(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 849 354 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
24.06.1998 Bulletin 1998/26

(51) Int. Cl.^{6}: **C11D 1/835**, C11D 1/825

(21) Application number: **96309419.8**

(22) Date of filing: **20.12.1996**

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV RO SI

(71) Applicant: **UNILEVER PLC**
London EC4P 4BQ (GB)

(72) Inventors:
- **Whaley, Christopher**
  Wirral, Merseyside L63 5NS (GB)
- **Khan-Lodhi, Abid Nadim**
  Chester, Cheshire CH2 3HJ (GB)
- **Sams, Philip John**
  South Wirral, Cheshire L64 1TB (GB)
- **Harirchian, Bijan**
  Warren, New Jersey 07059 (US)

(74) Representative:
Ford, Michael Frederick et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(54) Softening compositions

(57) A fabric softening composition contains a first nonionic surfactant which has a head group bearing at least three hydroxyl groups and is preferably from carbohydrate source and a lipophilic aliphatic tail of 10 to 40, especially 16 to 24 carbon atoms, plus a second nonionic surfactant of HLB not above 7, which may incorporate an aliphatic chain of 10 to 40, especially 16 to 24 carbon atoms.

Printed by Xerox (UK) Business Services
2.16.3/3.4

Description

This invention relates to compositions for use in softening of fabrics during the laundry process.

When fabrics are washed they acquire a rougher texture which feels harsh to the skin. Cotton fabrics are particularly affected. To counteract this, many consumers add fabric softening compositions to the rinse water. These fabric softening compositions generally contain a material with a cationic head group and 1 or 2 alkyl chains which are attached to the head group and are of sufficient length to make the cationic material insoluble in water. This cationic material is then deposited on the fabric, and causes the fabric to display a softer feel.

US 5401426 discloses that lactobionamides, which are nonionic surfactant materials, may be used as softening agent in a rinse conditioner composition.

There have also been proposals to formulate a detergent composition so that a fabric softening effect is provided during the washing of the fabrics rather than during a rinsing step. Such softening can be accomplished using certain clays which have ion exchange properties. It has also been proposed to use certain nonionic materials to give fabric softening during washing.

More specifically, GB-A-2185991 teaches a detergent composition in which fabric softening is provided by the incorporation of an alkyl glycoside as the sole softening agent. The composition also contains an anionic surfactant and a nonionic surfactant other than an alkyl glycoside. GB-A-2185992 discloses detergent compositions which also contain an alkyl glycoside jointly with a quaternary ammonium compound, a nonionic surfactant which is not an alkyl glycoside and an anionic surfactant. In both of these documents this nonionic surfactant may be a fatty alcohol containing 8 to 18 carbon atoms ethoxylated with 5 to 30 moles of ethylene oxide.

EP-A-380406 discloses a detergent composition containing anionic and nonionic surfactants together with a sugar ester as a fabric softening agent. The nonionic detergent (apart from the sugar ester) is preferably a fatty alcohol containing 8 to 22 carbon atoms alkoxylated with 3 to 20 moles of lower alkylene oxide. Among such materials it is stated to be preferred that the fatty alcohol has 11 to 15 carbon atoms and is alkoxylated with 5 to 13 lower alkoxy groups.

EP-A-325184 discloses detergent compositions containing acetylated sugar ether. This is stated to provide a fabric softening function as well as acting as a bleach activator and detergency booster.

A number of other documents teach detergent compositions in which an alkyl glycoside is used as one of the surfactants in a surfactant mixture. These documents generally recommend that a detergent composition includes anionic surfactant but in some experimental examples a composition is used which contains alkyl glycoside together with ethoxylated fatty alcohol.

We have now discovered that a surprisingly high degree of fabric softening can be achieved by means of a composition which contains two kinds of nonionic surface active materials (ie. surfactants). The present invention is thus able to provide alternative compositions in which fabric softening can be achieved without the use of cationic materials. Alternatively, the combination of nonionic softeners could be used jointly with cationic softener.

As mentioned above, fabric softening is frequently carried out using a cationic fabric softener which is deposited from rinse water onto the fabric. While these cationic materials are effective and widely used, one problem with them is that they tend to render the softened fabric hydrophobic with the result that the water absorbency of fabrics such as cotton towels is reduced. An advantage of the nonionic materials used in the present invention is that they do not render the softened fabrics hydrophobic to the same extent as cationic fabric softeners and thus provide a better combination of properties.

Rinse conditioner formulations which contain a cationic fabric softening material are generally formulated as aqueous dispersions. It is not a simple matter to formulate an aqueous dispersion which will be stable during storage under varying temperatures, possibly even including exposure to temperatures below freezing. For some markets it is desired or required to use a fabric softening agent which is biodegradable. For cationic fabric softeners this has been achieved by the use of materials containing an ester linkage but it is then necessary to guard against hydrolytic instability of the ester linkage, which is the subject of European Patent 239910).

The use of a combination of nonionic materials in accordance with the present invention can assist in the formulation of a product which is storage stable. Some forms of this invention can provide biodegradability without problems of hydrolytic instability.

Further advantages of a composition based on nonionic surfactants is that it will avoid interfering with detergency when the fabrics are next washed with a detergent composition containing anionic detergent; can assist perfume delivery, and can facilitate the preparation of concentrated products with good physical stability, even when subjected to frost or high ambient temperature.

In a first aspect, therefore, the present invention provides a composition containing

(i) a first nonionic surface active material (which maybe a mixture of such materials) having a head group bearing at least three free hydroxyl groups, and a lipophilic aliphatic radical of 10 to 40 carbon atoms attached to that head group, and

(ii) a second nonionic surface active material (which may also be a mixture of materials) with an HLB value which is not above 7.

In preferred forms of the invention the HLB value of this material is less than 5, e.g. 4.9 and below. It may in particular lie in a range from 0.5 to 5.

The mole ratio of (i) to (ii) is preferably in a range from 5:1 to 1:5. Usually it will be desirable that the mole ratio is from 3:1 to 1:5, and often the second nonionic surfactant will be in molar excess, e.g. a ratio of 1:1 to 1:4.

It is particularly envisaged that the compositions of this invention will be used as rinse conditioner compositions, although it is also possible to formulate a composition within this invention as a detergent composition for washing fabrics, and giving a softening benefit during this washing step.

In another aspect, this invention provides a method of washing and conditioning fabrics by steps of

(i) washing the fabrics in an aqueous wash liquor containing detergent, then

(ii) rinsing the fabrics with water

characterised by adding a composition as set forth above to the rinse water.

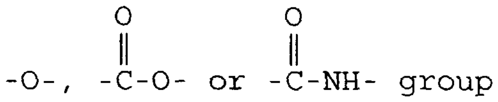
The washing and rinsing of fabrics may be carried out in an automatic washing machine which pumps a majority of the wash liquor away from the fabrics before contacting them with the rinse water. Such a machine may mix the rinse conditioner composition with the rinse water as that water is drawn into the machine - and therefore just before it is brought into contact with the fabrics. However, the above method could also be carried out using a different type of machine, or by hand, such that the wet fabrics are taken out of the wash liquor and allowed to drain before immersion in the rinse water.

The first nonionic surfactant (i) is required to have an aliphatic radical, especially an alkyl or alkenyl chain of at least 10 better at least 12 carbon atoms attached to a head group on which there are at least three hydroxyl groups. These are able to participate in hydrogen bonding, notably hydrogen bonding to cellulosic fabric. Such head groups with a plurality of hydroxyl groups can be provided by residues of sugars e.g. glucose, mannose, galactose, maltose and lactose, or by residues of the reduced counterparts of sugars e.g. mannitol and sorbitol.

This head group may be provided by a single saccharide or reduced saccharide residue or it may be provided by residue of more than one saccharide in which case of course the head group will have a greater number of hydroxyl groups remaining free and able to participate in hydrogen bonding. The head group may be provided by a mixture of saccharides, notably a mixture of mono and disaccharides so that the average number of saccharide residues is not an integer, but lies between 1 and 2. Preferably the head group has an average of at least four hydroxyl groups free and able to participate in hydrogen bonding.

It may not be essential that the head group is derived from saccharide. However, saccharides and reduced saccharides are a convenient source of chemical structures with multiple hydroxyl groups in proximity to one another.

Alkyl and alkenyl chain lengths up to 18 carbon atoms maximum are likely to be used. Chain lengths up to 22 and 24 carbon atoms are possible. Even longer chains are less easy to provide, but can be provided as shorter carbon chains connected through heteroatoms, thus providing a longer alkyl or alkenyl aliphatic chain interrupted by a heteroatom(s) such as in an



$$-O-,\ -\overset{\overset{\displaystyle O}{\|}}{C}-O-\ \text{or}\ -\overset{\overset{\displaystyle O}{\|}}{C}-NH-\ \text{group}$$

A nonionic surfactant having a head group and an alkyl or alkenyl chain in accordance with the parameters indicated above will generally have an HLB value of at least 7. It is preferred that it has an HLB value of at least 8, better at least 10 and the HLB value may well be greater than 12 or 13.

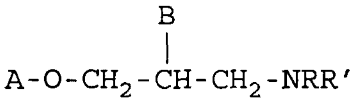
A number of types of nonionic material can serve as the first surfactant. One significant category of materials which may be used as this first nonionic surfactant are alkyl polyglycosides which have the formula

$$RO(R'O)_y(A)_x$$

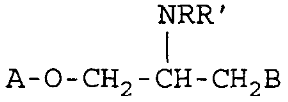
in which R denotes an alkyl or alkenyl group containing from 8 to 22 carbon atoms; each (R'O) contains from 2 to 4 carbon atoms, and is preferably an ethoxy, propoxy, or glyceryl group; each A is a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms; y is from 0 to 12, and x is a number from 1 to 5. Preferably y is from 0 to 3 and will usually be zero; preferably x ranges from 1 or 1.2 up to 2.7 or 3, more preferably from 1.2 up to 1.6 or 2.0.

Alkyl polyglycosides are discussed in a number of documents including European Patents 70074, 75995 and 317614 (WO 88/9369), GB 2185991, US 3598865, US 4011389 and US 4565647. Processes for their preparation are disclosed in US 3598865.

Another category of nonionic surfactants having multiple hydroxy groups at the head, are the glyceroglycolipid surfactants of formulae

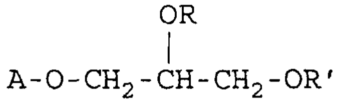


$$A\text{-}O\text{-}CH_2\text{-}\overset{\overset{\displaystyle B}{|}}{CH}\text{-}CH_2\text{-}NRR'$$



$$A\text{-}O\text{-}CH_2\text{-}\overset{\overset{\displaystyle NRR'}{|}}{CH}\text{-}CH_2B$$

and



$$A\text{-}O\text{-}CH_2\text{-}\overset{\overset{\displaystyle OR}{|}}{CH}\text{-}CH_2\text{-}OR'$$

where A is a saccharide residue, B is OH or NRR', R is an alkyl or alkenyl group having from 8 to 24 carbon atoms, and R' is hydrogen or a C_1 to C_4 alkyl group or C_3 to C_7 cycloalkyl.

These surfactants and their synthesis are disclosed in EP-A-550279 and 550280.

Aldobionamides are another category of nonionic surfactants with multiple hydroxy groups in a head group. These compounds may be represented by a general formula

$$ANR_1R_2$$

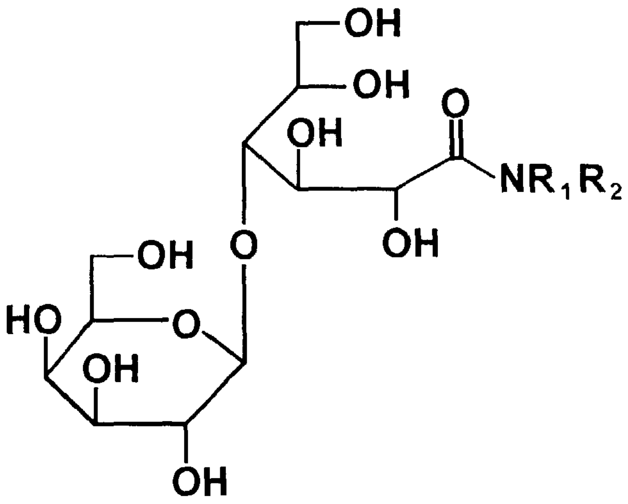
where A is a sugar-based moiety which is a residue of an aldobionic acid and NR_1R_2 replaces the OH group normally extending from the carbonyl group on the aldobionic acid;

R_1 is an alkyl or alkenyl group having from 8 to 24 carbon atoms, and R_2 is hydrogen, C_1 to C_4 alkyl or C_3 to C_7 cycloalkyl. In preferred compounds R_2 is hydrogen.

Aldobionic acids are disaccharides or polysaccharides in which the aldehyde group (generally found at the C_1 position of the sugar) has been replaced by a carboxylic acid. Upon drying they cyclise to aldobionolactones. Aldobionamides are amides of an aldobionic acid (or aldobionolactone).

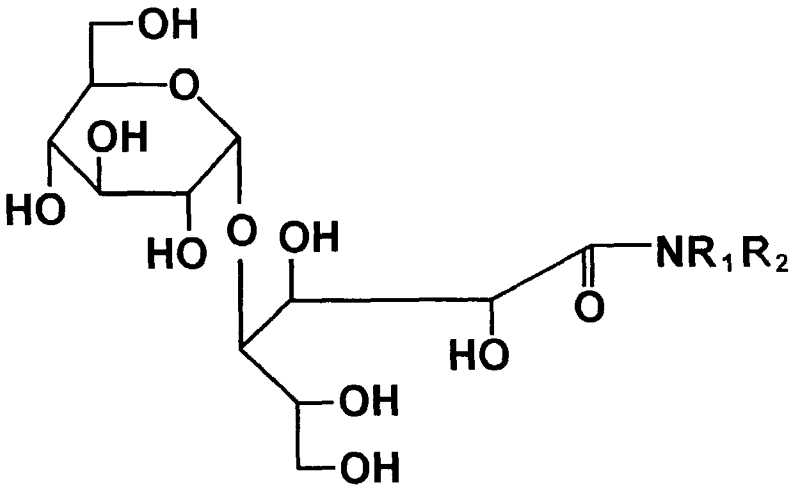
An aldobionamide may be based on compounds comprising two saccharide units or on compounds comprising more than two saccharide units, as long as the terminal sugar in the polysaccharide has an aldehyde group. Disaccharide compounds are preferred.

A specific example of an aldobionamide which may be used for purposes of the invention is the disaccharide lactobionamide set forth below:



wherein R_1 and R_2 are as specified above.

Another preferred aldobionamide is maltobionamide of the following formula:

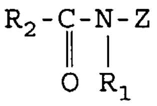


wherein R_1 and R_2 are as specified above.

Other examples of aldobionamides (disaccharides) which may be used include cellobionamides, melibionamides and gentiobionamides.

Aldobionamides and their preparation are described in EP-A-550278.

Another category of surfactants with hydroxyl groups in their head group is the polyhydroxy fatty acid amides discussed in WO 95/30729. These have a general formula



$$R_2-\underset{\underset{O}{\|}}{C}-\underset{\underset{R_1}{|}}{N}-Z$$

wherein R_1 is hydrogen, C_1-C_4 hydroxyalkyl such as 2-hydroxy ethyl or 2-hydroxy propyl, C_1-C_4 alkyl or mixture thereof, R_2 is a C_7-C_{23} alkyl or alkenyl group and Z is an aliphatic radical having at least one carbon chain with at least 3 hydroxyl groups directly connected to the chain, or an alkoxylated derivative of such a chain. Z is preferably derived from a reducing sugar in a reductive amination reaction. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose and xylose. As raw materials to provide the group Z, high dextrose corn syrup, high fructose corn syrup and high maltose corn syrup can be utilised as well as individual sugars listed above. It should be understood that these corn syrups may yield a mixture of sugar components for Z.

A further possibility for the first nonionic surfactant is a sugar ester consisting of a mono, di or polysaccharide esterified on one of its hydroxyl groups with a fatty acid of 8 to 24 carbon atoms. Esters of this general structure are mentioned in WO 89/01480.

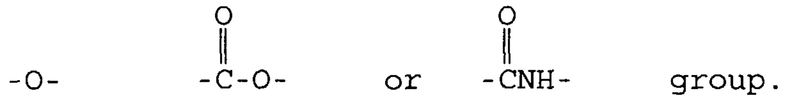
Any of the above nonionic surfactants may be ethoxylated, because of course when an ethylene oxide molecule adds on to a hydroxyl group, it also provides a new hydroxyl group able to take part in hydrogen bonding.

A category of ethoxylated surfactants which can be used as the first nonionic surfactant are the ethoxylated sorbitol esters. These are formed by ethoxylation of sorbitol or its cyclic derivative sorbitan, followed by esterification on one of the available hydroxy groups to introduce one long chain alkyl or alkenyl group, leaving the remaining hydroxy groups free. Compounds of this type are included in the range commercially available under the Registered Trade Mark TWEEN from Aldrich and from ICI United States Inc, but are also available from other suppliers.

Among these various possible compounds useful as the first nonionic surfactant, it is preferred to employ alkyl polyglycosides, glyceroglycolipids or one of the various bionamides. None of these incorporate an ester linkage which could be vulnerable to hydrolysis.

The second nonionic surfactant (ii) must be of low HLB. Generally, the second nonionic surfactant will have a polar group (which may be as small as a single hydroxyl group) attached to a lipophilic hydrocarbyl radical, especially a radical of 10 to 40 carbon atoms incorporating an aliphatic chain of at least 10 carbon atoms. The hydrocarbyl radical may be an alkyl or alkenyl chain, of at least 10, better at least 12 carbon atoms up to 24 carbon atoms. A preferred material is a fatty alcohol containing 11, better at least 12 up to 18 carbon atoms. It is also possible to use an ethoxylated or partially ethoxylated fatty alcohol provided the average degree of ethoxylation is low so as to give an overall low HLB value.

Chain lengths longer than 24 carbon atoms can be provided as shorter carbon chains connected through heteroatoms, thus providing a longer chain (preferably aliphatic) interrupted by a heteratom such as in an



$$-O- \qquad -\overset{\overset{\displaystyle O}{\|}}{C}-O- \qquad \text{or} \qquad -\overset{\overset{\displaystyle O}{\|}}{C}NH- \qquad \text{group.}$$

Other possibilities for a low HLB surface active material include sorbitan esters devoid of ethoxylation such as sorbitan monostearate, HLB 4.7; glycerol esters such as glycerol monostearate, esters of diglycerol and polyglycerol and monoesters of fatty acids with ethylene glycol (HLB typically 2.7-3.6).

Sorbitan esters which do not include ethoxy groups and which are of low HLB are marketed under the trade mark SPAN by ICI United States.

The second nonionic surfactant can be provided by a material with nitrogen in its head group, such as a fatty amine, fatty amide or slightly ethoxylated fatty amide, coconut monoethanolamide is an example of such a material.

If this second, low HLB, material does include some ethylene oxide residues, it will generally be the case that the average degree of ethoxylation is below 3, (e.g. 2.5 or below) so as to give an HLB value below 7; preferably the average degree of ethoxylation is less, such as below 1.8 so as to give an HLB value below 5.

Fatty acids containing 8 or more carbon atoms are also materials of low HLB. However, we have found it difficult to make formulations with them, so we prefer that more than half, better more than 75% of the nonionic detergent of low HLB is other than fatty acid.

Generally it will be desirable that neither of the surfactants includes residues of propylene oxide or any higher alkylene oxide.

In this invention it is desirable that the molar ratio of the first nonionic surfactant to the second, low HLB nonionic surfactant, lies in the range from 5:1 to 1:5, more preferably from 1:1 to 1:4 for most combinations of first and second surfactants.

The two categories of nonionic surfactant should interact with each other to form a fabric-substantive liquid crystalline phase which is not simply micellar in nature. This liquid crystalline phase may be such as to be described as hydrated solid, lamellar (L_α and L_β), hexagonal, cubic or some combination of these possibilities. Particularly preferred are the hydrated solid phase and the L_β phase. The nonionic non-micellar liquid crystalline phase should exist at the concentration of use. In practice the combination of nonionic surfactants should form liquid crystalline phase(s) at an overall concentration of 5% by weight in water at 20°C.

We have found that a liquid crystalline phase can be formed with a wide variety of nonionic surfactants as the first nonionic surfactant (incorporating at least three hydroxy groups in head group) provided the second nonionic surfactant is chosen to have a sufficiently low HLB. The formation of a suitable non-micellar liquid crystal phase can be checked by optical microscopy and other phase behaviour characterisation techniques as described by Small D M, "Handbook of Lipid Research, Vol 4: The Physical Chemistry of Lipids" Plenum Press NY, 1986.

For formation of the liquid crystalline phase it has proved desirable that either the first nonionic surfactant, the second nonionic surfactant or both of them should have an alkyl or alkenyl group of at least 16 carbon atoms.

Thus one or both surfactants may contain tallow alkyl chains rather than coconut alkyl chains or similar synthetic alkyl chains of 11 to 15 carbon atoms.

Frequently the second nonionic surfactant will contain an alkyl or alkenyl chain of at least 16 carbon atoms. Thus, the first nonionic surfactant will desirably be a material which forms an L_β or hydrated solid phase in a system consisting of 2.5% by weight of first nonionic surfactant, 2.5% by weight of stearyl alcohol and 95% by weight of water.

A characteristic of surfactant combinations which provide the preferred L_β or hydrated solid phases is that, an aqueous mixture, containing the nonionic surfactants at a total concentration of 5% by weight, undergoes an endothermic phase transition at a temperature above 0°C, better above 5°C or 10°C. This phase transition is detectable by differential scanning calorimetry and is attributable to "melting" the hydrated solid or the hydrocarbon chains of the L_β phase.

This invention may be embodied in various forms of fabric treatment product. Particularly envisaged is a rinse conditioner formulation for addition to water used for rinsing fabrics after washing. However, the invention can also be embodied in other product forms as will be mentioned again below.

Rinse conditioner compositions of this invention preferably do not include any substantial amount of synthetic anionic detergent because such detergent may dissolve the desired liquid crystalline phase. Water soluble soaps, with chain lengths of 14 or less carbon atoms should be avoided for the same reason. Thus the total amount of synthetic anionic detergent or water-soluble soap (if any) should preferably not exceed 10% by weight of the total amount of the required nonionic surfactants, indeed preferably not exceed 10% by weight of the total softener content.

Preferably, rinse conditioner compositions of this invention do not include other non-bionic surfactants, so that these cannot interfere with the interaction between the specified nonionic surfactants. In particular, the amount of ethoxylated fatty alcohols with five or more ethylene oxide residues may be no more than 10% (better not over 8%) weight of the amount of the said second non-ionic surface active material (ii).

When a composition of the present invention is a rinse conditioner, it may contain the aqueous surfactants as a dispersion or solution in water at a total concentration in the range from 2% to 30% by weight. Rinse conditioners can also be embodied in other forms such as powders and pastes.

A composition which is for use as a rinse conditioner will generally not include any significant amount of detergency builders. Thus, the total amount of insoluble aluminosilicate and water soluble tripolyphosphate (two common detergency builders) will generally be less than 5% by weight of the composition. Usually these will be entirely absent.

A rinse conditioner composition could include a cationic fabric softener, although certain forms of the present invention do not use cationic materials. Therefore, the total quantity of the required nonionic surfactants may be at least half, equal to or greater than the total quantity of cationic softeners, if any. Indeed, the total quantity of the required nonionic surfactants may be more than 3 or 4 times the total quantity, if any, of cationic softeners.

Other constituents which may be incorporated into such a rinse conditioning composition are perfumes, perfume carriers, polymeric thickeners, drape imparting agents, antistatic agents, germicides, fungicides and ironing aids.

Materials which enhance deposition on fabric may usefully be included. Such materials are often polymeric: GB-A-2266100 (case C3443) discloses certain cellulose ethers for this purpose and mentions earlier documents which proposed other materials able to bring about deposition.

A rinse conditioning composition may be manufactured by making a melt of the surfactant materials, adding this to hot water e.g. at a temperature of 70 - 85°C, with mixing, and then mixing the composition with high shear until it is homogenous.

The invention can also be utilised in compositions used on an industrial scale for finishing newly manufactured fabric. Another possible application is products for spraying directly onto fabric, for example when ironing the fabric after it has been dried. Yet another application is in products to be placed in a tumble dryer jointly with the fabrics, so that the nonionic surfactants transfer to the fabrics in their molten state. Conventional products in this category take the form of porous sheets impregnated with cationic fabric softener(s). This invention could be embodied as similar sheets impregnated with the solid surfactants of this invention.

The conditioning composition of the present invention may be coated onto a flexible substrate which is capable of releasing the composition in a tumble dryer. Such a product can be designed for single usage or for multiple uses. One such multi-use article comprises a sponge material releasably enclosing enough of the conditioning composition to effectively impart fabric softness during several drying cycles. The multi-use article can be made by filling a porous sponge with the composition. In use, the composition melts and leaches out through the pores of the sponge to soften and condition fabrics. A single use sheet may comprise the inventive compositions carried on a flexible substrate such as a sheet of paper or woven or non-woven cloth substrate. When such an article is placed in an automatic laundry dryer, the heat, moisture, distribution forces and tumbling action of the dryer removes the composition from the substrate and deposits it on the fabrics. Substrate materials for single use and multiple use articles, and methods of impregnating or coating them are discussed in US-A-5254269 and elsewhere.

Another possible form of product embodying the invention is a detergent composition which is formulated to give fabric softening jointly with fabric washing.

If the composition of the invention is a detergent composition for fabric washing, the composition will usually contain one or more detergency builders, suitably in an amount of from 5 to 60 or 80 wt%, preferably from 20 to 60 wt%. Various classes of detergency builders are well known.

One well known class of builders is the alkali metal (preferably sodium) aluminosilicates. These may suitably be incorporated in amounts of from 5 to 60% by weight (anhydrous basis) of the composition, and may be either crystalline or amorphous or mixture thereof. These materials have the general formula:

$$0.8 - 1.5\ Na_2O.Al_2O_3.\ 0.8 - 6\ SiO_2$$

contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above).

Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1429143 (Proctor & Gamble). The preferred sodium aluminosilicates of this type are the well known commercially available zeolites A and X, and mixtures thereof. Also of interest is the novel zeolite P described and claimed in EP 384070 (Unilever).

Other builders may also be included in a detergent composition, as necessary or desired. Water-soluble builders may be organic or inorganic. Inorganic builders that may be present include alkali metal (generally sodium) carbonate, orthophosphate, pyrophosphate and tripolyphosphate. Organic builders include polycarboxylate polymers, such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphorates, monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono- di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates; and organic precipitant builders such as alkyl- and alkenylmalonates and succinates.

Especially preferred supplementary builders for use jointly with aluminosilicate are polycarboxylate polymers, more especially polyacrylates and acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, especially from 1 to 10 wt%; and monomeric polycarboxylates, more especially citric acid and its salts, suitably used in amounts of from 3 to 20 wt%, more preferably from 5 to 15 wt% by weight of the composition.

Detergent compositions for fabric washing are customarily formulated using anionic surfactant as at least part of the detergent active. However, compositions are known in which the detergent active is wholly or largely nonionic. It is envisaged that the present invention may in particular be embodied in a built detergent composition where nonionic surfactants (including the nonionic surfactants required by this invention) are over 50%, probably at least 80% by weight of all surfactants present. Synthetic anionic surfactants may well be omitted entirely.

In a detergent composition for fabric washing the total amount of surfactant will generally lie in a range from 5 to 50%, more usually 5 to 40% by weight of the composition.

Detergent compositions according to the invention may also contain a bleach system. This preferably comprises one or more peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, which may be employed in conjunction with activators to improve bleaching action at low wash temperatures. If any peroxygen compound is present, the amount is likely to lie in a range from 10 to 25% by weight of the composition.

Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate, advantageously employed together with an activator. Bleach activators, also referred to as bleach precursors, have been widely disclosed in the art. Preferred examples include peracetic acid precursors, for example, tetraacetylethylene diamine (TAED), now in widespread commercial use in conjunction with sodium perborate. The quaternary ammonium and phosphonium bleach activators disclosed in US 4751015 and US 4818426 (Lever Brothers Company) are also of interest. Another type of bleach activator which may be used, but which is not a bleach precursor, is a transition metal catalyst as disclosed in EP-A-458397, EP-A-458398 and EP-A-549272.

Detergent compositions of the invention may also contain one or more of the detergency enzymes known in the art for their ability to degrade and aid in the removal of various soils and stains. Suitable enzymes include the various proteases, cellulases, lipases, amylases, and mixtures thereof.

Further ingredients which can optionally be employed in a detergent composition of the invention include antifoams, fluorescers, anti-redeposition agents such as sodium carboxymethylcellulose, heavy metal sequestrants such as EDTA; perfumes; pigments, colorants or coloured speckles; and inorganic salts such as sodium and magnesium sulphate.

EXAMPLES:

A number of experiments were carried out with the following materials:

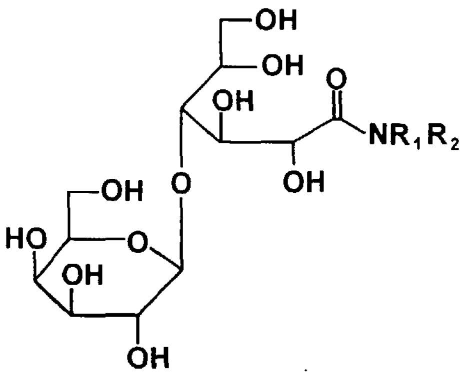
First nonionic surfactant (carbohydrate based)

APG = Glucopon 600CS, an alkylpolyglycoside available from Henkel and of formula

$$RO(A)_x,$$

where R is C_{12} - $_{14}$ alkyl, A denotes a glucose residue and x has an average value of 1.4.

CLB = Cocolactobionamide	}all
TLB = Tallow lactobionamide	}of
HTLB = Hardened tallow lactobioamide	}formula



where R_1 is coconut alkyl, tallow alkyl or hardened tallow alkyl respectively, and R_2 is hydrogen, prepared by the method given in US 5386018.

Second (low HLB) nonionic surfactant:

ROH = hardened tallow fatty alcohol
GMS = glycerol monostearate

Comparison

HT TMAPC = 1-trimethylammonio-2,3-di(hardened tallowoyloxy) propane chloride which is an effective cationic fabric softener.

Various formulations were prepared, as set out in tables below. The formulations all contained 1.33% by weight of the carbohydrate-based first nonionic surfactant. Each formulation was prepared by adding the nonionic surfactant(s) to water at 80-85°C, and allowing the mixture to equilibrate with occasional agitation, after which it was subjected to high shear mixing until homogenous.

After cooling, formulations were tested to evaluate their fabric softening efficacy, diluting the formulations with tap water (10°FH) so that they contained a total of 7.52 grams of the formulation per litre of water. This provided 0.1 g/litre by weight of the first nonionic surfactant. Comparative data were provided by formulations containing one of the carbohydrate-based first nonionic surfactants without a second nonionic surfactant. Here the concentration of each first nonionic surfactant in water was 0.1 g/litre or greater. A control was provided by HT TMAPC formulated at a concentration of 2.5% by weight, and then used at a concentration of 4 g/litre, so as again to provide 0.1 g/litre by weight in the treatment liquor. Another control was water only. The second nonionic surfactants are of such low HLB (i.e. non-polar) that they could not be dispersed in water. Consequently, if an attempt was made to use them without the first nonionic surfactant, the result was the same as with water alone.

The test fabric was terry towelling which had previously been washed to remove any filler or dressing applied during manufacture. The fabric was treated in Tergotometer pots. Three pieces of terry towelling (8cm x 8cm, 40g total weight) were added to each tergotometer pot. The treatment liquor was then dosed onto the cloths which were treated for 5 minutes while the agitator in the tergotometer rotated at 65 rpm, then spin dried to remove excess liquor and line dried overnight.

Softening of the fabrics was assessed by an expert panel of 4 people. Each panel member assessed cloths treated with test or comparative formulations, together with control cloths respectively treated with HT TMAPC or water only. Panel members were asked to assess softness on an 8 point scale, where a score of 8 represents unsoftened fabric and a score of 2 represents extremely soft fabric. Thus, lower values are indicative of better softening. Softness scores were calculated by averaging the scores of the individual panellists.

The results are tabulated below:

Ex. No	Formulations providing 0.1g APG per litre in rinse			
	APG (wt%)	ROH (wt%)	APG:ROH (molar ratio)	Softness Ranking
1	1.33	1.42	1:1.75	3
2	1.33	1.63	1:2	3.25
3	1.33	1.85	1:2.25	3.75
4	1.33	2.05	1:2.5	4.25
C	1.33	None		7.0

Ex. No	Formulations providing 0.1g CLB per			litre in rinse
	CLB (wt%)	ROH (wt%)	CLB:ROH (molar ratio)	Softness Ranking
5	1.33	1.17	1:2	3.25
6	1.33	1.34	1:2.25	3.75
7	1.33	1.49	1:2.5	3.5
8	1.33	1.79	1:3	3.5
	CLB (wt%)	GMS (wt%)	CLB:GMS (molar ratio)	Softness Ranking
9	1.33	1.46	1:1.75	4.5
10	1.33	1.67	1:2	5.25
11	1.33	2.09	1:2.5	5.25
12	1.33	2.50	1:3	6.25

Ex. No	Formulations providing 0.1g TLB per litre in rinse			
	TLB (wt%)	Second nonionic	Molar Ratio	Softness Ranking
13	1.33	ROH	1:1.33	2.75
14	1.33	GMS	1:0.5	3.25

(continued)

Ex. No	Formulations providing 0.1g TLB per litre in rinse			
	TLB (wt%)	Second nonionic	Molar Ratio	Softness Ranking
F	1.33	None		7.25

Ex. No	Formulations providing 0.1g HTLB per litre in rinse	
	HTLB:GMS (molar ratio)	Softness Ranking
15	1:0.5	3.5
16	1:1	3.75
17	1:1.5	2.2
18	1:2	3.5
	HTLB:ROH	Softness Ranking
19	1:0.5	3.5
20	1:1	3.75
21	1:1.5	2.25
22	1:2	3.5

Ex. No	Formulation provides in rinse	Softness Ranking
Control A	0.1g HT TMAPC per litre	2.75
Control B	Water only	8
D	0.2g CLB per litre	6.5
E	2.0g CLB per litre	6.5

In a second experiment some of the treated test cloths were divided into strips 3cm wide. These were tested for water absorbency by dipping an end portion in demineralised water and measuring the height of water rise up the strips after 15 minutes. The results are in the following table and show a dramatic difference from the HT TMAPC control.

Ex. No	Formulation		Wicking Height (mm)
	provides 0.1g/litre in rinse	Second nonionic	
1	1.33% APG	1.42% ROH	52
5	1.33% CLB	1.17% ROH	66

(continued)

Ex. No	Formulation		Wicking Height (mm)
	provides 0.1g/litre in rinse	Second nonionic	
Control A	HT TMAPC	none	3

In further experiments, pairs of first and second nonionic surfactants were tested at varying concentrations in the rinse liquor. Softness and wicking height were assessed as described for the Examples above. The results were:

Dose (g/l) in rinse liquor	Softness Ranking	Wicking Height (cm)
HTLB:GMS (1:1.5 mole ratio)		
0.05	4	10.0
0.1	2.5	10.0
0.2	2	9.2
HTLB:**ROH** (1:1.5 mole ratio)		
0.05	4.5	11.3
0.1	3	10.5
0.2	2	10.5
TLB:**ROH** (1:1.33 mole ratio)		
0.05	7	14.4
0.1	5.5	14.4
0.02	3.25	12.0
CLB:**ROH** (1:2 mole ratio)		
0.05	4.5	14.2
0.1	3	12.7
0.2	2	11.8

Claims

1. A composition containing

    (i) a first nonionic surfactant or mixture of surfactants, having a head group bearing at least three free hydroxyl groups, and having a lipophilic aliphatic radical of 10 to 40 carbon atoms attached to that head group, and
    (ii) a second nonionic surfactant or mixture of surfactants with an HLB value which is not above 7.

2. A composition according to Claim 1 wherein the HLB value of the second nonionic surfactant is less than 5.

3. A composition according to claim 1 or claim 2 wherein the head group of the first nonionic surfactant bears at least four free hydroxyl groups.

4. A composition according to claim 1, claim 2 or claim 3 wherein the aliphatic radical of the first nonionic surfactant is an alkyl or alkenyl chain of 12 to 24 carbon atoms.

5. A composition according to any one of the preceding claims wherein the mole ratio of (i) to (ii) is in a range from 5:1 to 1:5.

6. A composition according to claim 3 wherein the surface active materials (i) and (ii) when at a total concentration of 5% by weight in water at 20°C form a liquid crystalline phase.

7. A composition according to any one of the preceding claims wherein the first nonionic surface active material (i) has an HLB exceeding 11.

8. A composition according to any one of claims 1 to 7 which is an aqueous suspension for use as a rinse conditioner.

9. A composition according to claim 8 which contains from 2 to 30% of the said nonionic surfactants.

10. A porous sheet impregnated with a composition according to any one of claims 1 to 7.

11. A composition according to any one of claims 1 to 7 which is a detergent composition containing builder.

12. A method of washing and conditioning fabrics by steps of

(i) washing the fabrics in an aqueous wash liquor containing detergent, then
(ii) rinsing the fabrics with water characterised by adding a composition according to any one of claims 1 to 7 to the rinse water.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 9419

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X A	US 5 474 691 A (SEVERNS JOHN C.) 12 December 1995 * abstract * * column 13, line 20 - column 14, line 16 * * column 15, line 50 - column 18, line 57 * * claims 1,2,25 *	1-5,7,9, 10 8,12	C11D1/835 C11D1/825
X	WO 96 29977 A (HENKEL CORP.) 3 October 1996 * page 2, line 24 - page 9, line 35 * * page 13, line 19 - line 27 * * page 16, line 22 - line 37 * * claims 1-53,57,58 *	1-5,7, 10,11	
X	DE 44 08 503 A (HENKEL KGAA.) 21 September 1995 * page 2, line 39 - page 3, line 17 * * claims *	1,2,4,5	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
D,X	EP 0 550 280 A (UNILEVER PLC.) 7 July 1993 * page 6, line 22 - line 28 * * claims 1-12,14,21,22 *	1-4,7-9, 11	C11D
X	EP 0 694 608 A (THE PROCTER & GAMBLE CO.) 31 January 1996 * page 3, line 30 - page 4, line 49 * * claims 1-6 *	1-5,11	
X	WO 92 06160 A (THE PROCTER & GAMBLE CO.) 16 April 1992 * page 6, line 18 - page 10, line 34 * * claims 1-10 * -/--	1-5,7,11	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 May 1997	Serbetsoglou, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 9419

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)
D,A	US 5 401 426 A (GERLING KLAUS-GUENTER ET AL.) 28 March 1995 * abstract; claims 1-11 *	1,8	
D,A	GB 2 185 991 A (COLGATE-PALMOLIVE CO.) 5 August 1987 * page 2, line 9 - page 3, line 1 * * claims 1-11,17 *	1,8,12	
D,A	EP 0 380 406 A (COLGATE-PALMOLIVE CO.) 1 August 1990 * page 4, line 47 - line 50 * * page 5, line 15 - line 24 * * claims 1,10-14 *	1,3,4,8,11,12	
D,A	EP 0 325 184 A (COLGATE-PALMOLIVE CO.) 26 July 1989 * abstract; claims 1-11 * * page 8, line 5 - line 49 *	1,2,8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	29 May 1997	Serbetsoglou, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)