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(54) **Soaker compositions**

(57) Soaking compositions are disclosed which comprise a sorbitan ester in combination with a soil suspending agent selected from the group consisting of ethoxylated diamines, ethoxylated polyamines, ethoxylated amine polymers and mixtures thereof. Said compositions are diluted in water to form soaking liquors. In its broadest embodiment the present invention relates to a process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition comprising such a soil suspending agent, for more than 1 hour, then removed from said soaking liquor. The invention is particularly effective in removing particulate soils like silt and clay from fabrics as well as enzymatic stains.

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Description**Technical Field**

5 The present invention relates to the cleaning of fabrics in soaking conditions, i.e., in conditions where the fabrics are left to soak in a soaking liquor comprising water and detergent ingredients, either as a first step before a typical washing operation, or as a single step.

Background of the invention

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Fabric soaking operations have been described in the art. In such soaking operations, fabrics are left in contact with a soaking liquor for a prolonged period of time typically ranging from more than 1 hour to overnight or even 24 hours. This laundering process has the advantage that it maximises the contact time between the fabrics and the key active ingredients of the soaking liquor. It also has the advantage that it reduces or eliminates the need for a typical laundering operation involving the need for mechanical agitation, or that it improves the efficiency of the subsequent typical laundering operation.

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Such soaking operations are typically desirable to remove tough outdoor dirt from fabrics, such as particulate soil like mud, silt and/or clays. For example, clays usually have a microcrystalline mineral structure (e.g., hydrous aluminum silicate like illite, montmorillonite, kaolinite and the like) with the presence of an organic fraction. The organic fraction can contain a variety of compounds (e.g., humic acid, fulvic acid, plant/animal biomass and the like). Clays can also contain several kinds of metals (e.g., magnesium, calcium, potassium, iron and the like). However, such particulate soil is particularly difficult to remove from fabrics. Indeed, it is believed that the very fine dirt grains like clays or silt, typically below 0.002 mm in size, can insert among fabric fibers and steadily stick to the surface of the fibers. This problem is particularly acute with socks which are most exposed to silt and clay pick-up. Also such soaking operations are not fully satisfactory regarding the enzymatic stains removal performance delivered. Enzymatic stains are typically composed of carbohydrates and proteinaceous soil like blood. It has now been observed that enzymatic stains may act as a glue for particulate soil on fabrics, thus removing such enzymatic stains may facilitate the removal of particulate soil from fabrics.

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It is thus an object of the present invention to improve the removal of particulate soils, particularly silt, mud and/or clay, as well as enzymatic stains, from fabrics in a soaking operation.

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It has been found that this object can be met by soaking fabrics in an aqueous soaking liquor comprising an effective amount of a soaking detergent composition comprising a soil suspending agent selected from the group consisting of ethoxylated diamines, ethoxylated polyamines, ethoxylated amine polymers and mixtures thereof, as defined herein after. Indeed, it has been found that such a soil suspending agent, in a soaking composition, delivers improved stain removal performance on tough outdoor dirt like particulate soil and/or enzymatic stains under soaking conditions (i.e., when left in contact for prolonged period of time typically more than 1 hour up to 24 hours), as compared to the stain removal performance delivered with the same composition being free of such a soil suspending agent. Thus, in its broadest aspect the present invention encompasses a process of soaking fabrics, wherein said fabrics are immersed for more than one hour in a soaking liquor comprising water and an effective amount of a composition comprising a soil suspending agent, as defined herein, then removed from said soaking liquor.

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Furthermore, it has been found that the stain removal performance on particulate soil and/or enzymatic stains is further improved by combining said soil suspending agent with a sorbitan ester, as defined hereinafter, in a soaking detergent composition. Thus, the present invention encompasses a soaking detergent composition comprising a sorbitan ester and, a soil suspending agent, as defined herein, as well as a process of soaking fabrics in a soaking liquor formed with said soaking detergent composition.

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An advantage of the present invention is that not only improved particulate soil removal performance is delivered but also that the soil redeposition on fabrics in prolonged soaking condition is prevented. Furthermore, the soaking composition of the present invention comprising sorbitan ester and such a soil suspending agent provides effective stain removal performance on other types of stains like greasy stains, e.g., dirty motor oil, spaghetti sauce and even on bleachable stains like tea and/or coffee.

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Background art

EP-A- 112 593 discloses laundry detergent compositions (pH= 6 to 8.5) comprising ethoxylated mono- or diamines, ethoxylated polyamines and/or ethoxylated amine polymers as a clay soil removal/antiredeposition agent. No sorbitan esters are disclosed.

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European patent application number 95870028.8 discloses soaking compositions comprising a sorbitan ester in combination with a high amount of a building and soil suspending system comprising a compound selected from citric

acid or citrates, silicates, zeolites, polycarboxylates phosphates and mixtures thereof. No ethoxylated diamines, ethoxylated polyamines or ethoxylated amine polymers are disclosed.

US 3 755 201 discloses a laundry product with a blue dye stuff, surfactants, a compound selected from the group of builders, fillers, solvents and adjuvants. These compositions may be employed in pre-soaking laundry products. Polyoxyethylene sorbitan monostearate is disclosed. No ethoxylated diamines, ethoxylated polyamines or ethoxylated amine polymers are disclosed.

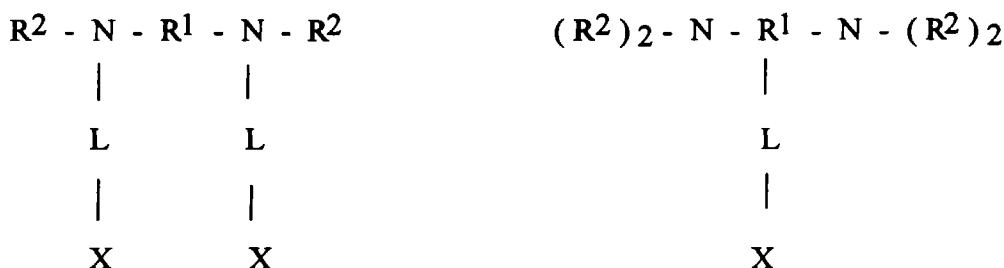
US 3 762 859 discloses laundry detergent compositions comprising surfactants, and particular dyestuff. Sorbitan esters like sorbitan monolaurate, sorbitan mono-oleate and mannitan monopalmitate are disclosed. No ethoxylated diamines, ethoxylated polyamines or ethoxylated amine polymers are disclosed.

Summary of the invention

The present invention encompasses a soaking composition comprising:

- a sorbitan ester according to the formula $C_6H_9O_2(C_2H_4O)_xR_1R_2R_3$, wherein x is an integer of from 0 to 40, R_1 , R_2 are independently OH or $(C_nH_{n+1})COO$, and R_3 is $(C_nH_{n+1})COO$ group, where n is an integer of from 11 to 17; and
- a soil suspending agent selected from the group consisting of:

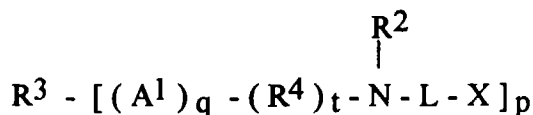
(1) ethoxylated diamines having the formula:



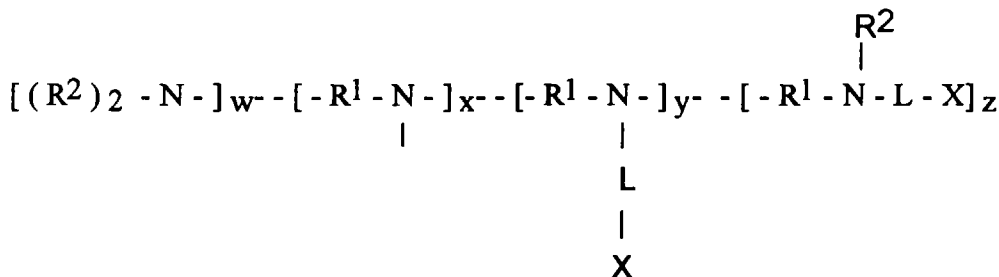
or



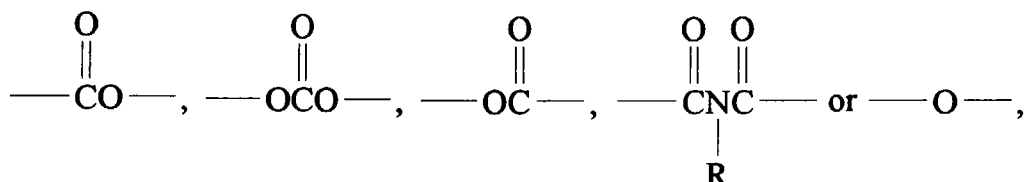
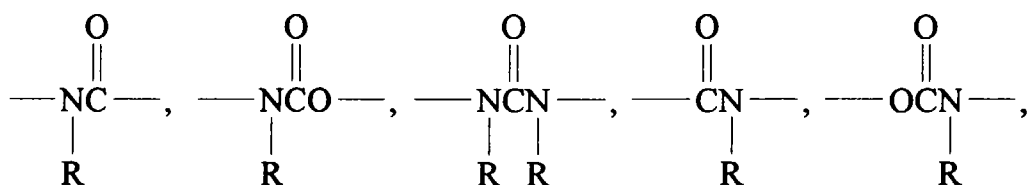
(2) ethoxylated polyamines having the formula:



(3) ethoxylated amine polymers having the general formula:



and (4) mixtures thereof, wherein A¹ is



R is H or C₁-C₄ alkyl or hydroxyalkyl; R¹ is C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to 20 oxyalkylene units provided that no O—N bonds are formed; each R² is C₁-C₄ alkyl or hydroxyalkyl, the moiety —L—X, or two R² together form the moiety —(CH₂)_r—A²—(CH₂)_s—, wherein A² is —O— or —CH₂—, r is 1 or 2, s is 1 or 2, and r+s is 3 or 4; X is a non-ionic group, an anionic group or mixture thereof; R³ is substituted C₃-C₁₂ alkyl, hydroxyalkyl, alkenyl, aryl, or alkaryl group having p substitution sites; R⁴ is C₁-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety have from 2 to 20 oxyalkylene units provided that no O—O or O—N bonds are formed; L is a hydrophilic chain which contains the polyoxyalkylene moiety —[(R⁵O)_m(CH₂CH₂O)_n]—, wherein R⁵ is C₃-C₄ alkylene or hydroxyalkylene and m and n are numbers such that the moiety —(CH₂CH₂O)_n— comprises at least 50% by weight of said polyoxyalkylene moiety; for said diamines, m is from 0 to 3, and n is at least 6 when R¹ is C₂-C₃ alkylene hydroxyalkylene, or alkenylene, and at least 3 when R¹ is other than C₂-C₃ alkylene, hydroxyalkylene or alkenylene; for said polyamines and amine polymers, m is from 0 to 10 and n is at least 3; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1; w is 1 or 0; x + y + z is at least 2; and y + z is at least 2.

The present invention further encompasses a process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition as described herein above, for an effective period of time, then removed from said soaking liquor.

In its broadest aspect the present invention encompasses a process of soaking fabrics, wherein said fabrics are immersed for more than one hour in a soaking liquor comprising water and an effective amount of a composition comprising a soil suspending agent as defined herein, then removed from said soaking liquor.

Detailed Description of the invention

The present invention encompasses a composition and a process of soaking fabrics. The composition, hereinafter referred to as the soaking composition, is used in the soaking process.

A - The composition:

The present invention encompasses a composition which comprises a sorbitan ester, and a soil suspending agent, as defined herein.

The sorbitan ester:

Accordingly, the first essential ingredient of the compositions of the present invention is a sorbitan ester according to the formula C₆H₉O₂(C₂H₄O)_xR₁R₂R₃, wherein x is an integer of from 0 to 40, R₁, R₂ are independently OH or (C_nH_{n+1})COO, and R₃ is (C_nH_{n+1})COO group, where n is an integer of from 11 to 17.

In the preferred compositions herein, x is 0 or 20, and the most preferred compositions herein comprise polyethox-

ylated (20) sorbitan tristearate, i.e. $C_6H_9O_2(C_2H_4O)_{20}(C_{17}H_{35}COO)_3$, or polyethoxylated (20) sorbitan monostearate, i.e. $C_6H_9O_2(C_2H_4O)_{20}(OH)_2(C_{17}H_{35}COO)$, or sorbitan monostearate, i.e. $C_6H_9O_2(OH)_2(C_{17}H_{35}COO)$, or sorbitan monopalmitate, i.e. $C_6H_9O_2(OH)_2(C_{15}H_{31}COO)$, or mixtures thereof.

All these materials are commercially available under several trade names, such as Glycosperse TS 20 from Lonza (polyethoxylated sorbitan tristearate), Glycosperse S 20 from Lonza (polyethoxylated sorbitan monostearate), Radiasurf 7145 from Fina (sorbitan monostearate), Radiasurf 7135 from Fina (sorbitan monopalmitate), Armotan MP from Akzo (sorbitan monopalmitate).

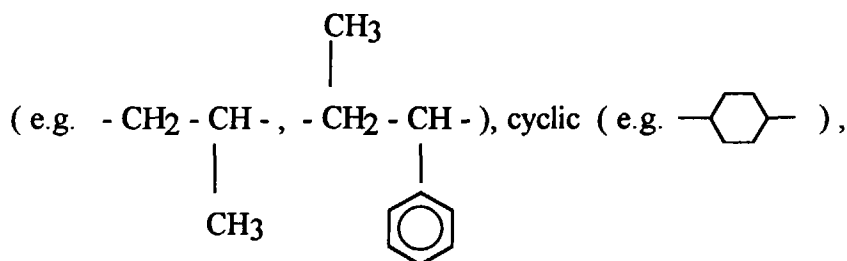
It has further been found that combining ethoxylated sorbitan esters with non-ethoxylated sorbitan esters provides better performance than either kind alone.

In the soaking composition herein, there should be from 0.01% to 10% of said sorbitan ester or mixtures thereof, preferably from 0.01% to 5%, most preferably from 0.5% to 5%.

The soil suspending agent

The second essential ingredient of the compositions of the present invention is a soil suspending agent selected from the group consisting of ethoxylated diamines, ethoxylated polyamines, ethoxylated amine polymers, as previously defined and mixtures thereof. Indeed, the presence of said soil suspending agent contributes to the excellent cleaning benefits of the compositions according to the present invention.

In the preceding formulas of the soil suspending agent used herein, R^1 can be branched



or most preferably linear

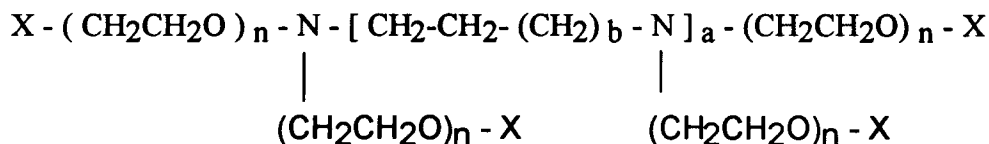
(e.g. $-\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{CH}_2-$)

alkylene, hydroxyalkylene, alkenylene, alkarylene or oxyalkylene. R^1 is preferably C_2 - C_6 alkylene for the ethoxylated diamines and amine polymers. For the ethoxylated diamines, the minimum degree of ethoxylation required for suitable soil removal/anti-redeposition properties decreases on going from C_2 - C_3 alkylene (ethylene, propylene) to hexamethylene. However, for the ethoxylated amine polymers, in particular the ethoxylated polyalkyleneamines and polyalkyleneimines, especially at higher molecular weights, C_2 - C_3 alkylene (ethylene, propylene) are preferred for R^1 with ethylene being most preferred. Each R^2 is preferably the moiety $-\text{L}-\text{X}$.

In the preceding formulas, hydrophilic chain L usually consists entirely of the polyoxyalkylene moiety $-\text{[(R}^5\text{O)}_m(\text{CH}_2\text{CH}_2\text{O)}_n]-$. The moieties $-(\text{R}^5\text{O)}_m-$ and $-(\text{CH}_2\text{CH}_2\text{O)}_n-$ of the polyoxyalkylene moiety can be mixed together or preferably form blocks of $-(\text{R}^5\text{O)}_m-$ and $-(\text{CH}_2\text{CH}_2\text{O)}_n-$ moieties. R^5 is preferably C_3H_7 (propylene). For the ethoxylated polyamines and amine polymers, m is preferably from 0 to 5. For all ethoxylated amines of the present invention, m is most preferably 0, i.e. the polyoxyalkylene moiety consists entirely of the moiety $-(\text{CH}_2\text{CH}_2\text{O)}_n-$. The moiety $-(\text{CH}_2\text{CH}_2\text{O)}_n-$ preferably comprises at least 85% by weight of the polyoxyalkylene moiety and most preferably 100% by weight (m is O).

In the preceding formula, X can be any compatible nonionic group, anionic group or mixture thereof. Suitable non-ionic groups include C_1 - C_4 alkyl or hydroxyalkyl ester or ether groups, preferably acetate or methyl ether, respectively; hydrogen (H); or mixtures thereof. The particularly preferred nonionic group is H. With regard to anionic groups, PO_3^{2-} and SO_3^- are suitable. The particularly preferred anionic group is SO_3^- . It has been found that the percentage of anionic groups relative to nonionic groups can be important to the soil removal/anti-redeposition properties provided by the ethoxylated amine. A mixture of from 0 to 30% anionic groups and from 70 to 100% nonionic groups provides preferred properties. A mixture of from 5 to 10% anionic groups and from 90 to 95% nonionic groups provides the most preferred properties. Usually, a mixture of from 0 to 80% anionic groups and from 20 to 100% nonionic groups provides suitable soil removal/anti-redeposition properties.

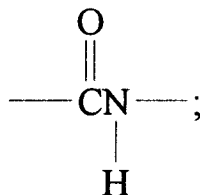
Preferred ethoxylated diamines have the formula:



wherein X and n are defined as before, a is 1 and b is from 0 to 4. For preferred ethoxylated diamines, n is at least 12 with a typical range of from 12 to 42.

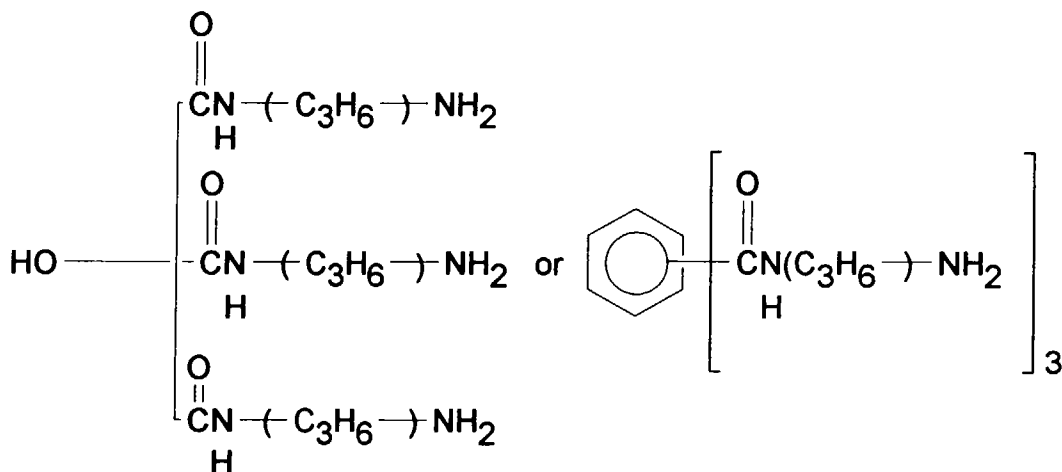
Methods for making ethoxylated diamines are for example described in EP-A-112 593.

In the preceding formula for the ethoxylated polyamines, R³ (linear, branched, or cyclic) is preferably a substituted C₃-C₆ alkyl, hydroxyalkyl or aryl group; A¹ is preferably

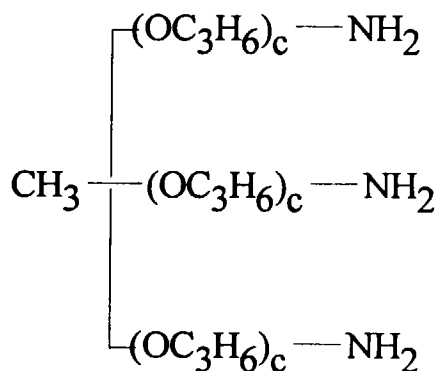


n is preferably at least 12, with a typical range of from 12 to 42; p is preferably from 3 to 6. When R³ is a substituted aryl or alkaryl group, q is preferably 1 and R⁴ is preferably C₂-C₃ alkylene. When R³ is an alkyl, hydroxyalkyl, or alkenyl group, and when q is 0, R¹ is preferably a C₂-C₃ oxyalkylene moiety; when q is 1, R⁴ is preferably C₂-C₃ alkylene.

These ethoxylated polyamines can be derived from polyamino amides such as:

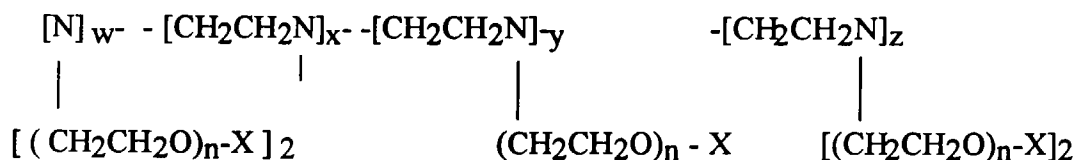


These ethoxylated polyamines can also be derived from polyaminopropyleneoxide derivatives such as:



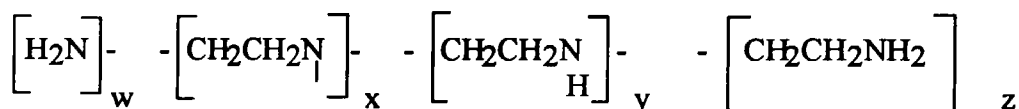
wherein each c is a number from 2 to 20.

Preferred ethoxylated amine polymers are the ethoxylated C₂-C₃ polyalkyleneamines and polyalkyleneimines. Particularly preferred ethoxylated polyalkyleneamines and polyalkyleneimines are the ethoxylated polyethyleneamines (PEA's) and polyethyleneimines (PEI's). These preferred compounds comprise units having the general formula:



wherein X, w, x, y, z and n are defined as before.

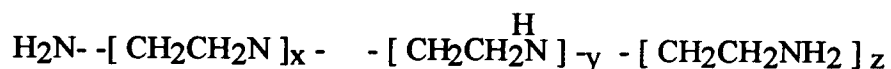
Prior to ethoxylation, the PEAs used in preparing compounds of the present invention have the following general formula:



wherein x + y + z is from 2 to 9, y + z is from 2 to 9 and w is 0 or 1 (molecular weight of from 100 to 400). Each hydrogen atom attached to each nitrogen atom represents an active site for subsequent ethoxylation. For preferred PEAs, y + z is from 3 to 7 (molecular weight of from 140 to 310) and most preferably from 3 to 4 (molecular weight of from 140 to 200). These PEA's can be obtained by reactions involving ammonia and ethylene dichloride, followed by fractional distillation. The common PEA's obtained are triethylenetetramine (TETA) and tetraethylenepentamine (TEPA). Above the pentamines, i.e., the hexamines, heptamines, octamines and possibly nonamines, the cogenerically derived mixture does not appear to separate by distillation and can include other materials such as cyclic amines and particularly piperazines. There can also be present cyclic amines with side chains in which nitrogen atoms appear. See US Patent 2,792,372 to Dickson, issued May 14, 1957, which describes the preparation of PEAs.

The minimum degree of ethoxylation required for preferred soil removal/anti-redeposition performance can vary depending upon the number of units in the PEA. Where y + z is 2 or 3, n is preferably at least about 6. Where y + z is from 4 to 9, suitable benefits are achieved when n is at least 3. For most preferred ethoxylated PEAs, n is at least 12, with a typical range of from 12 to 42.

The PEIs used in preparing the compounds of the present invention have a molecular weight of at least 440 prior to ethoxylation, which represents at least 10 units. Preferred PEIs used in preparing these compounds have a molecular weight of from 600 to 1800. The polymer backbone of these PEIs can be represented by the general formula:



wherein the sum of x, y, and z represents a number of sufficient magnitude to yield a polymer having the molecular weights previously specified. Although linear polymer backbones are possible, branch chains can also occur. The relative proportions of primary, secondary and tertiary amine groups present in the polymer can vary, depending on the manner of preparation. The distribution of amine groups is typically as follows:

- CH ₂ CH ₂ -NH ₂	30%
- CH ₂ CH ₂ -NH-	40%
- CH ₂ CH ₂ -N-	30%

Each hydrogen atom attached to each nitrogen atom of the PEI represents an active site for subsequent ethoxylation. These PEIs can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid or acetic acid. Specific methods for preparing PEIs are disclosed in U.S. Patent 2,182,306 to Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746 to Mayle et al., issued May 8, 1962; US Patent 2,208,095 to Esselmann et al., issued July 16, 1940; US Patent 2,806,839 to Crowther, issued Sept. 17, 1957; and US Patent. 2,553,696 to Wilson, issued May 21, 1951.

As defined in the preceding formulas, n is at least 3 for the ethoxylated PEIs. However, it should be noted that the minimum degree of ethoxylation required for suitable soil removal/anti-redeposition performance can increase as the molecular weight of the PEI increases, especially much beyond 1800. Also, the degree of ethoxylation for preferred compounds increases as the molecular weight of the PEI increases. For PEIs having a molecular weight of at least 600, n is preferably at least 12, with a typical range of from 12 to 42. For PEIs having a molecular weight of at least 1800, n is preferably at least 24, with a typical range of from 24 to 42.

Typically, the compositions according to the present invention comprise from 0.01% to 20% by weight of the total composition of such a soil suspending agent or mixtures thereof, preferably from 0.1% to 15%, more preferably 0.2% to 8% and most preferably from 0.5% to 5%.

Optional ingredients:

As an optional but highly preferred ingredient, the compositions according to the present invention may further comprise an oxygen bleach. Indeed, oxygen bleaches provide a multitude of benefits such as bleaching of stains, deodorization, as well as disinfectancy, and the sorbitan esters according to the present invention have a further particular advantage that they are resistant to oxydation by oxygen beaches. The oxygen bleach in the composition may come from a variety of sources such as hydrogen peroxide or any of the addition compounds of hydrogen peroxide, or organic peroxyacid, or mixtures thereof. By addition compounds of hydrogen peroxide it is meant compounds which are formed by the addition of hydrogen peroxide to a second chemical compound, which may be for example an inorganic salt, urea or organic carboxylate, to provide the addition compound. Examples of the addition compounds of hydrogen peroxide include inorganic perhydrate salts, the compounds hydrogen peroxide forms with organic carboxylates, urea, and compounds in which hydrogen peroxide is clathrated.

Other suitable oxygen bleaches include persulphates, particularly potassium persulphate K₂S₂O₈ and sodium persulphate Na₂S₂O₈. Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate and persulfate salts. The inorganic perhydrate salts are normally the alkali metal salts.

The alkali metal salt of percarbonate, perborate or mixtures thereof, are the preferred inorganic perhydrate salts for use herein. Preferred alkali metal salt of percarbonate is sodium percarbonate.

Soaking compositions in the present invention may comprise from 0.01% to 80% by weight of the total composition of an oxygen bleach or mixtures thereof, preferably from 5% to 45% and more preferably from 10% to 40%.

When the soaking compositions herein comprise an oxygen bleach, it is preferred for them to further comprise bleach activators up to 30% by weight of the total composition. Examples of suitable compounds of this type are dis-

closed in British Patent GB 1 586 769 and GB 2 143 231. Preferred examples of such compounds are tetracetyl ethylene diamine, (TAED), sodium 3, 5, 5 trimethyl hexanoyloxybenzene sulphonate, diperoxy dodecanoic acid as described for instance in US 4 818 425 and nonylamide of peroxyadipic acid as described for instance in US 4 259 201 and n-nonanoyloxybenzenesulphonate (NOBS), and acetyl triethyl citrate (ATC) such as described in European patent application 91870207.7. Also particularly preferred are N-acyl caprolactam selected from the group consisting of substituted or unsubstituted benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, hexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, formyl caprolactam, acetyl caprolactam, propanoyl caprolactam, butanoyl caprolactam pentanoyl caprolactam. The soaking compositions herein may comprise mixtures of said bleach activators.

Preferred mixtures of bleach activators herein comprise n-nonanoyloxybenzenesulphonate (NOBS) together with a second bleach activator having a low tendency to generate diacyl peroxide, but which delivers mainly peracid. Said second bleach activators may include tetracetyl ethylene diamine (TAED), acetyl triethyl citrate (ATC), acetyl caprolactam, benzoyl caprolactam and the like, or mixtures thereof. Indeed, it has been found that mixtures of bleach activators comprising n-nonanoyloxybenzenesulphonate and said second bleach activators, allow to boost particulate soil cleaning performance while exhibiting at the same time good performance on diacyl peroxide sensitive soil (e.g., beta-carotene) and on peracid sensitive soil (e.g., body soils).

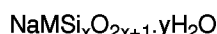
Accordingly, the soaking compositions herein may comprise from 0% to 15% by weight of the total composition of n-nonanoyloxybenzenesulphonate, preferably from 1% to 10% and more preferably from 3% to 7% and from 0% to 15% by weight of the total composition of said second bleach activator preferably from 1% to 10% and more preferably from 3% to 7%.

The compositions herein may comprise an acidifying system amongst the preferred optional ingredients. The purpose of said acidifying system is to control the alkalinity generated by the source of available oxygen and any alkaline compounds present in the wash solution. Said system comprises anhydrous acidifying agent, or mixtures thereof, which needs to be incorporated in the product in an anhydrous form, and to have a good stability in oxidizing environment. Suitable anhydrous acidifying agents for use herein are carboxylic acids such as citric acid, adipic acid, glutaric acid, 3 chetoglutaric acid, citramalic acid, tartaric acid and maleic acid or their salts or mixtures thereof. Other suitable acidifying agents include sodium bicarbonate, sodium sesquicarbonate and silicic acid. Highly preferred acidifying systems to be used herein comprise citric acid and/or sodium citrate. Indeed, citric acid can be used in its acidic form or in the form of its salts (mono-, di-, tri-salts) and in all its anhydrous and hydrated forms, or mixtures thereof. It may additionally act as a builder and a chelant, and it is biodegradable. The compositions according to the present invention comprise from up to 20% by weight of the total composition of anhydrous citric acid, preferably from 5% to 15%, most preferably about 10%.

The compositions herein may comprise an alkali metal salt of silicate, or mixtures thereof, amongst the preferred optional ingredients. Preferred alkali metal salt of silicate to be used herein is sodium silicate. In the preferred embodiment herein wherein the soaking compositions comprise an oxygen bleach, it has been found that the decomposition of available oxygen produced in the soaking liquors upon dissolution of the soaking compositions is reduced by the presence of at least 40 parts per million of sodium silicate in said soaking liquors.

Any type of alkali metal salt of silicate can be used herein, including the crystalline forms as well as the amorphous forms of said alkali metal salt of silicate or mixtures thereof.

Suitable crystalline forms of sodium silicate to be used are the crystalline layered silicates of the granular formula



wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20, or mixtures thereof. Crystalline layered sodium silicates of this type are disclosed in EP-A-164 514 and methods for their preparation are disclosed in DE-A-34 17 649 and DE-A-37 42 043. For the purposes of the present invention, x in the general formula above has a value of 2, 3 or 4 and is preferably 2. More preferably M is sodium and y is 0 and preferred examples of this formula comprise the a, b, g and d forms of $\text{Na}_2\text{Si}_2\text{O}_5$. These materials are available from Hoechst AG FRG as respectively NaSKS-5, NaSKS-7, NaSKS-11 and NaSKS-6. The most preferred material is d- $\text{Na}_2\text{Si}_2\text{O}_5$, NaSKS-6. Crystalline layered silicates are incorporated in soaking compositions herein, either as dry mixed solids, or as solid components of agglomerates with other components.

Suitable amorphous forms of sodium silicate to be used herein have the following general formula:

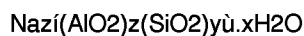


wherein M is sodium or hydrogen and x is a number from 1.9 to 4, or mixtures thereof. Preferred to be used herein are the amorphous forms of $\text{Si}_2\text{O}_5\text{Na}_2\text{O}$.

Suitable Zeolites for use herein are aluminosilicates including those having the empirical formula:

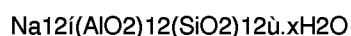


wherein M is sodium, potassium, ammonium or substituted ammonium, z is from about 0.5 to about 2; and y is 1; this material having a magnesium ion exchange capacity of at least about 50 milligram equivalents of CaCO₃ hardness per gram of anhydrous aluminosilicate. Preferred zeolites which have the formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

Useful materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from 20 to 30, especially about 27. This material is known as Zeolite A. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

Typically, the compositions herein may comprise from 0.5% to 15% by weight of the total composition of an alkali metal salt of silicate or mixtures thereof, preferably from 1% to 10% and more preferably from 2% to 7%.

The composition herein may also comprise a builder amongst the preferred optional ingredients. All builders known to those skilled in the art may be used herein. Suitable phosphate builders for use herein include sodium and potassium triphosphate, pyrophosphate, polymeric metaphosphate having a degree of polymerization of from about 6 to 21, and orthophosphate. Other phosphorus builder compounds are disclosed in U.S. Pat. Nos. 3,159,581; 3,213,030; 3,422,021; 3,422,137; 3,400,176 and 3,400,148, incorporated herein by reference.

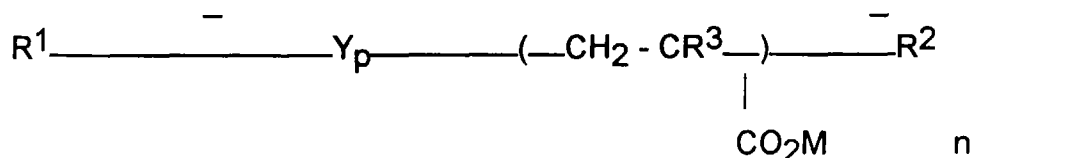
Suitable polycarboxylate builders for use herein include ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, 1,3,5-trihydroxy benzene-2,4,6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in European Patent Application 86200690.5/0,200,263, published November 5, 1986.

Other suitable polycarboxylate builders are disclosed in U.S. Patent 4,144,226, Crutchfield et al, issued March 13, 1979 and in U.S. Patent 3,308,067, Diehl, issued March 7, 1967. See also Diehl U.S. Patent 3,723,322.

Other suitable polycarboxylate builders for use herein include builders according to formula I



wherein Y is a comonomer or comonomer mixture; R¹ and R² are bleach- and alkali-stable polymer-end groups; R³ is H, OH or C₁₋₄ alkyl; M is H, alkali metal, alkaline earth metal, ammonium or substituted ammonium; p is from 0 to 2; and n is at least 10, or mixtures thereof.

Preferred polymers for use herein fall into two categories. The first category belongs to the class of copolymeric polymers which are formed from an unsaturated polycarboxylic acid such as maleic acid, citraconic acid, itaconic acid, mesaconic acid and salts thereof as first monomer, and an unsaturated monocarboxylic acid such as acrylic acid or an alpha-C₁₋₄ alkyl acrylic acid as second monomer. Referring to formula I hereinabove, the polymers belonging to said first class are those where p is not 0 and Y is selected from the acids listed hereinabove. Preferred polymers of this class are those according to formula I hereinabove, where Y is maleic acid. Also, in a preferred embodiment, R³ and M are H, and n is such that the polymers have a molecular weight of from 1000 to 400 000 atomic mass units.

The second category of preferred polymers for use herein belongs to the class of polymers in which, referring to formula I hereinabove, p is 0 and R³ is H or C₁₋₄ alkyl. In a preferred embodiment n is such that the polymers have a molecular weight of from 1000 to 400 000 atomic mass units. In a highly preferred embodiment, R³ and M are H.

The alkali-stable polymer end groups R¹ and R² in formula I hereinabove suitably include alkyl groups, oxyalkyl groups and alkyl carboxylic acid groups and salts and esters thereof.

In the above, n, the degree of polymerization of the polymer can be determined from the weight average polymer molecular weight by dividing the latter by the average monomer molecular weight. Thus, for a maleic-acrylic copolymer having a weight average molecular weight of 15,500 and comprising 30 mole % of maleic acid derived units, n is 182 (i.e. $15,500 / (116 \times 0.3 + 72 \times 0.7)$).

Temperature-controlled columns at 40°C against sodium polystyrene sulphonate polymer standards, available from Polymer Laboratories Ltd., Shropshire, UK, the polymer standards being 0.15M sodium dihydrogen phosphate and 0.02M tetramethyl ammonium hydroxide at pH 7.0 in 80/20 water/acetonitrile.

Of all the above, highly preferred polymers for use herein are those of the first category in which n averages from 100 to 800, preferably from 120 to 400.

Preferred builders for use herein are polymers of maleic or acrylic acid, or copolymers of maleic and acrylic acid.

Typically, the compositions of the present invention comprise up to 50% by weight of the total composition of a builder or mixtures thereof, preferably from 0.1% to 20% and more preferably from 0.5 to 11%.

When the soaking compositions herein comprise an oxygen bleach, it may be desirable for them to further comprise chelating agents which help to control the level of free heavy metal ions in the soaking liquors, thus avoiding rapid decomposition of the oxygen released by said source of available oxygen. Suitable amino carboxylate chelating agents which may be used herein include diethylene triamino pentacetic acid, ethylenediamine tetraacetates (EDTA), N-hydroxyethylethylenediamine triacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraamine hexaacetates, and ethanoldiglycines, alkali metal ammonium and substituted ammonium salts thereof or mixtures thereof. Further suitable chelating agents include ethylenediamine-N,N'-disuccinic acids (EDDS) or alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof. Particularly suitable EDDS compounds are the free acid form and the sodium or magnesium salt or complex thereof. Also others suitable chelating agents may be the organic phosphonates, including 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 in the form of their metal alkali salt. Preferably, the organic phosphonate compounds where present are in the form of their magnesium salt.

The soaking compositions in the present invention may accordingly comprise from 0% to 5% by weight of the total compositions of said chelating agents, preferably from 0% to 3%, more preferably from 0.05% to 2%.

The compositions herein may further comprise a filler like inorganic filler salts such as alkali metal carbonates, bicarbonates and sulphates. Such fillers for instance sodium bicarbonate, may also act as acidifying agent as described herein after. Accordingly, sodium bicarbonate and sodium sulphate are the preferred filler materials for use herein.

Typically, the compositions of the present invention comprise up to 50% by weight of the total composition of a filler or mixtures thereof, preferably from 0.1% to 20% and more preferably from 0.5 % to 10%

Soaking compositions in the present invention may further comprise other optional ingredients such as surfactants, optical brighteners, enzymes, other chelants, dispersants, soil release agents, photoactivated bleaches such as Zn phthalocyanine sulphonate, dyes, dye transfer inhibitors, pigments, perfumes and the like. Said optional ingredients can be added in varying amounts as desired.

The compositions herein can be manufactured in solid, preferably granular, or even in liquid form.

B - The process:

The present invention encompasses processes of soaking fabrics. Indeed, the present invention encompasses a process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective

amount of a composition as described hereinbefore, for an effective period of time, then removed from said soaking liquor.

As used herein, the expression "process of soaking fabrics" refers to the action of leaving fabrics to soak in a soaking liquor comprising water and a composition as described hereinabove, for a period of time sufficient to clean said fabrics. In contrast to typical laundering operation using a washing machine, the soaking process herein allows prolonged contact time between the fabrics and the soaking liquor, typically up to 24 hours. The soaking process can be performed independently from any other process, such as a typical laundering operation, or a first step before a second, typical laundering step. In the preferred soaking processes of the invention, fabrics are left to soak for a period of time ranging from 10 minutes to 24 hours, preferably from 30 min to 24 hours, more preferably more than 1 hour to 24 hours, even more preferably 2 hours to 24 hours, and most preferably 4 hours to 24 hours. After the fabrics have been immersed in said soaking liquor for a sufficient period of time, they can be removed and rinsed with water. The fabrics can also be washed in a normal laundering operation after they have been soaked, with or without having been rinsed inbetween the soaking operation and the subsequent laundering operation.

In the soaking process herein, a soaking composition described hereinabove is diluted in an appropriate amount of water to produce a soaking liquor. Suitable doses may range from 45 to 50 grams of soaking composition in 3.5 to 5 liters of water, down to 90 to 100 grams of soaking composition in 20 to 45 liters of water. Typically one dose is 45-50 grams in 3.5 to 5 liters for a concentrated soak (bucket/sink). For washing machine soaked, the dose is 90-100 grams in about 20 (Europe) to 45 (US) liters of water. The fabrics to be soaked are then immersed in the soaking liquor for an appropriate period of time. There are factors which may influence overall performance of the process on particulate dirt/soils. Such factors include prolonged soaking time. Indeed, the longer fabrics are soaked, the better the end results. Ideally, soaking time is overnight, i.e., 8 hours up to 24 hours, preferably 12 hours to 24 hours. Another factor is the initial warm or lukewarm temperature. Indeed, higher initial temperatures of the soaking liquors ensure large benefits in performance.

The process herein is suitable for cleaning a variety of fabrics, but finds a preferred application in the soaking of socks, which are particularly exposed to silt and clay pick-up.

In its broadest embodiment the present invention also encompasses a process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition comprising a soil suspending agent selected from the group consisting of ethoxylated diamines, ethoxylated polyamines, ethoxylated amine polymers and mixtures thereof as defined herein, for more than 1 hour, preferably 2 hours to 24 hours, and more preferably 4 hours to 24 hours, then removed from said soaking liquor. Indeed, it has been found that when adding such a soil suspending agent, in a soaking composition, improved particulate soil removal and/or improved enzymatic stain removal is obtained.

The stain removal performance test method:

The stain removal performance of a given composition on a soiled fabric under soaking conditions, may be evaluated by the following test method. Soaking liquors are formed by diluting for instance 45 g of the soaking compositions herein in 3.78 liter of water or 90g of the soaking composition in 45 liters of water. Fabrics are then immersed in the resulting soaking liquor for a time ranging from more than 1 hour to 18 hours. Finally, the fabrics are removed from the soaking liquors, rinsed with water and washed with a regular washing process, handwash or washing machine wash, with a regular detergent, with or without re-using the soaking liquor, then said fabrics are left to dry.

For example, typical soiled fabrics to be used in this stain removal performance test 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, blood on two different substrates: cotton (CW120) and polycotton (PCW28).

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 soil suspending agent 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.

The following examples will further illustrate the present invention.

Examples

The following compositions are prepared by mixing the listed ingredients in the listed proportions.

EP 0 832 968 A1

Ingredients	1 (%w/w)	2 (%w/w)	3 (%w/w)
Sorbitan mono-stearate (SMS)	0.5	0.5	0
Citric acid	11	11	8
NOBS	12	12	12
Polyacrylate (Acusol 445ND)	11	11	11
Sodium percarbonate	31	31	31
Ethoxylated 15-18 tetraethylenepentamine	1.0	2.0	2.0
NOBS	12	12	10
Anionic (LAS/AS/AES)	8	8	8
DTPA	0.2	0.2	0.2
Minors and inerts	up to 100	up to 100	up to 100

Ingredients	4 (%w/w)	5 (%w/w)	6 (%w/w)
Sorbitan mono-stearate (SMS)	2.50	0	0
Sorbitan monostearate EO 20 (SMS EO 20)	0	3.00	0
Sorbitan tristearate EO 20 (STS EO 20)	0.50	0	3.00
Citric acid	10	10	10
Ethoxylated 15-18 tetraethylenepentamine	1.0	2.0	2.0
Polyacrylate (Acusol 445 ND)	11	11	11
Silicate (amorphous; 1.6r)	0.4	0.4	0.4
Sodium perborate monohydrate	27	-	0
Sodium percarbonate	-	31	31
Sodium sulphate	24	24	24
NOBS	6	6	6
TAED	5	5	5
Anionic (LAS/AS/AES)	7	7	7
Others, inerts and minors	up to 100	up to 100	up to 100

Ingredients	7 (%w/w)	8 (%w/w)	9 (%w/w)
Sorbitan mono-stearate (SMS)	0.50	0.50	0.5
Citric acid	10	10	10
Polyacrylate (Acusol 445 ND)	11	11	11
Silicate (amorphous; 1.6r)	0.4	0.4	0.4
Ethoxylated 15-18 tetraethylenepentamine	-	5.0	-
Ethoxylated 15-18 polyethylenamine	5.0	-	-
Ethoxylated 15-18 ethylenediamine	-	-	5.0
Sodium perborate monohydrate	0	0	0
Sodium percarbonate	31	31	31
Sodium sulphate	24	24	24
NOBS	6	0	6
TAED	5	11	5
Anionic (LAS/AS/AES)	8	8	8
Others, inerts and minors	up to 100	up to 100	up to 100

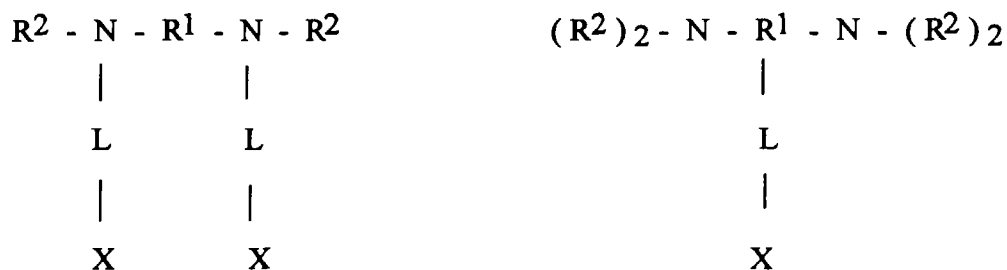
Soaking liquors are formed by diluting each time 45 g of the above compositions in between 3.5 lit. to 5.0 lit. of water. 0.5 to 2 Kg of fabrics are then each time immersed in said soaking liquor for a time ranging from 10 minutes to 24 hours. For the soaking liquor comprising composition 3 described hereinbefore, the soaking time according to the process of soaking of the present invention is of more than 1 hour and preferably 4 to 24 hours. Finally, the fabrics are removed from the soaking liquors, rinsed with water and washed with a regular washing process, handwash or washing machine wash, with a regular detergent, with or without re-using the soaking liquor, then said fabrics are left to dry. Excellent stain removal performance is obtained with these compositions on various stains including mud/clay stains, enzymatic stains, greasy stains, bleachable stains and the like.

Claims

1. A soaking composition comprising:

- a sorbitan ester according to the formula $C_6H_9O_2(C_2H_4O)_xR_1R_2R_3$, wherein x is an integer of from 0 to 40, R_1 , R_2 are independently OH or $(C_nH_{n+1})COO$, and R_3 is $(C_nH_{n+1})COO$ group, where n is an integer of from 11 to 17; and
- a soil suspending agent selected from the group consisting of

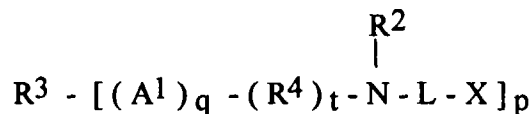
(1) ethoxylated diamines having the formula:



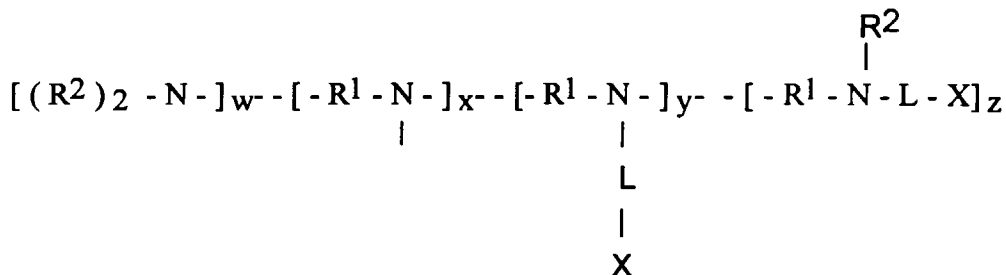
or



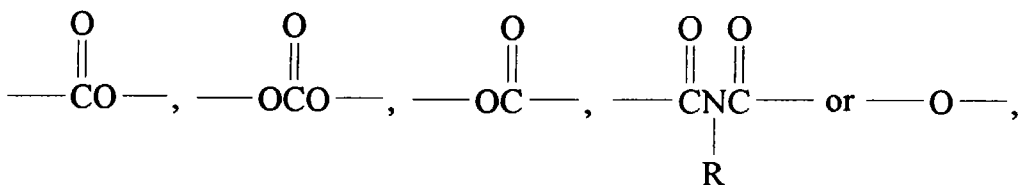
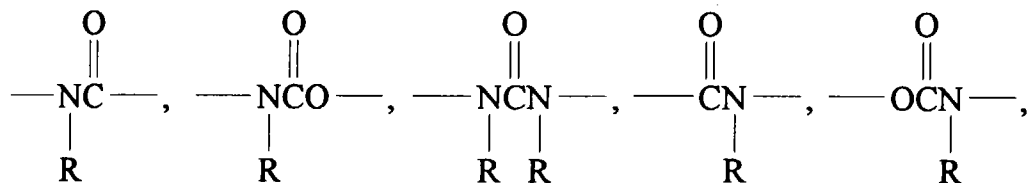
(2) ethoxylated polyamines having the formula:



(3) ethoxylated amine polymers having the general formula:



and (4) mixtures thereof, wherein A^1 is



R is H or C₁-C₄ alkyl or hydroxyalkyl; R¹ is C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to 20 oxyalkylene units provided that no O—N bonds are formed; each R² is C₁-C₄ alkyl or hydroxyalkyl, the moiety —L—X, or two R² together form the moiety —(CH₂)_r—A²—(CH₂)_s—, wherein A² is —O— or —CH₂—, r is 1 or 2, s is 1 or 2, and r+s is 3 or 4; X is a nonionic group, an anionic group or mixture thereof; R³ is substituted C₃-C₁₂ alkyl, hydroxyalkyl, alkenyl, aryl, or alkaryl group having p substitution sites; R⁴ is C₁-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety have from 2 to 20 oxyalkylene units provided that no O—O or O—N bonds are formed; L is a hydrophilic chain which contains the polyoxyalkylene moiety —[(R⁵O)_m(CH₂CH₂O)_n]—, wherein R⁵ is C₃-C₄ alkylene or hydroxyalkylene and m and n are numbers such that the moiety —(CH₂CH₂O)_n— comprises at least 50% by weight of said polyoxyalkylene moiety; for said diamines, m is from 0 to 3, and n is at least 6 when R¹ is C₂-C₃ alkylene hydroxyalkylene, or alkenylene, and at least 3 when R¹ is other than C₂-C₃ alkylene, hydroxyalkylene or alkenylene; for said polyamines and amine polymers, m is from 0 to 10 and n is at least 3; p is from 3 to 8; q is 1 or 0; t is 1 or

0, provided that t is 1 when q is 1; w is 1 or 0; x + y + z is at least 2; and y + z is at least 2, said composition being formulated either as an emulsion or a microemulsion.

2. A composition according to claim 1 wherein said soil suspending agent is an ethoxylated amine polymer wherein R¹ is C2-C3 alkylene, preferably ethylene, wherein L consists entirely of the moiety $-(CH_2CH_2O)_n-$ and n is of at least 12.
3. A composition according to claim 2 wherein said ethoxylated amine polymer is an ethoxylated polyethylenamine having a molecular weight of from 140 to 310 prior to ethoxylation.
4. A composition according to any of the preceding claims wherein said soil suspending agent is ethoxylated 15-18 tetraethylenepentamine.
5. A composition according to claim 2 wherein said ethoxylated amine polymer is an ethoxylated polyethyleneimine having a molecular weight of from 600 to 1800 prior to ethoxylation.
6. A composition according to any of the preceding claims which comprises from 0.01% to 20% by weight of the total composition of said soil suspending agent, or mixtures thereof, preferably from 0.1% to 10%, more preferably from 0.2% to 4%, and most preferably from 0.5% to 2%.
7. A composition according to any of the preceding claims where said sorbitan ester is polyethoxylated (20) sorbitan tristearate, or polyethoxylated (20) sorbitan monostearate, or sorbitan monostearate, or sorbitan monopalmitate, or mixtures thereof.
8. A composition according to any of the preceding claims which comprises a non-ethoxylated sorbitan ester and an ethoxylated sorbitan ester.
9. A composition according to any of the preceding claims which comprises from 0.01% to 10% of said sorbitan ester or mixtures thereof, preferably from 0.01% to 5%, and most preferably from 0.5% to 5%.
10. A composition according to any of the preceding claims which further comprises at least one optional ingredient selected from the group consisting of acidifying agents, alkali metal salt of silicate, builders, soils suspending polyamine polymers, fillers, surfactants, optical brighteners, enzymes, chelating agents, dispersants, soil release agents, dyes, dye transfer inhibitors, pigments, perfumes and mixtures thereof.
11. A composition according to any of the preceding claims which further comprises an oxygen bleach at a level of from 0.01% to 80% by weight of the total composition, preferably from 5% to 45% and more preferably from 10% to 40%.
12. A composition according to claim 11 which comprises an activator for said bleach up to a level of 30% by weight of the total composition.
13. A process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition according to any of the preceding claims, for an effective period of time, then removed from said soaking liquor.
14. A process according to claim 13 wherein said time ranges from 10 minutes to 24 hours, preferably 30 minutes to 24 hours, more preferably more than 1 hour up to 24 hours and most preferably 4 hours to 24 hours.
15. A process of soaking fabrics, wherein said fabrics are immersed in a soaking liquor comprising water and an effective amount of a composition comprising a soil suspending agent selected from the group consisting of

(1) ethoxylated diamines having the formula:



|

L

|

X

|

L

|

X



|

L

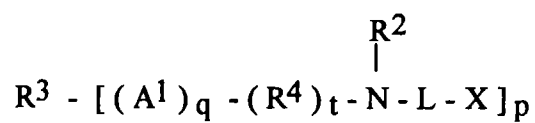
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X

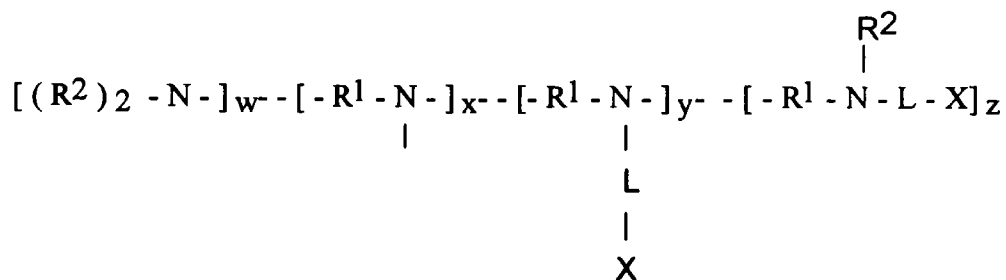
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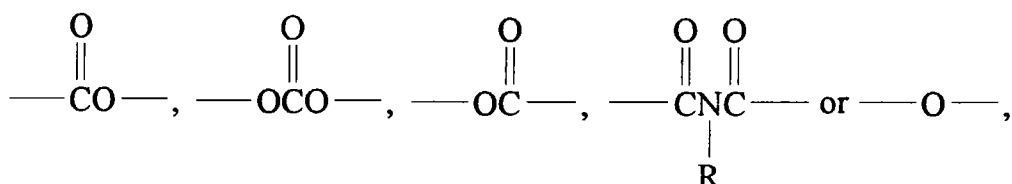
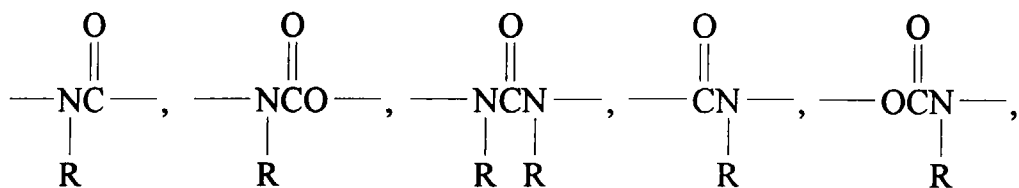


(2) ethoxylated polyamines having the formula:



(3) ethoxylated amine polymers having the general formula:

and (4) mixtures thereof,
wherein A¹ is



R is H or C₁-C₄ alkyl or hydroxyalkyl; R¹ is C₂-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety having from 2 to 20 oxyalkylene units provided that no O—N bonds are formed; each R² is C₁-C₄ alkyl or hydroxyalkyl, the moiety —L—X, or two R² together form the moiety —(CH₂)_r—A²—(CH₂)_s—, wherein A² is —O— or —CH₂—, r is 1 or 2, s is 1 or 2, and r+s is 3 or 4; X is a non-ionic group, an anionic group or mixture thereof; R³ is substituted C₃-C₁₂ alkyl, hydroxyalkyl, alkenyl, aryl, or alkaryl group having p substitution sites; R⁴ is C₁-C₁₂ alkylene, hydroxyalkylene, alkenylene, arylene or alkarylene, or a C₂-C₃ oxyalkylene moiety have from 2 to 20 oxyalkylene units provided that no O—O or O—N bonds are formed; L is a hydrophilic chain which contains the polyoxyalkylene moiety —[(R⁵O)_m(CH₂CH₂O)_n]—, wherein R⁵ is C₃-C₄ alkylene or hydroxyalkylene and m and n are numbers such that the moiety —(CH₂CH₂O)_n— comprises at least 50% by weight of said polyoxyalkylene moiety; for said diamines, m is from 0 to 3, and n is at least 6 when R¹ is C₂-C₃ alkylene hydroxyalkylene, or alkenylene, and at least 3 when R¹ is other than C₂-C₃ alkylene, hydroxyalkylene or alkenylene; for said polyamines and amine polymers, m is from 0 to 10 and n is at least 3; p is from 3 to 8; q is 1 or 0; t is 1 or 0, provided that t is 1 when q is 1; w is 1 or 0; x + y + z is at least 2; and y + z is at least 2, for more than 1 hour, preferably 2 hours to 24 hours, and more preferably 4 hours to 24 hours, then removed from said soaking liquor.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 87 0124

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)
A	US 3 676 341 A (GERECHT JOHN FRED ET AL) * column 4, line 64; claims * ---	1,6,7, 10-12	C11D3/37 C11D3/00 C11D1/66
A	FR 2 311 884 A (PROCTER & GAMBLE) * page 10 - page 14 * * claims * ---	1,6,7, 10-12	
A	WO 95 32272 A (PROCTER & GAMBLE) * page 2, line 18 - line 20 * * claims 1,2,10 * * page 4, line 10 - line 34 * * page 5 - page 7 * ---	1-6, 10-12	
A	EP 0 206 513 A (PROCTER & GAMBLE ET AL.) * claims * -----	1-6, 10-12	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 7 February 1997	Examiner Pelli Wablat, B
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