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(54) **Pretreatment compositions**

(57) The present invention relates to pretreater or laundry additive compositions which removes stains and as a laundry additive, whiten fabrics. The compositions contain 0.1 to 20 wt. % of a nonionic surfactant, 0.1% to 10 wt. % of a hydrophobically modified polymer and less than about 5 wt. % of an anionic soap. Methods of using the composition are also described.

Description

Field of the Invention

5   This invention relates to a laundry pretreatment composition in either a liquid, gel or stick form which contains a hydrophobically modified polar polymer and nonionic surfactants. These can be used to effect or enhance stain removal in lieu of or in advance of, the main wash. The liquid and gel compositions may also be used as laundry additives to boost whitening effects and improve stain removal in the wash.

10   Background of the Invention

Prewash stain remover compositions for the laundry have been in use for many years. Recently developed pre-treater compositions available in liquid, spray and gel forms are usually based on nonionic surfactants. The consumer applies the stain remover to the soiled portions of the garments before washing with a laundry detergent. The ingredients
15   in the prewash stain remover or in-wash whitener/stain remover work to remove stains, but either high levels of costly ingredients are required or a plateau in stain removal is observed with increasing concentration of the ingredient. A convenient application method for a pretreatment composition is by the stick form. So-called stick forms essentially comprise the composition in the form of a block (often bar-or-stick shaped or cylindrical in shape), which block is solid or else has the consistency of soap or hard wax. As used herein, the terms "stick", "stick form", stick composition" etc.
20   are to be construed as referring to pretreatment compositions having such a physical consistency. Stick compositions are conveniently sold often in a dispensing holder. It is difficult to produce stick forms which have optimal hardness to effectively deliver the pretreater compositions.

Stick form versions of such pretreaters are generally aqueous based rather than solvent based and contain both nonionic surfactants and anionic soaps such aqueous based systems, while exhibiting proper hardness characteristics,
25   often compromise cleaning performance (see U. S. No. 5,147,576 owned by S.C. Johnson.)

It has now been found that inclusion of hydrophobically modified polar polymers helps to significantly enhance the stain removal performance of the prewash stain remover. Similar compositions may also be used as in wash laundry additives to boost whitening effects and improve stain removal. It has also now been found that such formulations containing hydrophobically modified polar polymers when used in conjunction with a detergent significantly boosts
30   whitening and improve stain removal.

Deflocculating polymers which allow incorporation of more surfactants and/or electrolytes in a detergent composition are described in U.S. Patent No. 5,147,576 issued to Montague.

The polymers of the Montague reference comprise a hydrophilic backbone which is generally a linear branched or highly cross-linked molecular composition containing one or more types of hydrophilic monomer units; and hydro-
35   phobic side chains, for example, selected from the group consisting of siloxanes, saturated or unsaturated alkyl and hydrophobic alkoxy groups, aryl and alkylarlyl groups, and mixtures thereof.

These polymers were not, however, taught for use in pretreater or in-wash laundry boosting compositions which are designed for direct application to stains or for boosting the performance of detergents, respectively, and require compositions which are significantly different from detergents. These compositions are preferably based on nonionic
40   aqueous solutions.

Although U.S. Patent No. 5,308,530 does teach the use of these polymers in detergent formulas there is no suggestion or discussion that such combinations would provide improved pretreater or laundry additive compositions.

Thus, there still exists a need in the art for a stable pretreater compositions based on non-ionic surfactants for improved cleaning performance on stains. This improvement is effected by the present invention incorporating hydro-
45   phobically modified polar polymers which enable the composition to penetrate both oil and water based stains for improved cleaning performance.

It is therefore an object of the present invention to provide an aqueous laundry stain pretreater composition which provides outstanding cleaning performance on a variety of stains for a variety of fabrics.

Another object of the invention is to provide an aqueous nonionic based composition which boosts the fluorescer
50   whitening of detergents without added fluorescer and improves stain removal.

Another object of the invention is to provide a stick pretreater composition which has an effective hardness profile, is shelf stable and which is free of chelating agents yet does not compromise cleaning performance.

Summary of the Invention
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Thus, a first aspect of the present invention now provides a pretreatment composition comprising

(a) from 0.1 to 80% by weight of nonionic surfactant;

(b) from 0 to 20% by weight of an anionic soap; and
(c) from 0.1% to 10% by weight of a polymer having:

1) a hydrophilic backbone comprising one or more monomer units selected from:

i) one or more ethylenically unsaturated hydrophilic monomers selected from the group consisting of unsaturated C_{1-6} acids, ethers, alcohols, aldehydes, ketones or esters; and/or
ii) one or more polymerizable hydrophilic cyclic monomer units; and/or
iii) one or more non-ethylenically unsaturated polymerizable hydrophilic monomers selected from the group consisting of glycerol and other polyhydric alcohols;
wherein said monomer units are independently optionally substituted with one or more amino, amine, amide, sulphonate, sulphate, phosphonate, hydroxy, carboxyl or oxide groups; and

2) at least one monomer containing a pendant hydrophobic group and optionally also, a pendant hydrophilic group;

said polymer having a MW of 1,000 to 20,000;
wherein the molar ratio of backbone hydrophilic group to pendant hydrophobic group is less than 40, preferably 30, most preferably 20.

Liquid, paste and gel compositions of the invention achieve the aforementioned and other objects of the invention by virtue of containing from about 0.1 to about 20%, more preferably 10% by wt of a hydrophobically modified polar polymer which has a hydrophilic backbone (hydrophilic backbone made of one monomer only, e.g., acrylate) wherein there is a critical molar ratio of hydrophilic groups (e.g., the backbone) to hydrophobic "anchors" attached ("tail") to the backbone and about 0.1 to about 20% of a nonionic surfactant.

Thus, a second aspect of the present invention provides an aqueous pretreatment composition, preferably in liquid, paste or gel form which comprise from 0.1 to 20% by weight of nonionic surfactant, from 0 to 5% by weight of anionic soap and from 0.1 to 10% by weight of polymer having:-

1) a hydrophilic backbone comprising one or more monomer units selected from:

i) one or more ethylenically unsaturated hydrophilic monomers selected from the group consisting of unsaturated C_{1-6} acids, ethers, alcohols, aldehydes, ketones or esters; and/or
ii) one or more polymerizable hydrophilic cyclic monomer units; and/or
iii) one or more non-ethylenically unsaturated polymerizable hydrophilic monomers selected from the group consisting of glycerol and other polyhydric alcohols;

wherein said monomer units are independently substituted with one or more amino, amine amide, sulphonate, sulphate, phosphonate, hydroxy, carboxyl or oxide groups; and
2) a tail comprising a monomer comprising a pendant hydrophobic group and optionally also a pendant hydrophilic group;

said polymer having a MW of 1,000 to 20,000;
wherein the molar ratio of backbone hydrophilic group to pendant hydrophobic group is less than 20.

Stick compositions of the invention achieve the aforementioned and other objects by virtue of containing from about 0.1 to about 10% by wt. of a hydrophobically modified polar polymer which has a hydrophilic backbone (hydrophilic backbone made of one monomer only, e.g., acrylate) wherein there is a critical molar ratio of hydrophilic groups (e.g., the backbone) to hydrophobic "anchors" attached ("tail") to the backbone, and about 30 wt. % to about 80 wt. % of a nonionic surfactant, and from about 5 wt. % to about 20 wt. % of an anionic soap.

Thus, a third aspect of the present invention provides a stick pretreatment composition comprising from 30% to 80% by weight of nonionic surfactant, from 1 to 20% by weight of anionic soap and from 0. 1 to 10% by weight of a polymer having:

1) a hydrophilic backbone comprising one or more monomer units selected from:

i) one or more ethylenically unsaturated hydrophilic monomers selected from the group consisting of unsaturated C_{1-6} acids, ethers, alcohols, aldehydes, ketones or esters; and/or
ii) one or more polymerizable hydrophilic cyclic monomer units; and/or
iii) one or more non-ethylenically unsaturated polymerizable hydrophilic monomers selected from the group consisting of glycerol and other polyhydric alcohols;

wherein said monomer units are independently substituted with one or more amino, amine amide, sulphonate, sulphate, phosphonate, hydroxy, carboxyl or oxide groups; and

2) a tail comprising a monomer comprising a pendant hydrophobic group and optionally also a pendant hydrophilic group;

said polymer having a MW of 1,000 to 20,000;
wherein the molar ratio of backbone hydrophilic group to pendant hydrophobic group is less than 20.

Enzymes and an enzyme stabilising system are optionally incorporated into the composition for improved cleaning.

The compositions of the invention provide improved stain removal by the pretreater composition prior to the laundry wash. When used as an in wash additive, they also provide enhanced fluorescer effectiveness and stain removal.

Detailed Description of Preferred Embodiments

The present invention relates to compositions which may be used as either pretreaters in liquid, gel or spray form or in-wash laundry additives. It is understood that the terms "in-wash" or "in-wash laundry booster" are interchangeable with the terms "laundry additive" or. "in-wash laundry additive". The present invention also relates to compositions which may be used a pretreaters in stick form.

The compositions are based on nonionic surfactants and are preferably substantially free of synthetic (non-soap) anionic surfactants. They also contain specific polymers which have a critical molar ratio of a number of hydrophilic "backbone" groups (single monomer hydrophilic backbone) to a number of hydrophobic "anchor" or tail group.

When the polymers of the invention are added to the specific compositions, it has been unexpectedly found that the compositions have better stain removal efficacy compared to compositions which do not contain the polymers.
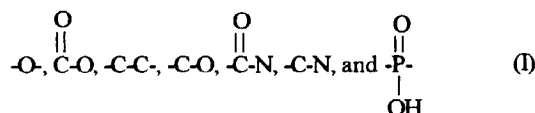
Hydrophobically Modified Polar Polymer

The polymer of the invention is one which, as noted above, has previously been used in structured (i.e., lamellar) compositions such as those described in U.S. Patent No. 5,147,576 to Montague et al., hereby incorporated by reference into the subject application.

In general, the polymer comprises a "backbone" component which is a monomer (single monomer) as discussed below and a "tail" portion which is a second monomer which is hydrophobic in nature (e.g., lauryl methacrylate or styrene).

The hydrophilic backbone generally is a linear, branched or highly cross-linked molecular composition containing one type of relatively hydrophobic monomer unit wherein the monomer is preferably sufficiently soluble to form at least a 1% by weight solution when dissolved in water. The only limitation to the structure of the hydrophilic backbone is that a polymer corresponding to the hydrophilic backbone made from the backbone monomeric constituents is relatively water soluble (solubility in water at ambient temperature and at pH of 3.0 to 12.5 is preferably more than 1 g/l). The hydrophilic backbone is also preferably predominantly linear, e.g., the main chain of backbone constitutes at least 50% by weight, preferably more than 75%, most preferably more than 90% by weight.

The hydrophilic backbone is composed of one monomer unit selected from a variety of units available for polymer preparation and linked by any chemical links including:

$$\text{-O-, } \overset{\overset{\text{O}}{\|}}{\text{C}}\text{-O, -C-C-, -C-O, } \overset{\overset{\text{O}}{\|}}{\text{C}}\text{-N, } \overset{\overset{\text{O}}{\|}}{\underset{\underset{\text{OH}}{|}}{\text{C}}}\text{-N, and -P-} \qquad \text{(I)}$$

The "tail" group comprises a monomer unit comprising hydrophobic side chains which are incorporated in the "tail" monomer. The polymer is made by copolymerizing hydrophobic monomers (tail group comprising hydrophobic groups) and the hydrophilic monomer making up the backbone. The hydrophobic side chains preferably include those which when isolated from their linkage are relatively water insoluble, i.e., preferably less than 1 g/l, more preferred less than 0.5 g/l, most preferred less than 0. g/l of the hydrophobic monomers, will dissolve in water at ambient temperature at pH of 3.0 to 12.5.

Preferably, the hydrophobic moieties are selected from siloxanes, saturated and unsaturated alkyl chains, e.g., having from 5 to 24 carbons, preferably 6 to 18, most preferred 8 to 16 carbons, and are optionally bonded to hydrophilic backbone via an alkoxylene or polyalkoxylene linkage, for example a polyethoxy, polypropoxy, or butyloxy (or mixtures

of the same) linkage having from 1 to 50 alkoxylene groups. Alternatively, the hydrophobic side chain can be composed of relatively hydrophobic alkoxy groups, for example, butylene oxide and/or propylene oxide, in the absence of alkyl or alkenyl groups.

Monomer units which make up the hydrophilic backbone include:

(1) unsaturated, preferably mono-unsaturated, C_{1-6} acids, ethers, alcohols, aldehydes, ketones or esters such as monomers of acrylic acid, methacrylic acid, maleic acid, vinyl-methyl ether, vinyl sulphonate or vinyl alcohol obtained by hydrolysis of vinyl acetate, acrolein;
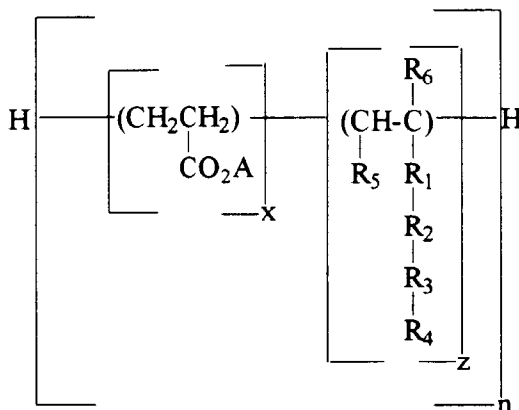
(2) cyclic units, unsaturated or comprising other groups capable of forming inter-monomer linkages, such as saccharides and glucosides, alkoxy units and maleic anhydride;

(3) glycerol or other saturated polyalcohols.

Monomeric units comprising both the hydrophilic backbone and hydrophobic side chain may be substituted with groups such as amino, amine, amide, sulphonate, sulphate, phosphonate, phosphate, hydroxy, carboxyl and oxide groups.

The hydrophilic backbone is composed of one unit. The backbone may also contain small amounts of relatively hydrophilic units such as those derived from polymers having a solubility of less than 1 g/l in water provided the overall solubility of the polymer meets the requirements discussed above. Examples include polyvinyl acetate or polymethyl methacrylate.

(II)

$$H \left[\left[(CH_2CH_2) \atop CO_2A \right]_x \left[\begin{array}{c} R_6 \\ | \\ (CH\text{-}C) \\ | \quad | \\ R_5 \quad R_1 \\ | \\ R_2 \\ | \\ R_3 \\ | \\ R_4 \end{array} \right]_z \right]_n H$$

wherein

z is 1;

x:z (i.e., hydrophilic backbone to hydrophobic tail) is less than 20, preferably less than 17, more preferably less than 10;

in which the monomer units may be in random order; and

n is at least 1:

R_1 represents -CO-O-, -O-, -O-CO-, -CH$_2$-, -CO-NH- or is absent;

R_2 represents from 1 to 50 independently selected alkyleneoxy groups preferably ethylene oxide or propylene oxide groups, or is absent, provided that when R_3 is absent and R_4 represents hydrogen or contains no more than 4 carbon atoms, then R_2 must contain an alkyleneoxy group with at least 3 carbon atoms;

R_3 represents a phenylene linkage, or is absent;

R_4 represents hydrogen or a C_{1-24} alkyl or C_{2-24} alkenyl group, with the provisos

a) when R_1 represents -O-CO-, R_2 and R_3 must be absent and R_4 must contain at least 5 carbon atoms;
b) when R_2 is absent, R_4 is not hydrogen and when R_3 is absent, then R_4 must contain at least 5 carbon atoms;

R_5 represents hydrogen or a group of formula -COOA;
R_6 represents hydrogen or C1-4 alkyl; and A is independently selected from hydrogen, alkali metals, alkaline earth metals, ammonium and amine bases and C_{1-4}.

Alternatively, the group such as,

$$
\begin{array}{c}
R_6 \\
| \\
(CH\text{-}C) \\
| \quad | \\
R_5 \quad R_1 \\
| \\
R_2 \\
| \\
R_3 \\
| \\
R_4
\end{array}
$$
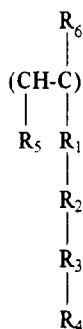
group (defined by z) can be substituted with benzene, for example styrene.

The present invention is direct to the observation that, when polymers such as those described above (known as deflocculating or decoupling polymers in the "structured liquid" art) are used in pretreater or laundry additive booster formulations they provide enhanced stain removal and, when used in the wash with a detergent containing fluorescer, they enhance the fluorescer whitening.

The polymer should be used in an amount comprising 0.01 to 10% by wt., preferably 0.1% to 5% by wt. of the composition.

Nonionic Surfactants

The nonionic surfactants useful in the present invention are those compounds produced by the condensation of alkylene oxide groups with an organic hydrophobic material which may be aliphatic or alkyl or aromatic in nature. The link of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. Illustrative, but not limiting examples, of various suitable non-ionic surfactant types are:

(a) polyoxyethylene or polyoxypropylene condensates of aliphatic alcohols, whether linear-or branched-chain and unsaturated or saturated, containing from about 6 to about 24 carbon atoms and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable alcohols include "coconut" fatty alcohol, "tallow" fatty alcohol, lauryl alcohol, myristyl alcohol and oleyl alcohol. Particularly preferred nonionic surfactant compounds in this category are the "Neodol" type products, a registered trademark of the Shell Chemical Company.

Also included within this category are nonionic surfactants having a formula:

$$
R-(CH_2CHO)_X(CH_2CH_2)_Y(CH_2CHO)_ZH \quad (III)
$$
$$
\qquad \quad \begin{array}{cc} R^1 & \qquad\qquad R^2 \end{array}
$$
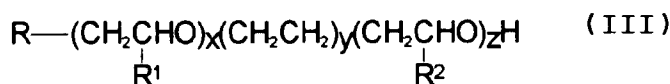
wherein R is a linear alkyl hydrocarbon radical having an average of 6 to 18 carbon atoms, R^1 and R^2 are each linear alkyl hydrocarbons of about l to about 4 carbon atoms, x is an integer of from l to 6, y is an integer of from 4 to 20 and z is an integer from 4 to 25.

A preferred nonionic surfactant included within this category are compounds of formula:
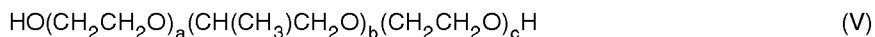
$$R^3\text{-}(CH_2CH_2O)_aH \qquad\qquad (IV)$$

wherein R^3 is a C_6-C_{24} linear or branched alkyl hydrocarbon radical and a is a number from 2 to 50; more preferably R^3 is a C_8-C_{18} linear alkyl mixture and a is a number from 2 to 15.

(b) polyoxyethylene or polyoxypropylene condensates of aliphatic carboxylic acids, whether linear- or branched-chain and unsaturated or saturated, containing from about 8 to about 18 carbon atoms in the aliphatic chain and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units. Suitable carboxylic acids include "coconut" fatty acids (derived from coconut oil) which contain an average of about 12 carbon atoms, "tallow" fatty acids (derived from tallow-class fats) which contain an average of about 18 carbon atoms, palmitic acid, myristic acid, stearic acid and lauric acid.
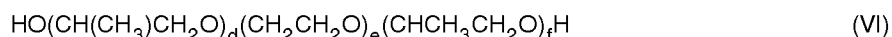
(c) polyoxyethylene or polyoxypropylene condensates of alkyl phenols, whether linear- or branched-chain and unsaturated or saturated, containing from about 6 to 12 carbon atoms and incorporating from about 2 to about 25 moles of ethylene oxide and/or propylene oxide.

(d) polyoxyethylene derivatives of sorbitan mono-, di-, and tri-fatty acid esters wherein the fatty acid component has between 12 and 24 carbon atoms. The preferred polyoxyethylene derivatives are of sorbitan monolaurate, sorbitan trilaurate, sorbitan monopalmitate, sorbitan tripalmitate, sorbitan monostearate, sorbitan monoisostearate, sorbitan tripalmitate, sorbitan monostearate, sorbitan monoisostearate, sorbital tristearate, sorbitan monooleate, and sorbitan trioleate. The polyoxyethylene chains may contain between about 4 and 30 ethylene oxide units, preferably about 20. The sorbitan ester derivatives contain 1, 2 or 3 polyoxyethylene chains dependent upon whether they are mono-, di- or tri-acid esters.

(e) polyoxyethylene-polyoxypropylene block copolymers having formula:

$$HO(CH_2CH_2O)_a(CH(CH_3)CH_2O)_b(CH_2CH_2O)_cH \qquad\qquad (V)$$

or

$$HO(CH(CH_3)CH_2O)_d(CH_2CH_2O)_e(CHCH_3CH_2O)_fH \qquad\qquad (VI)$$

wherein a, b, c, d, e and f are integers from 1 to 350 reflecting the respective polyethylene oxide and polypropylene oxide blocks of said polymer. The polyoxyethylene component of the block polymer constitutes at least about 10% of the block polymer. The material preferably has a molecular weight of between about 1,000 and 15,000, more preferably from about 1,500 to about 6,000. These materials are well-known in the art. They are available under the trademark "Pluronic" and "Pluronic R", a product of BASF Corporation.

(f) Alkyl glycosides having formula:

$$R^4O(R^5O)_n(Z^1)p \qquad\qquad (VII)$$
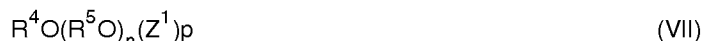
wherein R^4 is a monovalent organic radical (e.g., a monovalent saturated aliphatic, unsaturated aliphatic or aromatic radical such as alkyl, hydroxyalkyl, alkenyl, hydroxyalkenyl, aryl, alkylaryl, hydroxyalkylaryl, arylalkyl, alkenylaryl, arylalkenyl, etc.) containing from about 6 to about 30 (preferably from about 8 to 18 and more preferably from about 9 to about 13) carbon atoms; R^5 is a divalent hydrocarbon radical containing from 2 to about 4 carbon atoms such as ethylene, propylene or butylene (most preferably the unit $(R^5O)_n$ represents repeating units of ethylene oxide, propylene oxide and/or random or block combinations thereof); n is a number having an average

value of from 0 to about 12; Z^1 represents a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms (most preferably a glucose unit); and p is a number having an average value of from 0.5 to about 10 preferably from about 0.5 to about 5.

Examples of commercially available materials from Henkel Kommanditgesellschaft Aktien of Dusseldorf, Germany include APG® 300, 325 and 350 with R^4 being C_9-C_{11}, n is 0 and p is 1.3, 1.6 and 1.8-2.2 respectively; APG® 500 and 550 with R^4 is C_{12}-C_{13}, n is 0 and p is 1.3 and 1.8-2.2, respectively; and APG® 600 with R^4 being C_{12}-C_{14}, n is 0 and p is 1.3. Particularly preferred is APG® 600.

The nonionic surfactant which are most preferred are the polyoxyalkylene condensates of paragraphs "(a)" and "(b)" and the alkyl glycosides. Most preferred are the polyoxyalkylene condensates.

The nonionic is used in an amount of about 0.1 to about 20 wt. % in liquid, paste or gel products and from about 30 to about 80 wt.%, preferably up to 60, more preferably up to 40wt.% in stick products..

Optional Polymers

Conventional Polymers also referred to as antiredeposition polymers may also be incorporated in the formulations of the invention. Such polymers include polycarboxylates (e.g. copolymers of acrylate/maleate commercially available as Sokolan® copolymers supplied by BASF; polyoxyalkylene copolymers (e.g. Pluronic Series supplied by BASF); carboxymethylcelluloses (e.g. CMC Series supplied by Union Carbide); methylcellulose (e.g. Methocel from Dow Chemical) and ethoxylated polyamines (e.g. ethoxylated tetra ethylene pentamine from Shell Chemical Co).

Especially preferred are the polycarboxylate polymers. The polymers should be incorporated in the formulations of the invention in an amount of up to about 5 wt. %, preferably 0.1 wt. % to 3 wt. %, most preferably 0.5 wt. % to 1 wt. %.

Anionic Soaps

The pretreater formulations of the invention are preferably substantially free of synthetic (non-soap) anionic surfactants. It is possible, however, to add less from about 5 wt. %, preferably less than 3 wt. % of an anionic soap to liquid, paste or gel compositions according to the invention, particularly for some in-wash formulations intended to boost whitening of fabrics. Compositions according to the present invention which are in stick form contain from about 1wt.% to about 20wt.% of anionic soap.

The term "soap" is used herein in its popular sense, i.e., the alkali metal or alkanol ammonium salts of aliphatic alkane- or alkene monocarboxylic acids. Sodium, potassium, mono-, dipand tri-ethanol ammonium cations, or combinations thereof, are suitable for purposes of this invention. In general, sodium soaps are used in the compositions of this invention, but from about 1% to about 25% of the soap may be potassium soaps. The soaps useful herein are the well known alkali metal salts of natural or synthetic aliphatic (alkanoic or alkanoic) acids having about 8 to 22 carbons, preferably about 12 to about 18 carbon atoms. They may be described as alkali metal carboxylates of acrylic hydrocarbons having about 12 to about 22 carbon atoms. They also include soaps derived from natural carboxylic acids such as "coconut" fatty acids (derived from coconut oil) which contain an average of about 12 carbon atoms, "tallow" fatty acids (derived from tallow-class fats) which contain an average of about 18 carbon atoms, palmitic acid, myristic acid, stearic acid and lauric acid. The soaps preferably contain saturated or partially saturated fatty acids. Excessive unsaturation should be avoided.

Typical stick form stain remover compositions according to the present invention will comprise about 1-20 wt. %, preferably 5-15 wt. % of normally distributed stearic soap (nominally >95% $C_{18}H_{36}O_2$) as the gelling agent. The current invention preferably uses blends of saturated soaps (carbon chain lengths of C_8-C_{18}) as the coagel structurant which solidifies the stain treatment sticks. The coagel structuring is used in the margarine industry to solidify oil and water mixtures. A coagel solid relies on the structuring of alternating water and oil bi-layer lamellar sheets to form a macroscopically solid phase. Without being limited to a theory, it is believed that the blend of saturated soaps modifies the surfactant and oil interface in order to form the bi-layer lamellar sheets necessary for the coagel structuring. For stick formulations according to the present invention it is preferred to use blends of soaps neutralized (in-situ) from the following table:

As % of Total Fatty Acid in Formulation	Caprylic $C_8H_{16}O_2$	Capric $C_{10}H_{20}O_2$	Lauric $C_{12}H_{24}O$	Myristic $C_{14}H_{28}O_2$	Palmitic $C_{16}H_{32}O_2$	Stearic $C_{18}H_{36}O_2$	Unsaturated
Preferred Range	0-6.0	0-5.0	5.0-40.0	0-18.0	10.0-60.0	5.0-60.0	0-5.0

(continued)

As % of Total Fatty Acid in Formulation	Caprylic $C_8H_{16}O_2$	Capric $C_{10}H_{20}O_2$	Lauric $C_{12}H_{24}O$	Myristic $C_{14}H_{28}O_2$	Palmitic $C_{16}H_{32}O_2$	Stearic $C_{18}H_{36}O_2$	Unsaturated
Most Preferred Range	3.5-5.5	3.0-4.8	24.5-37.5	10.8-15.2	17.5-29.5	15.2-26.0	0-2.8
Example [1]	0	0	0	0	0-5	95-100	0-2.0

[1] as described in U.S. Patent No. 5,147,576.

The novel benefits of the current invention which uses a blend of saturated soaps and coagel structuring are as follows:

1) When the coagel stick is applied to a stain on cloth and then washed, the mixed saturated soaps helps to avoid a cubic surfactant phase between the stick and the stain in the aqueous phase. A cubic phase is very impermeable which inhibits the transfer of cleaning ingredients and the release of the stain from the cloth. Avoiding this cubic phase by using the blended saturated soaps improves the stain performance on oil stains compared to conventional stain sticks.

2) due to the bi-layer structuring of a coagel stick the dissolution rate in an aqueous solution (i.e., wash liquor) is much greater then with conventional stain sticks. This improves performance and ensures that no treatment stick remains on the cloth after washing.

3) The coagel structurant breaks down under the friction of contact with the cloth. Thus, under the friction of application to a dry stain, the localized region of contact for the coagel stick liquefies. This ensures that the treatment stick is easy to apply, the stick has a user friendly glide texture, and on application the liquefied stick formula can penetrate deeper into the stain, removing the stain more completely than with conventional stick formulations.

Formulations containing the preferred blend of saturated soaps may or may not also contain the hydrophobically modified polar polymer of the invention.

Anionic Surfactants

Synthetic anionic surfactants are preferably substantially or completely excluded from compositions according to the present invention. If present at all, then they are only included in minor amounts such as less than 10%, preferably less than 5%, more preferably less than 2%, still more preferably less than 1%, especially less than 0.5%, e.g. less than 0.1% by weight of the total composition. If present, such anionic surfactants may be chosen from any of those known in the art of formulating detergent compositions, such as the usual linear alkyl benzene sulphonates, primary alkyl sulphates, alkyl ether sulphates etc. Though, most preferred of all is total exclusion of synthetic anionic surfactants.

Enzymes

Enzymes may optionally be included in the pretreater or in wash formulations to enhance the removal of soils from fabrics. If present, the enzymes are in an amount of from about 0 to 10 weight %, preferably 1 to about 5 wt. %. Such enzymes include proteases (e.g. Alcalase®, Savinase® and Esperase® from Novo Industries A/S), amylases (e.g. Termamyl® from Novo Industries A/S), lipolases (e.g. Lipolase® from Novo Industries A/S) and cellulases, (e.g. Celluzyme® from Novo Industries A/S).

Enzyme Stabilising System

Stabilizers or stabilizer systems may be used in conjunction with enzymes and generally comprise from about 1 to 15% by weight of the composition.

The enzyme stabilization system may comprise calcium ion; boric acid, propylene glycol and/or short chain carboxylic acids. The composition preferably contains from about 0.01 to about 50, preferably from about 0.1 to about 30, more preferably from about I to about 20 millimoles of calcium ion per litre.

When calcium ion is used, the level of calcium ion should be selected so that there is always some minimum level available for the enzyme after allowing for complexation with builders, etc., in the composition. Any water-soluble calcium salt can be used as the source of calcium ion, including calcium chloride, calcium formate, calcium acetate and calcium propionate.

A small amount of calcium ion, generally from about 0.05 to about 2.5 millimoles per litre, is often also present in the composition due to calcium in the enzyme slurry and formula water.

Another enzyme stabilizer which may be used is propionic acid or a propionic acid salt capable of forming propionic acid. When used, this stabilizer may be used in an amount from about 0.1% to about 15% by weight of the composition.

Another preferred enzyme stabilizer is polyols containing only carbon, hydrogen and oxygen atoms. They preferably contain from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups. Examples include propylene glycol (especially 1,2 propanediol which is preferred), ethylene glycol, glycerol, sorbitol, mannitol and glucose. The polyol generally represents from about 0.5% to about 15%, preferably from about 1.0% to about 8% by weight of the composition.

The composition herein may also optionally contain from about 0.25% to about 5%, most preferably from about 0.5% to about 3% by weight of boric acid. The boric acid may be, but is preferably not, formed by a compound capable of forming boric acid in the composition. Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g. sodium ortho-, meta- and pyroborate and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid and a p-bromo phenylboronic acid) can also be used in place of boric acid.

One especially preferred stabilization system is a polyol in combination with boric acid. Preferably, the weight ratio of polyol to boric acid added is at least 1, more preferably at least about 1.3.

Preparation of Formulations

The formulations of the invention may be prepared in any form known in the art such as liquid, (including in spray form), paste or gel. Those compositions should be prepared by conventional formulation methods such as those described in U.S. 5,186,856, particularly directed to an aqueous form, herein incorporated by reference.

In general, aqueous liquid, paste or gel formulations are prepared by mixing the nonionic and selected polymers together and heating the mixture to a temperature of up to 160°F. The mixture is then cooled and the enzymes and enzyme stabilising system may be added. Optional ingredients, such as preservatives, dyes and perfumes are added to the cooled mixtures. The compositions are then packaged and stored.

Those formulations of the invention which are in stick forms are prepared as follows, but may be prepared in any form known in the art for stick forms.

The fatty acid(s) used are typically neutralized to soap in-situ. The nonionic surfactant, the blend of fatty acid(s) and the polyols such as sorbital, glycerol, propylene glycol are heated to about 70°C to form a homogeneous melt mixture. Water and neutralizing base (typically caustic) are then added to neutralize the fatty acid(s). The polymer is then added and mixed until the mixture is homogeneous. The homogenous mixture is than cooled to just above the mixtures dropping point. Any heat labile additional ingredients (i.e., enzymes, fragrance, preservatives) are then added. The composition is then packaged, cooled and stored.

Alternatively, the initial melt mixture can be added to a premixed mixture of water, caustic and polymer to perform the in-situ neutralization.

Thickeners

Thickeners may be incorporated into the formulations of the invention-particularly to import viscosity to liquid or to produce gel or paste consistency. Such thickeners include, but are not limited to natural thickeners such as xanthan gums and other conventional polymeric thickeners as known in the art. The thickeners may comprise up to 5% of the formulation. Preferably, 0.1 wt. % to 3 wt. %, most preferably 0.3 wt. % to 1 wt. %.

Optionally, an antifoam agent may be incorporated into formulations according to the invention in an amount of up to 2 wt. %, preferably 0.05 to 1 wt. %, to reduce the level of air entrapped in the solidified sticks. Suitable antifoams include mono- and distearyl acid phosphate, silicone oil, silicon emulsion, silicon compounds and mineral oil. Preferably, silicon emulsions are used.

Optional Ingredients

One or more optional additives may be included in the formulations including perfumes, dyes, pigment, opacifiers, germicides, optical brighteners, anticorrosional agents and preservatives. Each additive incorporated in the composition should be present in an amount of up to about 0.5% by wt.

The following examples will serve to distinguish this invention from the prior art and illustrate its embodiments

more fully. Unless otherwise indicated, all parts, percentages and proportions referred to are by weights.

Examples

Example 1

A aqueous pretreater formulation according to the invention was prepared as Sample A below. As a comparison, an aqueous pretreater formulation without the selected hydrophobically modified polymer was prepared as Sample B.

Table 1

Ingredient	Samples	
	A	B
boric acid	1.4	1.4
propylene glycol	3.0	3.0
alcohol ethoxylate[2]	4.7	4.7
Narlex® DC-1[3]	0.5	0
enzyme	0.7	0.7
xanthan gum	0.3	0.3
preservative	.003	.003
deionized water to 100%		

[2] a nonionic surfactant having 12-15 carbon atoms in the hydrophobic group and 9 EOs and supplied as Neodol 25-9 by Shell Chemical Co.

[3] a copolymer of acrylic acid and lauryl methacrylic acid supplied by National Starch and Chemical Co.

The liquid composition of the invention was made by charging a vessel with water and heating to 160°F, adding the boric acid and stirring the liquid until a clear solution was obtained. The surfactant was then added, and the heater turned off. The polymer of Sample A was then added when the solution temperature was between 120-150°F. The enzymes were added when the solution temperature was below 120°F, then preservative was added. The pH of the formulation was then adjusted to 7.0 (± 0.5).

Example 2

The stain removal performance of the inventive composition (Sample A) versus Sample B without the selected polymer was evaluated on four (4) different stains and on three types of fabric as follows.
The three types of fabrics used to evaluate the compositions were:

1) 100% cotton
2) 50%/50% polyester/cotton blend
3) double knit 100% polyester

Cloths 1 and 2 were obtained from Textile Innovators (Windsor, North Carolina), and the polyester cloth 3 was obtained from Test Fabrics (Middlesex, New Jersey). Prior to staining the cloths were prewashed five times with a fluorescer free detergent at 130°F (and dried) to remove spinning oils and increase the absorbency of the cloth. Swatches were cut to 4-3/4" x 8-3/4", and a 2" diameter circle inscribed in the middle.
Four different stains were used as follows:

1) Grass (1:2 gram of water by wt. blended and filtered).
2) Liquid foundation make-up
3) Cows blood
4) Mud (strained dirt mixed 1:1 with water and blended)

The stains were applied over the 2" circle on each swatch as outlined in Table 2:

Table 2

Stain	Dosage			Treatment
	Cotton	Blend	Polyester	
grass	8 drops (2x)	8 drops (2x)	1/4 tsp.	overnight
blood	7 drops	7 drops	18 drops	overnight
make-up	7 drops	6 drops	28 drops	overnight
mud	1/8 tsp	1/8 tsp	1/4 tsp	overnight

Stained clothes were treated with the liquid pretreater and washed in 17 gallons of 95°F tap water with a commercial laundry detergent followed by a cold rinse. The cloths were then placed in a static dryer until dry. Eight replicates of each stain with each cloth were performed.

Stain removal was measured by reflectometry and colour change using a Pacific Scientific Colorgard System model 5 colorimeter. The stain removal index (SRI) gives a numerical value for stain removal and is defined as:

$$SRI = 100 - [(L_c-L_w)^2 + (a_c-a_w)^2 + (b_c - b_w)^2]^{1/2}$$

Where:

L = measured lightness (reflectance) value
a = measured greenness/redness value
b = measured blueness/yellowness value
c = clean cloth
w = stained and washed cloth

Results were reported as SRI index values.

Stain removal data for Samples A and B for the four stains on the three types of cloth were observed and are reported in Table 3 below:

Table 3

STAIN REMOVAL INDEX VALUE									
Sample	100% Cotton			50/50 Polyester/Cotton			100% Polyester		
Stain	A	B	LSD[4]	A	B	LSD[1]	A	B	LSD[1]
Grass	94.89	89.34	0.52	80.97	76.29	0.27	96.79	92.91	0.50
Mud	78.32	77.99	0.94	83.18	79.70	2.08	88.87	85.94	1.74
Make-up	77.65	75.36	1.03	84.37	79.33	2.11	99.28	99.29	0.05
Blood	91.01	90.42	0.23	94.31	93.96	0.15	99.00	98.76	0.16

[4]LSD = Least Significant Difference at 95% confidence level.

It was thus observed that the inventive Sample A was significantly more effective at stain removal than observed with Sample B which did not contain the selected polymer.

Example 3

The following gel compositions were prepared as described in Example 1.

Table 4

Ingredient	Sample C	Sample D
boric acid	1.4	1.4

Table 4   (continued)

Ingredient	Sample C	Sample D
propylene glycol	3.0	3.0
alcohol ethoxylate	14	14
enzyme	1.5	1.5
xanthan gum	0.7	0.7
Narlex® DC-1	0	0.5
water	to 100%	

Sample C did not contain the hydrophobically modified polymer while Sample D contained Narlex® DC-1, a co-polymer of acrylic acid and lauryl methacrylic acid supplied by National Starch and Chemical Co. The cleaning performance of Sample C versus Sample D was evaluated as described in Example 2 on 2 different stains and three types of fabrics with the results presented in Table 5:

Table 5

STAIN REMOVAL INDEX VALUES									
Stain	100% Cotton			50/50 Polyester/cotton			100% Polyester		
	C	D	LSD[5]	C	D	LSD[1]	C	D	LSD[1]
grass	92.16	94.03	0.29	94.46	94.91	0.23	95.94	96.78	0.29
mud	76.71	78.89	0.91	79.85	79.94	1.63	90.09	92.5	0.85

[5]LSD = Least Significant Difference at 95% confidence level.

From the results described in Table 5, it was observed that the inventive formulation was significantly better in stain removal than the sample without the polymer of the invention.

Example 4

A gel form of the inventive formulation incorporating a styrene containing acrylic acid copolymer was prepared as described in Example 1 and presented in Table 6 below:

Table 6

Ingredient	% Active
boric acid	1.4
propylene glycol	3.0
alcohol ethoxylate	14
enzyme	1.5
xanthan gum	0.7
ALCO EXP 2499[6]	0.5
Deionized water	to 100%

[6]a styrene containing acrylic acid copolymer supplied by Alco under the Series H100.

Example 5

An aqueous composition incorporating a styrene containing acrylic acid copolymer was prepared as described in Example 1 having the formula described in Table 7:

Table 7

Ingredient	% Active
boric acid	1.4
propylene glycol	3.0
alcohol ethoxylate[7]	4.7
enzyme	0.7
xanthan gum	0.3
ALCO EXP 2499[8]	0.5
Deionized water	to 100%

[7] a nonionic surfactant supplied by Shell as Neodol 25-9.

[8] a styrene containing acrylic acid copolymer supplied by Alco under the Series H100.

Example 6

The following laundry additive compositions were prepared as described in Example 1:

Table 8

	E	F
boric acid	1.4	1.4
propylene glycol	4.0	4.0
alcohol ethoxylate[9]	2.0	2.0
enzyme	0.7	0.7
xanthan gum	0.3	0.3
Narlex DC-1[10]	1.0	1.0
monoethanolamine	-	0.4
coconut fatty acid	-	2.0
deionized water to 100%		

[9] a nonionic surfactant supplied by Shell as Neodol 25-9.

[10] a styrene containing acrylic acid copolymer supplied by Alco under the Series H100.

Samples of composition E were prepared as described in Example 1. Samples of composition F were prepared by adding the monoethanolamine and coconut fatty acid to the alcohol ethoxylate (as described in Example 1), adding the monoethanolamine first followed by the fatty acid.

Example 7

The fluorescent whitening of the inventive compositions used as laundry additives with a commercial detergent containing fluorescer whitening agents versus the detergent alone was evaluated on soiled cloths. Soil cloths were obtained from EMPA, St. Gallen, Switzerland. EMPA 112 is composed of cocoa, milk and sugar on cotton. EMPA 116 is composed of blood, milk, and indian ink on cotton. EMPA 117 has the same soil as EMPA 116 but it is on polyester/cotton. VCD is composed of vacuum cleaner dust on polyester/cotton. AS-10 is composed of milk powder, ground nut oil, carboxymethylcarubin and small levels of dyes on cotton.

The inventive products were used at a conventional booster level together with the commercial detergent. The composition of the detergent is shown in Table 9. Four of each soil cloth type were washed at the same time and the evaluation was done twice. The results are shown in Table 9. Fluorescer values are calculated using the following equation form reflectance data taken on a Gardner reflectometer with and without an ultraviolet filter.

$$F = 0.08 + 2.61(Z_{wo} - Z_w)$$

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where:

F = fluorescer value
0.08 and 2.61 are instrumental parameters
wo = without ultraviolet filter
w = with ultraviolet filter
Z = (0.7a - b)L/59.27
L = reflectance
b = yellow-blue value
a = green-red value

Fluorescent whitening of inventive formulations:

Table 9

FLUORESCENT WHITENING					
Product	VCD	AS-10	EMPA 112	EMPA 116	EMPA 117
detergent alone	5.39	3.94	1.13	0.43	0.04
+ formula G	6.01	5.41	1.77	1.55	0.33
+ formula H	5.97	5.34	1.87	1.61	0.43
least sig. diff.	0.26	0.26	0.16	0.16	0.16

The inventive formulations increase the fluorescent whitening of the detergent significantly. The boost in fluorescent whitening due to the inventive formulations is unexpected because these do not contain fluorescer.

Example 8

A stick formulation according to the invention was prepared as Sample G below. As a comparison, an aqueous pretreater formulation without the selected hydrophobically modified polymer was prepared as Sample H.

Table 10

	Samples	
Ingredient	G	H
propylene glycol	11.0	11.0
alcohol ethoxylate[11]	57.9	57.9
Narlex® DC- 1[12]	0.3	0
stearic acid[13]	4.4	4.4
coconut fatty acid[14]	7.9	7.9
sodium hydroxide	2.1	2.1
deionized water	to 100%	

[11]a nonionic surfactant having 12-15 carbon atoms in the hydrophobic group and 9 EOs and supplied as Neodol 25-9 by Shell Chemical Co.

[12]a copolymer of acrylic acid and lauryl methacrylic acid supplied by National Starch and Chemical Co.

[13]stearic acid containing a mixture of C_{12-18} saturated fatty acids supplied as Emersol 132 by Henkle.

[14]partially hydrogenated coconut fatty acid C_8-C_{22} saturated fatty acids supplied by Henkle.

The nonionic surfactant, the anionic surfactant, the polymer and the propylene glycol were added together in a mixture with low to medium agitation. The batch was heated up 40°C. The fatty acid was then added and heating was continued until the batch reached 55°C. Once the fatty acid was completely melted, the water was added with heating to maintain the batch at 50-55°C. Once the batch was homogeneous, the sodium hydroxide was added. The batch was then mixed for 45 minutes to ensure full neutralization of the fatty acid. The batch was then cooled to 50°C. The batch was then placed in a package and allowed to air cool with chilling.

Example 9

The stain removal performance of the inventive composition (Sample F) versus Sample G without the selected polymer was evaluated on three (3) different stains and on three types of fabric as follows.

The three types of test cloths used to evaluate the compositions were:

1) 100% cotton
2) 50%/50% polyester/cotton blend
3) double knit 100% polyester

Cloths 1 and 2 were obtained from Textile Innovators (Windsor, North Carolina), and the polyester cloth 3 was obtained from Test Fabrics (Middlesex, New Jersey). Prior to staining, the cloths were prewashed 5 times in Dye Free Liquid "all" at 130°F (and dried) to remove spinning oils and increase the absorbency of the cloth. Swatches were cut to 4-3/4" x 8-3/4", and a 2" diameter circle inscribed in the middle.

Three different stains were used as follows:

1) Grass (100g grass clippings added to 200g water, blended, filtered through cotton ballast, 100g more clippings and 200g more water added to filtrate, and new mixture filtered).
2) Cooking Oil/Food Colorant (17 gms. of annato seed colorant are dissolved in 400 gms. of cooking oil and the mixture is passed through a cheese cloth filter).
3) Mud (strained dirt mixed 1 : 1 with water and blended).

The stains were applied over the 2" circle on each swatch as outlined in Table 11:

Table 11

Stain	Dosage			Treatment
	Cotton	Blend	Polyester	
mud	1/8 tsp	1/8 tsp	1/4 tsp	overnight
grass	8 drops (2x)	8 drops (2x)	1/4 tsp.	overnight
cooking oil/food colorant	12 drops	12 drops	----	overnight

The stain cloth were pretreated (by rubbing) with the stick. Application of the stick is done using minimal force, allowing the natural gliding tendency of the stick to drive the movement. The stained and treated clothes were allowed to sit for 5 minutes before washing. The washes were done using the recommended dosages of a laundry liquid detergent in warm, 95°F water and rinsed in cold water. The cloths were then placed in a static dryer until dry. Four replicates of each stain with each cloth were performed.

Stain removal was measured by reflectometry and color change using a Pacific Scientific Colorgard System model 5 colorimeter. The stain removal index (SRI) gives a numerical value for stain removal and is defined as:

$$SRI = 100 - [(L_c - L_w)^2 + (a_c - a_w)^2 + (b_c - b_w)^2]^{1/2}$$

Where:

L = measured lightness (reflectance) value
a = measured greenness/redness value
b = measured blueness/yellowness value
c = clean cloth
w = stained and washed cloth

Stain removal data for Samples G and H for the three stains on the three types of cloth were observed and are reported in Table 12 below:

Table 12

Stain Removal Index Values									
Stain	**100% Cotton**			**50/50 Polyester/Cotton**			**100% Polyester**		
Stain	G	H	LSD	G	H	LSD	G	H	LSD
Mud	74.49	72.63	1.08	78.52	77.38	1.53	94.91	94.50	0.39
Grass	88.82	88.7	1.66	93.56	93.45	0.34	96.21	96.94	0.71
Cooking Oil/Food Colorant	90.599	90.411	1.12	92.055	91.299	0.27	N/A	N/A	N/A
LSD = Least Significant Difference at 95% confidence level.									

It was thus observed that the inventive Sample G consistently gave directionally better stain removal than observed with Sample H which did not contain the selected polymer.

Example 10

Stick forms of the inventive formulation incorporating a styrene containing acrylic acid copolymer were prepared as described in Example 8 and presented in Table 13 below:

Table 13

Ingredient	% Active
propylene glycol	11.0
alcohol ethoxylate[15]	57.9
ALCO EXP 2499[16]	0.5
stearic acid[17]	4.4
coconut fatty acid[18]	7.9
sodium hydroxide	2.1
deionized water	to 100%

[15]a nonionic surfactant supplied by Shell as Neodol 25-9.

[16]a styrene containing acrylic acid copolymer supplied by Alco under the Series H100.

[17]stearic acid containing a mixture of C_{2-18} saturated fatty acids supplied as Emersol 132 by Henkle.

[18]partially hydrogenated coconut fatty acid C_8-C_{22} saturated fatty acids supplied by Henkle.

Claims

1. A pretreatment composition comprising

  (a) from 0.1 to 80% by weight of nonionic surfactant;
  (b) from 0 to 20% by weight of an anionic soap; and
  (c) from 0.1% to 10% by weight of a polymer having:-

    1) a hydrophilic backbone comprising one or more monomer units selected from:

      i) one or more ethylenically unsaturated hydrophilic monomers selected from the group consisting of unsaturated C_{1-6} acids, ethers, alcohols, aldehydes, ketones or esters; and/or
      ii) one or more polymerizable hydrophilic cyclic monomer units; and/or
      iii) one or more non-ethylenically unsaturated polymerizable hydrophilic monomers selected from the group consisting of glycerol and other polyhydric alcohols ;
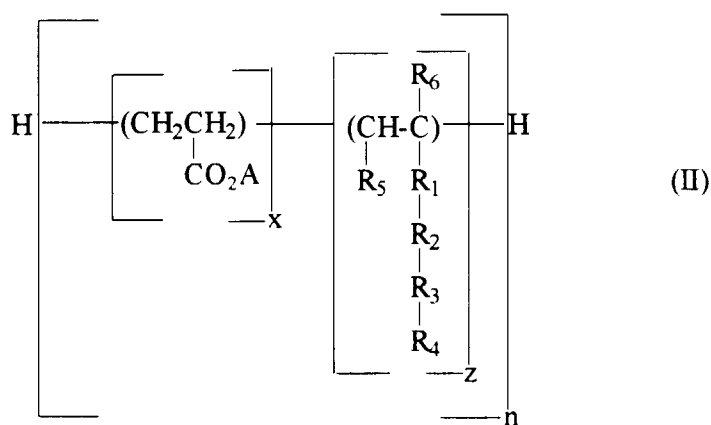
    wherein said monomer units are independently optionally substituted with one or more amino, amine, amide, sulphonate, sulphate, phosphonate, hydroxy, carboxyl or oxide groups; and

2) at least one monomer containing a pendant hydrophobic group and optionally also, a pendant hydrophilic group;

said polymer having a MW of 1,000 to 20,000;
wherein the molar ratio of backbone hydrophilic group to pendant hydrophobic group is less than 40, preferably 30, most preferably 20.

2. A composition according to claim 1, being in the form of an aqueous liquid, aqueous paste or aqueous gel, which composition comprises from 0.1 to 20% by weight of the nonionic surfactant and from 0 to 5% by weight of the anionic soap.

3. A composition according to claim 1, being in the form of a solid, which composition comprises from 30 to 80% by weight of the nonionic surfactant and from 1 to 20% by weight of the anionic soap.

4. A composition according to any preceding claim, wherein the composition further comprises an enzyme and an enzyme stabilising is selected from the group consisting of propylene glycol, ethylene glycol, glycerol, sorbitol, mannitol, glucose and mixtures thereof.

5. A composition according to claim 4, wherein the stabilizer is propylene glycol.

6. A composition according to any preceding claim, wherein the anionic soap is an alkalimetal salt of an aliphatic acid having from 8 to 22 carbon atoms.

7. A composition according to claim 6, wherein the alkali metal soap is a mixture of saturated fatty acids.

8. A composition according to any preceding claim, wherein the composition further comprises: 0.01 - 0.5% by weight of an antifoam agent.

9. A polymer for use as the polymer comprised in any preceding claim, the polymer having the formula:

$$H - \left[\left[(CH_2CH_2) \underset{CO_2A}{\big|} \right]_x \left[(CH\text{-}C) \begin{matrix} R_6 \\ | \\ R_5 \ R_1 \\ | \\ R_2 \\ | \\ R_3 \\ | \\ R_4 \end{matrix} \right]_z \right]_n H \qquad (II)$$

wherein

z is 1;
x:z is less than 20
n is at least 1
R^1 represents -CO-O-, -O-, -O-CO-, -CH$_2$-, -CO-NH- or is absent;
R^2 represents from 1 to 50 independently selected alkyleneoxy groups preferably ethylene oxide or propylene oxide groups, or is absent, provided that when R^3 is absent and R^4 represents hydrogen or contains no more

than 4 carbon atoms, then R^2 must contain an alkyleneoxy group with at least 3 carbon atoms;
R^3 represents a phenylene linkage, or is absent;
R^4 represents hydrogen or a C_{1-24} alkyl or C_{2-24} alkenyl group, with the provisos that

    a) when R^1 represents -O-CO-, R^2 and R^3 must be absent and R^4 must contain at least 5 carbon atoms;
    b) when R^2 is absent, R^4 is not hydrogen and when R^3 is absent, then R^4 must contain at lest 5 carbon atoms;

    R^5 represents hydrogen or a group of formula -COOA;
    R^6 represents hydrogen or C_{1-4} alkyl; and

is independently selected from hydrogen, alkali metals, alkaline earth metals, ammonium and amine bases and C_{1-4}.
wherein the monomer units may be in random order.

10. A polymer according to claim 9, wherein the backbone monomer is acrylate and the monomer comprising hydrophobic pendant group is lauryl methacrylate.

11. A polymer according to claim 9 or claim 10, wherein molar ratio is less than 17.

12. A polymer according to any of claims 9 to 11, wherein molar ratio is less than 10.

13. A method of pretreating stained fabric before a wash, the method comprising applying to said fabric, a composition according to any of claims 1-8.