indeed, it has been found that such liquid compositions comprising an enzyme, a surfactant and a solvent system as defined herein, when used in a laundry operation, boost the removal of various types of stains including greasy 30 stains, mud/clay-containing stains, enzymatic stains, as well as bleachable stains.

An advantage of the present invention is that excellent performance is provided in a variety of laundry applications, e.g., laundry detergent, or laundry additive, and preferably laundry pretreater.

Another advantage of the present invention is that when such a solvent system, as described herein, is added in a liquid composition of the present invention, the viscosity of said composition is reduced, whatever the viscosity was 35 before the addition of said solvent system. Thus, the present invention also provides liquid compositions, as described herein, wherein the viscosity can be conveniently controlled while maintaining adequate physical stability, without the need to add any viscosity control agent which would raise the formula cost, and add bulk to the compositions without contributing to the cleaning performance of said compositions. Thus the solvent system herein has a dual function, i.e., stain removing agent and viscosity controlling agent.

Background art

40 EP-A-137616 discloses laundry liquid compositions formulated in the form of an emulsion having a pH of 6.5 or above and comprising at least 5 % by weight of solvents. Such solvents include terpene and terpenoid solvents (e.g., pinene, d-limonene) as well as other solvents like benzyl alcohol, paraffins. Pretreating of fabrics and through the wash treatment with such compositions are disclosed. However, none of these compositions comprise a solvent system with a hydrophilic solvent and a hydrophobic solvent at a weight ratio of the hydrophilic solvent to the hydrophobic solvent of 10:1 to 2:1.

50 Summary of the invention

The present invention encompasses a liquid composition suitable for cleaning fabrics, comprising:

- a surfactant,
- 55 - from 0.0001% to 5% by weight of the total composition of an enzyme,
- and a solvent system comprising a hydrophilic solvent having a hydrophilic index of more than 15, and a hydrophobic solvent having a hydrophilic index of less than 15, at a weight ratio of said hydrophilic solvent to said hydrophobic solvent of 10:1 to 2:1,

wherein the hydrophilic index is defined by the equation

$$\frac{\text{molecular weight of the hydrophilic part of the solvent}}{\text{total molecular weight of the solvent}} * 100.$$

5

The present invention also encompasses a process of cleaning a fabric with a liquid composition as described herein, said process comprising the steps of applying said composition in its neat form onto said fabric, preferably only soiled portions thereof, before rinsing, or washing then rinsing said fabric.

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The present invention further encompasses a process of cleaning fabrics which includes the steps of diluting in an aqueous bath a liquid composition in its neat form, as described herein, contacting said fabrics with said aqueous bath comprising said liquid composition, and subsequently rinsing, or washing then rinsing said fabrics.

#### Detailed description of the Invention

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##### Liquid compositions

The present invention is based on the finding that by adding a solvent system comprising a hydrophilic solvent having a hydrophilic index of more than 15, and a hydrophobic solvent having a hydrophilic index of less than 15, at a weight ratio of said hydrophilic solvent to said hydrophobic solvent of 10:1 to 2:1, in a liquid composition comprising an enzyme (0.0001%-5%) and a surfactant, improved stain removal performance is obtained with said composition when used to treat a soiled fabric, especially in pretreatment application, as compared to the stain removal performance delivered with the same composition without said solvent system, or comprising only one type of solvent, i.e., a hydrophilic solvent or a hydrophobic solvent as defined herein, or comprising both a hydrophilic solvent and a hydrophobic solvent but not at the specific weight ratios from one to the other as defined herein.

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By "stain removal performance" it is meant herein stain removal performance on a variety of stains/soils such as greasy/oily stains, and/or enzymatic stains and/or mud/clay stains and/or bleachable stains.

By "greasy/oily stains" it is meant herein any soil and stain of greasy nature that can be found on a fabric like dirty motor oil, mineral oil, make-up, lipstick vegetal oil, spaghetti sauce, mayonnaise and the like. Indeed, the liquid compositions herein have been found to be particularly effective on make-up and spaghetti sauce.

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Examples of enzymatic stains include grass, chocolate and blood. Examples of bleachable stains include tea, coffee, wine and the like.

The stain removal performance of a given composition on a soiled fabric, for example under pretreatment conditions, may be evaluated by the following test method. A composition according to the present invention is first applied neat on the stained portion of a fabric, left to act thereon from about 1 to about 10 minutes, preferably 5 minutes, after which the pretreated fabric is washed according to common washing conditions with a conventional detergent composition, at a temperature of from 30°C to 70°C for a period of time sufficient to bleach said fabric. For example, typical soiled fabrics to be used in this stain removal performance test method may be commercially available from EMC (Empirical Manufacturing Company) Cincinnati, Ohio, USA, such as clay, grass, spaghetti sauce, gravy, dirty motor oil, make-up, barbecue sauce, tea, on two different substrates: cotton (CW120) and polycotton (PCW28).

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The stain removal performance may be evaluated by comparing side by side the soiled fabrics pretreated with the composition according to the present invention with those pretreated with the reference, e.g. the same composition without such a solvent system according to the present invention. A visual grading scale may be used to assign differences in panel score units (psu), in a range from 0 to 4.

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As a first essential element, the liquid compositions according to the present invention comprise a solvent system comprising a hydrophobic solvent, as defined herein, and a hydrophilic solvent, as defined herein, at a weight ratio of said hydrophilic solvent to said hydrophobic solvent of 10:1 to 2:1.

By "solvent" it is meant herein any hydrocarbon including aliphatic saturated or unsaturated hydrocarbons or aromatic hydrocarbons that contain or not, one or more alcoholic groups, one or more ether groups and/or one or more ketone groups.

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To define the hydrophilic or hydrophobic character of a solvent herein, the following hydrophilic index (HI) is used:

$$\frac{\text{molecular weight of the hydrophilic part of the solvent}}{\text{total molecular weight of the solvent}} * 100$$

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By "hydrophilic part" of a given solvent it is meant herein all the groups O, CO, OH, of a given solvent.

By "molecular weight of the hydrophilic part of a solvent" it is meant herein the total molecular weight of all the

hydrophilic parts of a given solvent.

The hydrophilic solvents to be used herein have a hydrophilic index of more than 15, preferably more than 18, more preferably more than 25 and most preferably more than 30, and the hydrophobic solvents to be used herein have a hydrophilic index of less than 15, preferably 14 or less and more preferably 13 or less.

It is essential that these solvents are present in the liquid compositions herein at a weight ratio of said hydrophilic solvent to said hydrophobic solvent of 10:1 to 2:1, preferably 7:1 to 3:1, more preferably 6:1 to 4:1 and most preferably about 5:1. Indeed, such a solvent system provides improved overall stain removal performance when added in a liquid composition comprising an enzyme and a surfactant, on various types of stains like greasy stains (e.g. dirty motor oil), enzymatic stains (e.g. blood) and clay stains as well as on bleachable stains (e.g. tea). It is speculated that said solvents can be a vehicle to the other active ingredients present in said liquid compositions, helping them to penetrate the stains.

Typically, the liquid compositions herein comprise from 0.1% to 20% by weight of the total composition of said solvent system, preferably from 0.1% to 10%, more preferably from 0.2% to 4%, and most preferably from 0.5% to 3.5%.

Suitable hydrophobic solvents to be used herein include paraffins, terpenes or terpene derivatives, as well as alkoxylated aliphatic or aromatic alcohols, aliphatic or aromatic alcohols, glycols or alkoxylated glycols, and mixtures thereof, all these solvents have a hydrophilic index of less than 15.

Suitable terpenes (hydrophilic index of 0) are mono- and bicyclic monoterpenes, especially those of the hydrocarbon class, which include the terpinenes, terpinolenes, limonenes and pinenes and mixtures thereof. Highly preferred materials of this type are d-limonene, dipentene, alpha-pinene and/or beta-pinene. For example, pinene is commercially available from SCM Glidco (Jacksonville) under the name Alpha Pinene P&F®.

Terpene derivatives such as alcohols, aldehydes, esters, and ketones which have a hydrophilic index of less than 15 can also be used herein. Such materials are commercially available as, for example, the  $\alpha$  and  $\beta$  isomers of terpineol and linalool.

All type of paraffins (hydrophilic index of 0) can be used herein, both linear and not, containing from 2 to 20 carbons, preferably from 4 to 10, more preferably from 6 to 8. Preferred herein is octane. Octane is commercially available for example from BASF.

Suitable hydrophobic alkoxylated aliphatic or aromatic alcohols to be used herein are according to the formula  $R(A)_n-OH$  wherein R is a linear or branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, or an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Suitable hydrophobic alkoxylated alcohol to be used herein is 1-methoxy-11-dodecanol (HI=14).

Suitable hydrophobic aliphatic or aromatic alcohols to be used herein are according to the formula  $R-OH$  wherein R is a linear or branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, or an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10. Suitable aliphatic alcohols to be used herein include linear alcohols like decanol (HI=7). Suitable aromatic alcohol to be used herein is 3-phenyl-1-butanol (HI= 13).

Suitable hydrophobic glycols to be used herein are according to the formula  $HO-CR_1R_2-OH$  wherein R1 and R2 are independently H or a C2-C10 saturated or unsaturated aliphatic hydrocarbon chain and/or cyclic. Suitable glycol to be used herein is octadecaneglycol (HI=12).

Suitable hydrophobic alkoxylated glycols to be used herein are according to the formula  $R-(A)_n-R_1-OH$  wherein R is H, OH, a linear saturated or unsaturated alkyl of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein R1 is H or a linear saturated or unsaturated alkyl of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, and A is an alkoxy group preferably ethoxy, methoxy, and/or propoxy and n is from 1 to 5, preferably 1 to 2. Suitable alkoxylated glycol to be used herein is methoxy octadecanol (HI=11).

Particularly preferred hydrophobic solvents to be used herein include d-limonene, dipentene, alpha-pinene, beta-pinene, octane or mixtures thereof.

Suitable hydrophilic solvents to be used herein include alkoxylated aliphatic or aromatic alcohols, aliphatic or aromatic alcohols, glycols or alkoxylated glycols, and mixtures thereof, all these solvents having a hydrophilic index of more than 15.

Suitable hydrophilic alkoxylated aliphatic or aromatic alcohols to be used herein are according to the formula  $R(A)_n-OH$  wherein R is a linear or branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, or an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein A is an alkoxy group preferably butoxy, propoxy and/or ethoxy, and n is an integer of from 1 to 5, preferably 1 to 2. Particularly suitable alkoxylated aliphatic alcohols to be used herein include methoxy propanol (HI= 37), ethoxy propanol (HI=32), propoxy propanol (HI=28) and/or butoxy propanol (HI= 27). Particularly suitable alkoxylated aromatic alcohol to be used herein include 1-methoxy-2-phenyl-1-ethanol (HI=23).

Suitable hydrophilic aliphatic or aromatic alcohols to be used herein are according to the formula  $R-OH$  wherein R

is a linear or branched saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, or an alkyl substituted or non-alkyl substituted aryl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10. Particularly suitable aliphatic alcohols to be used herein include linear alcohols like ethanol (HI=37) and/or propanol (HI=28). Particularly suitable aromatic alcohol to be used herein is benzyl alcohol (HI= 16).

Suitable hydrophilic glycols to be used herein are according to the formula HO-CR<sub>1</sub>R<sub>2</sub>-OH wherein R<sub>1</sub> and R<sub>2</sub> are independently H or a C<sub>2</sub>-C<sub>10</sub> saturated or unsaturated aliphatic hydrocarbon chain and/or cyclic. Particularly suitable glycol to be used herein are propanediol (HI=45) and/or dodecaneglycol (HI=16).

Suitable hydrophilic alkoxyated glycols to be used herein are according to the formula R-(A)<sub>n</sub>-R<sub>1</sub>-OH wherein R is H, OH, a linear saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, wherein R<sub>1</sub> is H or a linear saturated or unsaturated alkyl group of from 1 to 20 carbon atoms, preferably from 2 to 15 and more preferably from 2 to 10, and A is an alkoxy group preferably ethoxy, methoxy, and/or propoxy and n is from 1 to 5, preferably 1 to 2. Particularly suitable alkoxyated glycols to be used herein is ethoxyethoxyethanol (HI=37).

Particularly preferred hydrophilic solvents to be used herein are benzyl alcohol and/or 1-methoxy-2-propanol.

As a second essential element, the liquid compositions according to the present invention comprise an enzyme or mixtures thereof at a level of active enzyme of from 0.0001% to 5% by weight of the total composition, preferably from 0.001% to 2%, and more preferably from 0.01% to 1%. The enzymes are desirable herein as they contribute to the stain removal performance of the liquid compositions.

Suitable enzymes to be used herein include any enzyme known to those skilled in the art. Particularly suitable enzymes to be used herein include those selected from the group consisting of cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxygenases, ligninases, pullulanases, tannases, pentosanases, malanases, β-glucanases, arabinosidases and mixtures thereof.

A preferred combination of enzymes is for example protease, amylase, lipase, cutinase and/or cellulase. More preferably protease and/or amylase are used in combination with the lipolytic enzyme variant D96L, as the lipase.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgaard et al, which discloses fungal cellulase produced from *Humicola insolens*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

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

Other suitable cellulases are cellulases originated from *Humicola insolens* having a molecular weight of about 50KDa, an isoelectric point of 5.5 and containing 415 amino acids. Especially suitable cellulases are the cellulases having color care benefits. Examples of such cellulases are cellulases described in European patent application No. 91202879.2, filed November 6, 1991 (Novo).

Preferred commercially available protease enzymes include those sold under the tradenames Alcalase<sup>®</sup>, Savinase<sup>®</sup>, Primase<sup>®</sup>, Durazym<sup>®</sup>, and Esperase<sup>®</sup> by Novo Nordisk A/S (Denmark), those sold under the tradename Maxatase<sup>®</sup>, Maxacal<sup>®</sup> and Maxapem<sup>®</sup> by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean<sup>®</sup> and Optimase<sup>®</sup> by Solvay Enzymes. Also proteases described in our co-pending application USSN 08/136,797 can be included in the liquid composition of the invention.

A preferred protease herein referred to as "Protease D" is a carbonyl hydrolase variant having an amino acid sequence not found in nature, which is derived from a precursor carbonyl hydrolase by substituting a different amino acid for the amino acid residue at a position in said carbonyl hydrolase equivalent to position +76, preferably also in combination with one or more amino acid residue positions equivalent to those selected from the group consisting of +99, +101, +103, +104, +107, +123, +27, +105, +109, +126, +128, +135, +156, +166, +195, +197, +204, +206, +210, +216, +217, +218, +222, +260, +265, and/or +274 according to the numbering of *Bacillus amyloliquefaciens* subtilisin, as described in the concurrently filed patent application of A. Baeck et al. entitled "Protease-Containing Cleaning Compositions" having U.S. Serial No. 08/322,676, filed October 13, 1994, which is incorporated herein by reference in its entirety.

Highly preferred enzymes that can be included in the compositions of the present invention include lipases. It has been found that the cleaning performance on greasy soils is synergistically improved by using lipases. Suitable lipase enzymes include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. Suitable lipases include those which show a positive immunological cross-reaction with the antibody of the lipase, produced by the microorganism *Pseudomonas fluorescens* IAM 1057. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P<sup>®</sup> "Amano" hereinafter referred to as "Amano-P". Further suitable lipases are lipases such as M1 Lipase<sup>®</sup> and Lipomax<sup>®</sup> (Gist-Brocades). Highly preferred lipases are the D96L lipolytic enzyme variant of the native lipase derived from Humi-

cola lanuginosa as described in US Serial No. 08/341,826. Preferably the Humicola lanuginosa strain DSM 4106 is used. This enzyme is incorporated into the composition in accordance with the invention at a level of from 50 LU to 8500 LU per liter wash solution. Preferably the variant D96L is present at a level of from 100 LU to 7500 LU per liter of wash solution. More preferably at a level of from 150 LU to 5000 LU per liter of wash solution.

5 By D96L lipolytic enzyme variant is meant the lipase variant as described in patent application WO 92/05249 viz. wherein the native lipase ex Humicola lanuginosa aspartic acid (D) residue at position 96 is changed to Leucine (L). According to this nomenclature said substitution of aspartic acid to Leucine in position 96 is shown as : D96L.

10 Also suitable are cutinases [EC 3.1.1.50] which can be considered as a special kind of lipase, namely lipases which do not require interfacial activation. Addition of cutinases to detergent compositions have been described in, e.g. WO-A-88/09367 (Genencor).

Amylases (& and/or  $\beta$ ) can be included for removal of carbohydrate-based stains. Suitable amylases are Ter-mamyl<sup>®</sup> (Novo Nordisk), Fungamyl<sup>®</sup> and BAN<sup>®</sup> (Novo Nordisk).

The above-mentioned enzymes may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin.

15 As a third essential element, the liquid compositions according to the present invention comprise a surfactant or mixtures thereof.

Any surfactant known to those skilled in the art may be suitable herein including nonionic, anionic, cationic, zwitter-ionic, and/or amphoteric surfactants. Such surfactants contribute to the stain removal properties of the compositions according to the present invention.

20 The liquid compositions herein comprise from 0.1% to 50% by weight of the total composition of a surfactant or mixtures thereof, preferably from 5% to 30% and more preferably from 8% to 20%.

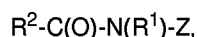
25 Nonionic surfactants are highly preferred herein for performance reasons. Suitable nonionic surfactants to be used herein are fatty alcohol ethoxylates and/or propoxylates which are commercially available with a variety of fatty alcohol chain lengths and a variety of ethoxylation degrees. Indeed, the HLB values of such alkoxyated nonionic surfactants depend essentially on the chain length of the fatty alcohol, the nature of the alkoxylation and the degree of alkoxylation. Surfactant catalogues are available which list a number of surfactants, including nonionics, together with their respec-tive HLB values.

30 Suitable chemical processes for preparing the nonionic surfactants for use herein include condensation of corre-sponding alcohols with alkylene oxide, in the desired proportions. Such processes are well-known to the man skilled in the art and have been extensively described in the art. As an alternative, a great variety of alkoxyated alcohols suitable for use herein is commercially available from various suppliers.

Particularly suitable to be used herein as nonionic surfactants are hydrophobic nonionic surfactants having an HLB (hydrophilic-lipophilic balance) below 16, preferably below 15, more preferably below 12, and most preferably below 10. Those hydrophobic nonionic surfactants have been found to provide good grease cutting properties.

35 Preferred hydrophobic nonionic surfactants to be used in the compositions according to the present invention are surfactants having an HLB below 16 and being according to the formula  $RO-(C_2H_4O)_n(C_3H_6O)_mH$ , wherein R is a  $C_6$  to  $C_{22}$  alkyl chain or a  $C_6$  to  $C_{28}$  alkyl benzene chain, and wherein  $n+m$  is from 0 to 20 and  $n$  is from 0 to 15 and  $m$  is from 0 to 20, preferably  $n+m$  is from 1 to 15 and,  $n$  and  $m$  are from 0.5 to 15, more preferably  $n+m$  is from 1 to 10 and,  $n$  and  $m$  are from 0 to 10. The preferred R chains for use herein are the  $C_8$  to  $C_{22}$  alkyl chains. Accordingly, suitable hydrophobic nonionic surfactants for use herein are Dobanol<sup>®</sup> 91-2.5 (HLB= 8.1; R is a mixture of  $C_9$  and  $C_{11}$  alkyl chains,  $n$  is 2.5 and  $m$  is 0), or Lutensol<sup>®</sup> TO3 (HLB=8; R is a  $C_{13}$  alkyl chains,  $n$  is 3 and  $m$  is 0), or Lutensol<sup>®</sup> AO3 (HLB=8; R is a mixture of  $C_{13}$  and  $C_{15}$  alkyl chains,  $n$  is 3 and  $m$  is 0), or Tergitol<sup>®</sup> 25L3 (HLB= 7.7; R is in the range of  $C_{12}$  to  $C_{15}$  alkyl chain length,  $n$  is 3 and  $m$  is 0), or Dobanol<sup>®</sup> 23-3 (HLB=8.1; R is a mixture of  $C_{12}$  and  $C_{13}$  alkyl chains,  $n$  is 3 and  $m$  is 0), or Dobanol<sup>®</sup> 23-2 (HLB=6.2; R is a mixture of  $C_{12}$  and  $C_{13}$  alkyl chains,  $n$  is 2 and  $m$  is 0), or Doba-nol<sup>®</sup> 45-7 (HLB=11.6; R is a mixture of  $C_{14}$  and  $C_{15}$  alkyl chains,  $n$  is 7 and  $m$  is 0) Dobanol<sup>®</sup> 23-6.5 (HLB=11.9; R is a mixture of  $C_{12}$  and  $C_{13}$  alkyl chains,  $n$  is 6.5 and  $m$  is 0), or Dobanol<sup>®</sup> 25-7 (HLB=12; R is a mixture of  $C_{12}$  and  $C_{15}$  alkyl chains,  $n$  is 7 and  $m$  is 0), or Dobanol<sup>®</sup> 91-5 (HLB=11.6; R is a mixture of  $C_9$  and  $C_{11}$  alkyl chains,  $n$  is 5 and  $m$  is 0), or Dobanol<sup>®</sup> 91-6 (HLB=12.5; R is a mixture of  $C_9$  and  $C_{11}$  alkyl chains,  $n$  is 6 and  $m$  is 0), or Dobanol<sup>®</sup> 91-8 (HLB=13.7; R is a mixture of  $C_9$  and  $C_{11}$  alkyl chains,  $n$  is 8 and  $m$  is 0), Dobanol<sup>®</sup> 91-10 (HLB=14.2; R is a mixture of  $C_9$  to  $C_{11}$  alkyl chains,  $n$  is 10 and  $m$  is 0), or mixtures thereof. Preferred herein are Dobanol<sup>®</sup> 91-2.5, or Lutensol<sup>®</sup> TO3, or Lutensol<sup>®</sup> AO3, or Tergitol<sup>®</sup> R 25L3, or Dobanol<sup>®</sup> 23-3, or Dobanol<sup>®</sup> 23-2, or mixtures thereof. These Doba-nol<sup>®</sup> surfactants are commercially available from SHELL. These Lutensol<sup>®</sup> surfactants are commercially available from BASF and these Tergitol<sup>®</sup> surfactants are commercially available from UNION CARBIDE. Nonionic surfactants may also be available from Hoechst under the name Surfonic<sup>®</sup>.

55 Other suitable nonionic surfactants for use herein include polyhydroxy fatty acid amide surfactants, or mixtures thereof, according to the formula



wherein R<sup>1</sup> is H, or C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R<sup>2</sup> is C<sub>5</sub>-C<sub>31</sub> hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxyated derivative thereof.

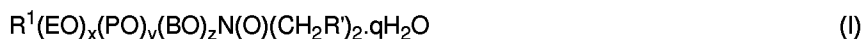
Preferably, R<sup>1</sup> is C<sub>1</sub>-C<sub>4</sub> alkyl, more preferably C<sub>1</sub> or C<sub>2</sub> alkyl and most preferably methyl, R<sup>2</sup> is a straight chain C<sub>7</sub>-C<sub>19</sub> alkyl or alkenyl, preferably a straight chain C<sub>9</sub>-C<sub>18</sub> alkyl or alkenyl, more preferably a straight chain C<sub>11</sub>-C<sub>18</sub> alkyl or alkenyl, and most preferably a straight chain C<sub>11</sub>-C<sub>14</sub> alkyl or alkenyl, or mixtures thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilised as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH<sub>2</sub>-(CHOH)<sub>n</sub>-CH<sub>2</sub>OH, -CH(CH<sub>2</sub>OH)-(CHOH)<sub>n-1</sub>-CH<sub>2</sub>OH, -CH<sub>2</sub>-(CHOH)<sub>2</sub>-(CHOR')(CHOH)-CH<sub>2</sub>OH, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxyated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly CH<sub>2</sub>-(CHOH)<sub>4</sub>-CH<sub>2</sub>OH.

In formula R<sup>2</sup> - C(O) - N(R<sup>1</sup>) - Z, R<sup>1</sup> can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. R<sup>2</sup> - C(O) - N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide and the like. Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxylactyl, 1-deoxygalactyl, 1-deoxymannityl, 1-deoxymaltotriosityl and the like.

Suitable polyhydroxy fatty acid amide surfactants to be used herein may be commercially available under the trade name HOE<sup>®</sup> from Hoechst.

Methods for making polyhydroxy fatty acid amide surfactants are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed for example in GB patent specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., US patent 2,965,576, issued December 20, 1960 to E.R. Wilson, US patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, US patent 1,985,424, issued December 25, 1934 to Piggott and WO92/06070, each of which is incorporated herein by reference.

Other nonionic surfactants to be used herein are amine oxide surfactants. The compositions of the present invention may comprise amine oxide in accordance with the general formula I:



In general, it can be seen that the structure (I) provides one long-chain moiety R<sup>1</sup>(EO)<sub>x</sub>(PO)<sub>y</sub>(BO)<sub>z</sub> and two short chain moieties, CH<sub>2</sub>R'. R' is preferably selected from hydrogen, methyl and -CH<sub>2</sub>OH. In general R<sup>1</sup> is a primary or branched hydrocarbyl moiety which can be saturated or unsaturated, preferably, R<sup>1</sup> is a primary alkyl moiety. When x+y+z = 0, R<sup>1</sup> is a hydrocarbyl moiety having chain length of from about 8 to about 18. When x+y+z is different from 0, R<sup>1</sup> may be somewhat longer, having a chainlength in the range C<sub>12</sub>-C<sub>24</sub>. The general formula also encompasses amine oxides wherein x+y+z = 0, R<sub>1</sub> = C<sub>8</sub>-C<sub>18</sub>, R' = H and q = 0-2, preferably 2. These amine oxides are illustrated by C12-14 alkyldimethyl amine oxide, hexadecyl dimethylamine oxide, octadecylamine oxide and their hydrates, especially the dihydrates as disclosed in U.S. Patents 5,075,501 and 5,071,594, incorporate herein by reference.

The invention also encompasses amine oxides wherein x+y+z is different from zero, specifically x+y+z is from about 1 to about 10, R<sup>1</sup> is a primary alkyl group containing 8 to about 24 carbons, preferably from about 12 to about 16 carbon atoms; in these embodiments y + z is preferably 0 and x is preferably from about 1 to about 6, more preferably from about 2 to about 4; EO represents ethyleneoxy; PO represents propyleneoxy; and BO represents butyleneoxy. Such amine oxides can be prepared by conventional synthetic methods, e.g., by the reaction of alkylethoxysulfates with dimethylamine followed by oxidation of the ethoxylated amine with hydrogen peroxide.

Highly preferred amine oxides herein are solids at ambient temperature, more preferably they have melting-points in the range 30°C to 90°C. Amine oxides suitable for use herein are made commercially by a number of suppliers, including Akzo Chemie, Ethyl Corp., and Procter & Gamble. See McCutcheon's compilation and Kirk-Othmer review article for alternate amine oxide manufacturers. Preferred commercially available amine oxides are the solid, dihydrate ADMOX 16<sup>®</sup> and ADMOX 18<sup>®</sup>, ADMOX 12<sup>®</sup> and especially ADMOX 14<sup>®</sup> from Ethyl Corp.

Preferred amine oxides to be used herein include hexadecyldimethylamine oxide dihydrate, dodecyldimethylamine oxide dihydrate, octadecyldimethylamine oxide dihydrate, hexadecyltris(ethyleneoxy)dimethylamine oxide, and tetradecyldimethylamine oxide dihydrate.

Whereas in certain of the preferred embodiments R' = H, there is some latitude with respect to having R' slightly larger than H. Specifically, the invention further encompasses embodiments wherein R' = CH<sub>2</sub>OH, such as hexadecylbis(2-hydroxyethyl)amine oxide, tallowbis(2-hydroxyethyl)amine oxide, stearylbis(2-hydroxyethyl)amine oxide and oley-

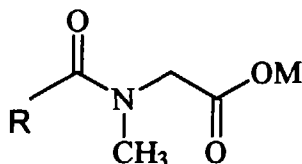
lbis(2- hydroxyethyl)amine oxide, dodecyldimethylamine oxide dihydrate.

The liquid compositions according to the present invention may comprise other surfactants like an anionic surfactant, or mixtures thereof. Anionic surfactants are suitable herein as they act as wetting agent, i.e., in a laundry application they wet the stains on the fabrics, especially on hydrophilic fabrics. Furthermore, anionic surfactants allow to obtain clear compositions even when said compositions comprise hydrophobic ingredients such as hydrophobic surfactants.

Particularly suitable for use herein are sulfonate and sulfate surfactants. The like anionic surfactants are well-known in the art and have found wide application in commercial detergents. These anionic surfactants include the C<sub>8</sub>-C<sub>22</sub> alkyl benzene sulfonates (LAS), the C<sub>8</sub>-C<sub>22</sub> alkyl sulfates (AS), unsaturated sulfates such as oleyl sulfate, the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates (AES) and the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy carboxylates. The neutralising cation for the anionic synthetic sulfonates and/or sulfates is represented by conventional cations which are widely used in detergent technology such as sodium, potassium or alkanolammonium. Preferred herein are the alkyl sulphate, especially coconut alkyl sulphate having from 6 to 18 carbon atoms in the alkyl chain, preferably from 8 to 15, or mixtures thereof.

Other anionic surfactants useful for deterative purposes can also be used herein. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C<sub>8</sub>-C<sub>22</sub> primary or secondary alkanesulfonates, C<sub>8</sub>-C<sub>24</sub> olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C<sub>8</sub>-C<sub>24</sub> alkylpolyglycoethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as C<sub>14-16</sub> methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C<sub>12</sub>-C<sub>18</sub> monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C<sub>6</sub>-C<sub>14</sub> diesters), sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below). Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. Further examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

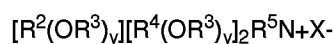
Other suitable anionic surfactants to be used herein also include acyl sarcosinate or mixtures thereof, in its acid and/or salt form, preferably long chain acyl sarcosinates having the following formula:



wherein M is hydrogen or a cationic moiety and wherein R is an alkyl group of from 11 to 15 carbon atoms, preferably of from 11 to 13 carbon atoms. Preferred M are hydrogen and alkali metal salts, especially sodium and potassium. Said acyl sarcosinate surfactants are derived from natural fatty acids and the amino-acid sarcosine (N-methyl glycine). They are suitable to be used as aqueous solution of their salt or in their acidic form as powder. Being derivatives of natural fatty acids, said acyl sarcosinates are rapidly and completely biodegradable and have good skin compatibility.

Accordingly, particularly preferred long chain acyl sarcosinates to be used herein include C<sub>12</sub> acyl sarcosinate (i.e. an acyl sarcosinate according to the above formula wherein M is hydrogen and R is an alkyl group of 11 carbon atoms) and C<sub>14</sub> acyl sarcosinate (i.e. an acyl sarcosinate according to the above formula wherein M is hydrogen and R is an alkyl group of 13 carbon atoms). C<sub>12</sub> acyl sarcosinate is commercially available, for example, as Hamposyl L-30<sup>®</sup> supplied by Hampshire. C<sub>14</sub> acyl sarcosinate is commercially available, for example, as Hamposyl M-30<sup>®</sup> supplied by Hampshire.

Cationic surfactants particularly suitable for use in the liquid compositions of the present invention are those having one long-chain hydrocarbonyl group. Examples of such cationic surfactants include the ammonium surfactants such as alkyldimethylammonium halogenides, and those surfactants having the formula:



wherein R<sup>2</sup> is an alkyl or alkyl benzyl group having from about 8 to about 18 carbon atoms in the alkyl chain, each R<sup>3</sup> is selected from the group consisting of -CH<sub>2</sub>CH<sub>2</sub>-, -CH<sub>2</sub>CH(CH<sub>3</sub>)-, -CH<sub>2</sub>CH(CH<sub>2</sub>OH)-, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, and mixtures

thereof; each R<sup>4</sup> is selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl, benzyl ring structures formed by joining the two R<sup>4</sup> groups, -CH<sub>2</sub>CHOH-CHOHCOR<sup>6</sup>CHOHCH<sub>2</sub>OH wherein R<sup>6</sup> is any hexose or hexose polymer having a molecular weight less than about 1000, and hydrogen when y is not 0; R<sup>5</sup> is the same as R<sup>4</sup> or is an alkyl chain wherein the total number of carbon atoms of R<sup>2</sup> plus R<sup>5</sup> is not more than about 18; each y is from 0 to about 10 and the sum of the y values is from 0 to about 15; and X is any compatible anion.

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



wherein R<sub>1</sub> is C<sub>8</sub>-C<sub>16</sub> alkyl, each of R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> is independently C<sub>1</sub>-C<sub>4</sub> alkyl, C<sub>1</sub>-C<sub>4</sub> hydroxy alkyl, benzyl, and - (C<sub>2</sub>H<sub>4</sub>O)<sub>x</sub>H where x has a value from 1 to 5, and X is an anion. Not more than one of R<sub>2</sub>, R<sub>3</sub> or R<sub>4</sub> should be benzyl.

The preferred alkyl chain length for R<sub>1</sub> is C<sub>12</sub>-C<sub>15</sub> particularly where the alkyl group is a mixture of chain lengths derived from coconut or palm kernel fat or is derived synthetically by olefin build up or OXO alcohols synthesis. Preferred groups for R<sub>2</sub>R<sub>3</sub> and R<sub>4</sub> are methyl and hydroxyethyl groups and the anion X may be selected from halide, methosulphate, acetate and phosphate ions.

Examples of suitable quaternary ammonium compounds of formulae (i) for use herein are:

coconut trimethyl ammonium chloride or bromide;  
 coconut methyl dihydroxyethyl ammonium chloride or bromide;  
 decyl triethyl ammonium chloride;  
 decyl dimethyl hydroxyethyl ammonium chloride or bromide;  
 C<sub>12-15</sub> dimethyl hydroxyethyl ammonium chloride or bromide;  
 coconut dimethyl hydroxyethyl ammonium chloride or bromide;  
 myristyl trimethyl ammonium methyl sulphate;  
 lauryl dimethyl benzyl ammonium chloride or bromide;  
 lauryl dimethyl (ethenoxy)<sub>4</sub> ammonium chloride or bromide;  
 choline esters (compounds of formula (i) wherein R<sub>1</sub> is -CH<sub>2</sub>-O-C(O)-C<sub>12-14</sub> alkyl and R<sub>2</sub>R<sub>3</sub>R<sub>4</sub> are methyl).

Other cationic surfactants useful herein are also described in U.S. Patent 4,228,044, Cambre, issued October 14, 1980.

The compositions to be used according to the present invention must be liquids. As used herein, "liquid" includes "pasty" compositions, and liquid compositions herein preferably have a viscosity of from 1 cps to 10000 cps when measured with a Brookfield viscometer at 50 rpm shear rate with a spindle n°2 at 20°C or with a Carri-med rheometer at 50 dyne/cm<sup>2</sup> at 20°C, preferably from 100 cps to 1000 cps, more preferably from 150 cps to 600 cps and most preferably 200 cps to 500 cps.

Preferably, the compositions to be used herein are aqueous. Said aqueous compositions have a pH as is of from 5 to 12, preferably from 6 to 10, and more preferably from 7 to 9. The pH of the compositions can be adjusted for instance by using organic or inorganic acids, or alkalizing agents.

The liquid compositions according to the present invention are physically stable. By "physically stable" it is meant herein that the compositions of the present invention do not split in two or more phases when exposed in stressed conditions, e.g., at a temperature of 50 °C during 2 weeks.

The compositions according to the present invention may further comprise other optional ingredients like builders, stabilizers, chelating agents, dye transfer agents, radical scavengers, solvents, brighteners, foam suppressors, perfumes, soil suspending polyamine polymers, polymeric soil release agents, catalysts, bleach, bleach activators and dyes.

#### Processes for cleaning a fabric

The present invention also encompasses processes of cleaning fabrics, starting from a liquid composition, as described herein.

The processes of cleaning fabrics of the present invention include the steps of contacting fabrics with a liquid composition, as described herein before, neat or diluted, and subsequently rinsing said fabrics. In the preferred embodiment, when the fabrics are "pretreated", the liquid composition is applied neat on the fabrics, and the fabrics are subsequently rinsed, or washed and then rinsed in a normal wash cycle. We have observed that the stain removal performance improvement is particularly noticeable with the liquid compositions herein when contacted directly with the soiled portion of fabrics, before they are washed/rinsed.

In the cleaning processes of the present invention, the liquid composition comprising an enzyme, a surfactant and

said solvent system needs to be contacted with the fabrics to be cleaned. This can be done either in a so-called "pretreatment mode", where the liquid composition is applied neat onto said fabrics before the fabrics are rinsed, or washed then rinsed, or in a "soaking mode" where the liquid composition is first diluted in an aqueous bath and the fabrics are immersed and soaked in the bath, before they are rinsed, or in a "through the wash mode", where the liquid composition is added on top of a wash liquor formed by dissolution or dispersion of a typical laundry detergent. As discussed earlier, the composition to perform the processes herein is in the form of a liquid as opposed to a solid or a gas.

It is also essential in these processes according to the present invention, that the fabrics be rinsed after they have been contacted with said liquid composition, before said composition has completely dried off.

In the pretreatment mode, the process comprises the steps of applying said liquid composition in its neat form onto said fabrics, or at least soiled portions thereof (i.e., directly applying said liquid composition as described herein onto said fabrics without undergoing any dilution), and subsequently rinsing, or washing then rinsing said fabrics. In this mode, the neat compositions can optionally be left to act onto said fabrics for a period of time ranging from 1 min. to 1 hour, preferably from 1 minute to 30 minutes, before the fabrics are rinsed, or washed then rinsed, provided that the composition is not left to dry onto said fabrics. For particularly tough stains, it may be appropriate to further rub or brush said fabrics by means of a sponge or a brush, or by rubbing two pieces of fabrics against each other.

In another mode, generally referred to as "soaking", the process comprises the steps of diluting said liquid composition in its neat form in an aqueous bath so as to form a diluted composition. The dilution level of said liquid composition in an aqueous bath is typically up to 1:85, preferably up to 1:50 and more preferably about 1:25 (composition:water). The fabrics are then contacted with the aqueous bath comprising the liquid composition, and the fabrics are finally rinsed, or washed then rinsed. Preferably in that embodiment, the fabrics are immersed in the aqueous bath comprising the liquid composition, and also preferably, the fabrics are left to soak therein for a period of time ranging from 30 minutes to 48 hours, preferably from 1 hour to 24 hours.

In yet another mode which can be considered as a sub-embodiment of "soaking", generally referred to as "bleaching through the wash", the liquid composition is used as a so-called laundry additive. And in that embodiment the aqueous bath is formed by dissolving or dispersing a conventional laundry detergent in water. The liquid composition in its neat form is contacted with the aqueous bath, and the fabrics are then contacted with the aqueous bath containing the liquid composition. Finally, the fabrics are rinsed.

#### Optional ingredients

The compositions according to the present invention may comprise a chelating agent as an optional but highly preferred ingredient. Indeed, such chelating agents further contribute to the benefit of the liquid compositions herein, i.e., they further improve the stain removal properties of the liquid compositions herein. Also they contribute to the safety profile of the liquid compositions of the present invention which may be used for pretreating a soiled colored fabric upon prolonged contact times before washing said fabric.

Suitable chelating agents to be used herein include chelating agents selected from the group of phosphonate chelating agents, amino carboxylate chelating agents, polyfunctionally-substituted aromatic chelating agents, and further chelating agents like glycine, salicylic acid, aspartic acid, glutamic acid, malonic acid, or mixtures thereof. Chelating agents when used, are typically present herein in amounts ranging from 0.001% to 5% by weight of the total composition and preferably from 0.05% to 2% by weight.

Suitable phosphonate chelating agents to be used herein may include ethydrionic acid as well as amino phosphonate compounds, including aminotri(methylene phosphonic acid) (ATMP), amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates. The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonates and aminotri(methylene phosphonic acid). Phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST®.

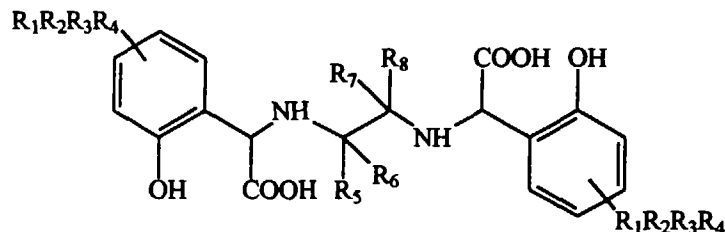
Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzene such as 1,2-dihydroxy-3,5-disulfobenzene.

A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'-disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N'-disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4,704,233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N'-disuccinic acids is, for instance, commercially available under the trade name ssEDDS® from Palmer Research Laboratories.

Suitable amino carboxylates to be used herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA), N-hydroxyethylethylenediamine triacetates, nitrilotri-acetates, ethyl-

enediamine tetrapropionates, triethylenetetraaminehexa-acetates, ethanoldiglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine di-acetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium, and substituted ammonium salt forms. Particularly suitable amino carboxylates to be used herein are diethylene triamine penta acetic acid, propylene diamine tetracetic acid (PDTA) which is, for instance, commercially available from BASF under the trade name Trilon FS<sup>®</sup> and methyl glycine di-acetic acid (MGDA).

Another preferred chelating agent for use herein is of the formula:

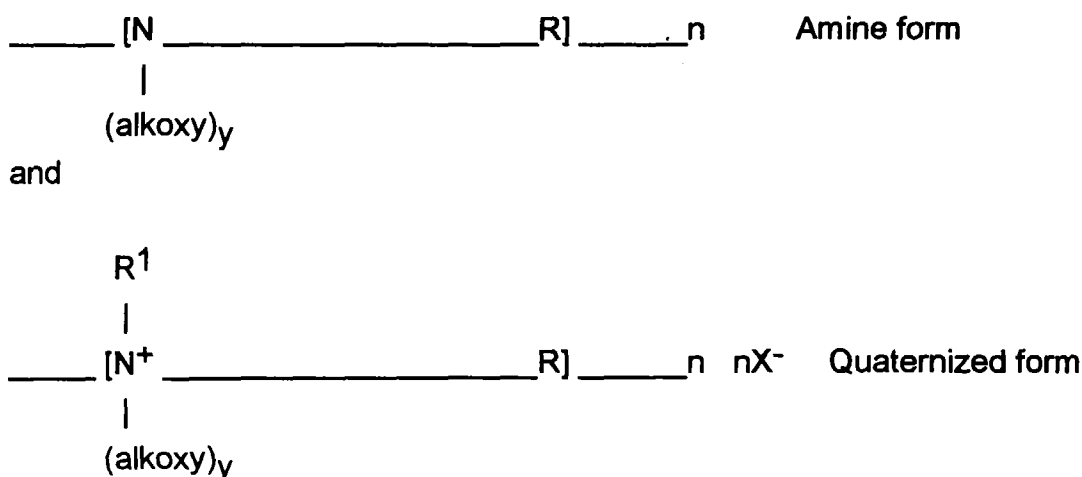


wherein R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, and R<sub>4</sub> are independently selected from the group consisting of -H, alkyl, alkoxy, aryl, aryloxy, -Cl, -Br, -NO<sub>2</sub>, -C(O)R', and -SO<sub>2</sub>R''; wherein R' is selected from the group consisting of -H, -OH, alkyl, alkoxy, aryl, and aryloxy; R'' is selected from the group consisting of alkyl, alkoxy, aryl, and aryloxy; and R<sub>5</sub>, R<sub>6</sub>, R<sub>7</sub>, and R<sub>8</sub> are independently selected from the group consisting of -H and alkyl.

Particularly preferred chelating agents to be used herein are ATMP, diethylene triamine methylene phosphonate, ethylene N,N'-disuccinic acid, diethylene triamine pentaacetate, glycine, salicylic acid, aspartic acid, glutamic acid, malonic acid or mixtures thereof.

The compositions according to the present invention may comprise a radical scavenger as an optional ingredient. Suitable radical scavengers for use herein include the well-known substituted mono and dihydroxy benzenes and their analogs, alkyl and aryl carboxylates and mixtures thereof. Preferred such radical scavengers for use herein include di-tert-butyl hydroxy toluene (BHT), hydroquinone, di-tert-butyl hydroquinone, mono-tert-butyl hydroquinone, tert-butyl-hydroxy anisole, benzoic acid, toluic acid, catechol, t-butyl catechol, benzylamine, 1,1,3-tris(2-methyl-4-hydroxy-5-tert-butylphenyl) butane, n-propylgallate or mixtures thereof and highly preferred is di-tert-butyl hydroxy toluene. Radical scavengers when used, are typically present herein in amounts ranging from 0.001% to 2% by weight of the total composition and preferably from 0.001% to 0.5% by weight.

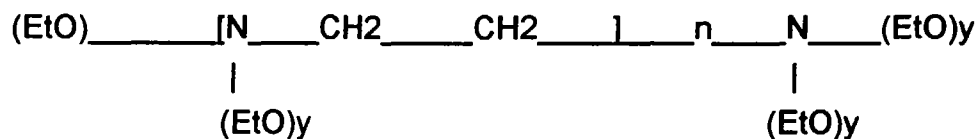
The liquid compositions according to the present invention may further comprise a soil suspending polyamine polymer or mixtures thereof, as optional but highly preferred ingredient. Any soil suspending polyamine polymer known to those skilled in the art may also be used herein. Particularly suitable polyamine polymers for use herein are polyalkoxylated polyamines. Such materials can conveniently be represented as molecules of the empirical structures with repeating units:



wherein R is a hydrocarbyl group, usually of 2-6 carbon atoms; R<sup>1</sup> may be a C<sub>1</sub>-C<sub>20</sub> hydrocarbon; the alkoxy groups are ethoxy, propoxy, and the like, and y is 2-30, most preferably from 10-20; n is an integer of at least 2, preferably from 2-

20, most preferably 3-5; and X<sup>-</sup> is an anion such as halide or methylsulfate, resulting from the quaternization reaction.

The most highly preferred polyamines for use herein are the so-called ethoxylated polyethylene amines, i.e., the polymerized reaction product of ethylene oxide with ethyleneimine, having the general formula:



when y = 2-30. Particularly preferred for use herein is an ethoxylated polyethylene amine, in particular ethoxylated tetraethylenepentamine, and quaternized ethoxylated hexamethylene diamine.

It has surprisingly been found that said soil suspending polyamine polymers contribute to the benefits of the present invention, i.e., that when added on top of said solvent system in a liquid composition comprising an enzyme and a surfactant, they further improve the stain removal performance of said composition, especially under laundry pretreatment conditions. Indeed, they allow to improve the stain removal performance on a variety of stains including greasy stains, enzymatic stains, clay/mud stains as well as on bleachable stains.

Typically, the compositions comprise up to 10% by weight of the total composition of such a soil suspending polyamine polymer or mixtures thereof, preferably from 0.1% to 5% and more preferably from 0.3% to 2%.

The compositions herein may also comprise other polymeric soil release agents known to those skilled in the art. Such polymeric soil release agents are characterised by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibres, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibres and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophile 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 hydrophile 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 hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile 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 hydrophobe components comprising (i) C<sub>3</sub> oxyalkylene terephthalate segments, wherein, if said hydrophobe components also comprise oxyethylene terephthalate, the ratio of oxyethylene terephthalate:C<sub>3</sub> oxyalkylene terephthalate units is about 2:1 or lower, (ii) C<sub>4</sub>-C<sub>6</sub> alkylene or oxy C<sub>4</sub>-C<sub>6</sub> 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<sub>1</sub>-C<sub>4</sub> alkyl ether or C<sub>4</sub> hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C<sub>1</sub>-C<sub>4</sub> alkyl ether or C<sub>4</sub> hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C<sub>1</sub>-C<sub>4</sub> alkyl ether and/or C<sub>4</sub> hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber 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 1 to about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C<sub>4</sub>-C<sub>6</sub> alkylene hydrophobe segments include, but are not limited to, end-caps of polymeric soil release agents such as MO<sub>3</sub>S(CH<sub>2</sub>)<sub>n</sub>OCH<sub>2</sub>CH<sub>2</sub>O<sup>-</sup>, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.

Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, co-polymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C<sub>1</sub>-C<sub>4</sub> alkyl and C<sub>4</sub> hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

Soil release agents characterised by poly(vinyl ester) hydrophobe segments include graft co-polymers of poly(vinyl ester), e.g., C<sub>1</sub>-C<sub>6</sub> vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as poly-



fer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate co-polymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO". The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which has an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Co-polymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI co-polymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These co-polymers can be either linear or branched.

The present invention compositions may also employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

If high sudsing is desired, suds boosters such as C<sub>10</sub>-C<sub>16</sub> alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C<sub>10</sub>-C<sub>14</sub> monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl<sub>2</sub>, MgSO<sub>4</sub>, and the like, can be added at levels of, for example, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Any optical brighteners, fluorescent whitening agents or other brightening or whitening agents known in the art can be incorporated in the instant compositions when they are designed for fabric treatment or laundering, at levels typically from about 0.05% to about 1.2%, by weight, of the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acids, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocyclic brighteners, this list being illustrative and non-limiting. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis-(1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bispheyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl-amino coumarin; 1,2-bis(-benzimidazol-2-yl)ethylene; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-naphth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho-[1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972, to Hamilton. Anionic brighteners are typically preferred herein.

Depending on the end-use envisioned, the liquid compositions herein can be packaged in a variety of containers including conventional bottles, bottles equipped with roll-on, sponge, brusher or sprayers, or sprayers.

Although the preferred application of the liquid compositions described herein is laundry application, as a laundry detergent or as a laundry additive and especially as a pretreater such compositions may also be used to clean hard-surfaces.

The invention is further illustrated by the following examples.

## Examples

Liquid compositions were prepared which comprise the indicated ingredients in the indicated proportions (weight%):

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	Ingredients	1 (%w/w)	2 (%w/w)	3 (%w/w)
5	Neodol® 45.7	12	-	5
	Neodol® 23.3	-	5	5
	Benzyl alcohol (HI=16)	1.0	-	-
	1-methoxy propanol (HI=37)	-	2.0	-
10	Ethanol (HI=37)	-	-	3.0
	Limonene (HI=0)	0.2	-	-
	Pinene (HI=0)	-	0.5	-
15	Octane (HI=0)	-	-	0.4
	Lipolase D96/L(100KNU/g)	0.12	0.10	0.05
	Protease (34g/l)	0.9	0.9	0.3
	Amylase (300KNU/g)	0.1	0.2	0.3
20	Ethoxylated 15-18 tetraethylenepentamine	1.0	2.0	0.5
	DTPA*	0.4	-	-
	DTPMP**	-	0.3	-
25	ATMP***	-	-	0.16
	Water and minors	up to 100	up to 100	up to 100
NaOH to pH 7.5				
	Ingredients	4 (%w/w)	5 (%w/w)	6 (%w/w)
30	Surfonic® 24.4	12	8	4
	Neodol® 23.65	-	-	4
	Na alkyl sulphate	12	15	10
35	Benzyl alcohol (HI=16)	-	1.5	-
	1-methoxy propanol (HI=37)	-	-	3.0
	Ethoxy ethoxy ethanol (HI=37)	0.5	-	-
40	Limonene (HI=0)	-	0.4	-
	Pinene (HI=0)	-	-	0.8
	Octane (HI=0)	0.2	-	-
45	Lipolase D96/L(100KNU/g)	0.10	0.12	0.8
	Protease (34g/l)	0.7	0.7	0.9
	Amylase (300KNU/g)	0.15	0.12	0.07
	Ethoxylated 15-18 tetraethylenepentamine	-	0.8	2.0
50	DTPA*	0.5	-	-
	DTPMP**	-	0.5	-
	Water and minors	up to 100	up to 100	up to 100
NaOH to pH 7.5				
55	DTPA* is diethylene triamine pentaacetate.			
	DTPMP** is diethylene triamine penta methylene phosphonic acid.			
	ATMP*** is aminotri(methylene phosphonic acid).			

Compositions 1 to 3 can be used in a pretreatment mode. In this mode, such a composition is applied neat on the stained portion of a fabric and left to act thereon for 5 minutes. Then the fabric is washed with a conventional detergent and rinsed. Excellent stain removal is obtained therewith on various stains including greasy stains, enzymatic stains, clay stains and bleachable stains.

5 Compositions 4 to 5 can be used in a through-the-wash mode. In this mode such a composition is contacted with an aqueous bath formed by dissolution of a conventional detergent in water. Fabrics are then contacted with the aqueous bath comprising the liquid detergent, and the fabrics are rinsed. Excellent stain removal is obtained on various stains including greasy stains, enzymatic stains, clay stains and bleachable stains.

10 Composition 6 can be used in a soaking mode. In this mode 100 ml of such a liquid composition is diluted in 10 liters of water. The fabrics are then contacted with this aqueous bath containing the composition, and left to soak therein for a period of time of 24 hours. The fabrics are eventually rinsed. Excellent stain removal is obtained therewith on various stains including greasy stains, enzymatic stains, clay stains and bleachable stains.

## Claims

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1. A liquid composition suitable for cleaning fabrics, comprising:

- from 0.0001% to 5% by weight of the total composition of an enzyme,
- a surfactant,
- 20 - and a solvent system comprising a hydrophilic solvent having a hydrophilic index of more than 15, and a hydrophobic solvent having a hydrophilic index of less than 15, at a weight ratio of said hydrophilic solvent to said hydrophobic solvent of 10:1 to 2:1,

wherein the hydrophilic index is defined by the equation

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$$\frac{\text{molecular weight of the hydrophilic part of the solvent}}{\text{total molecular weight of the solvent}} * 100.$$

30 2. A composition according to claim 1 wherein said hydrophilic solvent is an alkoxyated aliphatic or aromatic alcohol having a hydrophilic index of more than 15, an aliphatic or aromatic alcohol having a hydrophilic index of more than 15, glycol or alkoxyated glycol having a hydrophilic index of more than 15, or mixtures thereof, preferably is ethanol, propanol, methoxy propanol, ethoxy propanol, propoxy propanol, butoxy propanol, 1-methoxy-2-phenyl-1-ethanol, propanediol, dodecaneglycol, ethoxy-ethoxy-ethanol, benzyl alcohol or mixtures thereof, and more preferably is benzyl alcohol and/or 1-methoxy-2-propanol.

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3. A composition according to any of the preceding claims wherein said hydrophobic solvent is a paraffin, a terpene or a terpene derivative having a hydrophilic index of less than 15, an alkoxyated aliphatic or aromatic alcohol having a hydrophilic index of less than 15, an aliphatic or aromatic alcohol having a hydrophilic index of less than 15, glycol or alkoxyated glycol having a hydrophilic index of less than 15, or mixtures thereof, and preferably is d-limonene, dipentene, alpha-pinene, beta-pinene, octane or mixtures thereof.

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4. A composition according to any of the preceding claims wherein said hydrophilic and hydrophobic solvents are present at a weight ratio of said hydrophilic solvent to said hydrophobic solvent of 7:1 to 3:1 and preferably 6:1 to 4:1.

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5. A composition according to any of the preceding claims wherein said enzyme is selected from the group consisting of cellulases, hemicellulases, peroxidases, proteases, gluco-amylases, amylases, lipases, cutinases, pectinases, xylanases, reductases, oxidases, phenoloxidases, lipoxigenases, ligninases, pullulanases, tannases, pentosanases, malanases,  $\beta$ -glucanases, arabinosidases and mixtures thereof, and preferably is a protease, amylase, lipase, cutinase, cellulase or mixtures thereof.

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6. A composition according to any of the preceding claims which comprises from 0.001% to 2% by weight of the total composition of an enzyme, or mixtures thereof, and preferably from 0.01 % to 1%.

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7. A composition according to any of the preceding claims which comprises from 0.1% to 50% by weight of the total composition of a surfactant, or mixtures thereof, preferably from 5% to 30%, and more preferably from 8% to 20%, and wherein said surfactant is selected from the group consisting of nonionic surfactant, anionic surfactant, cationic

surfactant, zwitterionic surfactant, amphoteric surfactant and mixtures thereof.

- 5 8. A composition according to any of the preceding claims wherein said surfactant is a hydrophobic nonionic surfactant having an HLB below 16, or mixtures thereof, and more preferably is an alkoxyated nonionic surfactant according to the formula  $RO-(C_2H_4O)_n(C_3H_6O)_mH$ , wherein R is a  $C_6$  to  $C_{22}$  alkyl chain or a  $C_6$  to  $C_{28}$  alkyl benzene chain, and wherein  $n+m$  is from 0 to 20, n is from 0 to 15 and m is from 0 to 20, preferably  $n+m$  is from 1 to 15 and, n and m are from 0.5 to 15, more preferably  $n+m$  is from 1 to 10 and, n and m are from 0 to 10, or mixtures thereof.
- 10 9. A composition according to any of the preceding claims which is aqueous and has a pH of from 5 to 12, preferably from 6 to 10 and more preferably from 7 to 9.
- 15 10. A process of cleaning a fabric with a liquid composition according to any of the preceding claims, said process comprising the steps of applying said composition in its neat form onto said fabric, preferably only soiled portions thereof, before rinsing, or washing then rinsing said fabric.
- 20 11. A process according to claim 10, wherein said neat composition is allowed to remain in contact with said fabric for a period of time ranging from 1 minute to 1 hour, and preferably from 1 minute to 30 minutes.
- 25 12. A process of cleaning fabrics which includes the steps of diluting in an aqueous bath a liquid composition according to any of the preceding claims 1 to 9, in its neat form, contacting said fabrics with said aqueous bath comprising said liquid composition, and subsequently rinsing, or washing then rinsing said fabrics.
- 30 13. A process according to claim 12, wherein the fabrics are left to soak in said aqueous bath comprising said liquid composition for a period of time ranging from 30 minutes to 48 hours, preferably from 1 hour to 24 hours.
- 35 14. A process according to claims 12 or 13, wherein said aqueous bath is formed by dissolving or dispersing a conventional laundry detergent in water.
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## EUROPEAN SEARCH REPORT

Application Number  
EP 96 87 0125

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 5 374 372 A (BROZE GUY ET AL) * column 4, line 13 * * column 7; example * ---	1-7	C11D3/43 C11D3/18 C11D3/20
X,D	EP 0 137 616 A (PROCTER & GAMBLE ET AL.) * claims 1-3; examples * ---	1-3,5-7	
X	EP 0 164 467 A (PROCTER & GAMBLE ET AL.) * claim 1; examples * ---	1-3,5-7	
Y	DATABASE WPI Section Ch, Week 8851 Derwent Publications Ltd., London, GB; Class D25, AN 88-365232 XP002027060 & JP 63 275 697 A (KAO CORP) , 14 November 1988 * abstract * ---	1-14	
Y	EP 0 106 266 A (PROCTER & GAMBLE ET AL.) * claims * -----	1-14	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
BERLIN		6 March 1997	Pelli Wablat, B
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	

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