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Detergent composition.

A detergent composition for fabric washing contains dialkylsulphosuccinate whose alkyl groups contain 12 to 20 carbon atoms and are preferably both C<sub>7</sub>. This is accompanied by nonionic surfactant of HLB below 10.5 and detergency builder.

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## **DETERGENT COMPOSITION**

This invention relates to a detergent composition for cleaning soiled materials using a built aqueous wash liquor, and in particular but not exclusively to a detergent composition for washing fabrics.

Fabric washing compositions contain, as an essential ingredient, a detergent active system whose role is to assist in the removal of soil from fabric and its suspension in the wash liquor. Suitable detergent active materials fall into a number of classes, including anionic, nonionic and cationic materials and marketed products contain materials selected from one or more of these classes.

A known group of compounds which fall into the class of anionic detergent active materials are the dialkylsulphosuccinates. These materials have been used as detergent active materials in products for other cleaning purposes, such as in dishwashing compositions. However, dialkylsulphosuccinates have not found favour in detergent compositions intended to give a built wash liquor, such as compositions intended for washing fabrics.

We have now discovered that enhanced performance from dialkylsulphosuccinates in solution in a built wash liquor can be achieved by specific selection of alkyl substituent groups and by mixing with a specific nonionic detergent active material. Thus, according to the invention there is provided a detergent composition comprising:

1 to 50% by weight of a surfactant system which is a mixture of:

- i) a dialkylsulphosuccinate, the alkyl substituent groups of which contain at least 4 carbon atoms each and contain 12 to 20 carbon atoms in total; and
- ii) an alkoxylated nonionic surfactant which has an HLB value not above 10.5, preferably below this as indicated below, the ratio of i) to ii) lying between 7:1 and 1:7; and

5 to 60% by weight of detergency builder.

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The balance of any detergent composition may be selected from water and other ingredients conventionally encountered in detergent compositions.

According to a second aspect of this invention there is provided a method of washing which comprises contacting soiled material with a built aqueous wash liquor which is a solution of surfactant system comprising a mixture of:

- i) dialkylsulphosuccinate, the alkyl substituent groups of which contain at least 4 carbon atoms each and contain 12 to 20 carbon atoms in total; and
- ii) an alkoxylated nonionic surfactant which has an HLB value not above 10.5; the ratio of i) to ii) lying between 7:1 and 1:7.

For a given total number of carbon atoms in the two alkyl groups of the sulphosuccinate, it is advantageous that the alkyl groups contain the same number of carbon atoms so that the dialkylsulphosuccinate is symmetrical. It is then possible for other dialkylsulphosuccinate molecules, with alkyl substituents of different chain length or with unsymmetrical substituents, to be present also. It is preferred however, that of all dialkylsulphosuccinate molecules present in the composition at least 55% of the alkyl chains, preferably at least 70% of the alkyl chains are of the same length.

We have found that the optimum chain length for the alkyl substituents is seven carbon atoms, especially when these  $C_7$  alkyl groups are of straight chain formation.

Suitable nonionic surfactants which may be used are alkoxylated materials which are the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific alkoxylated nonionic detergent compounds are alkyl ( $C_6$ - $C_{22}$ ) phenols- ethylene oxide condensates, the condensation products of aliphatic ( $C_8$ - $C_{18}$ ) primary or secondary linear or branched alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine.

Alkylene oxide adducts of fatty materials are preferably used as the nonionic surfactants. The number of alkylene oxide groups per molecule has a considerable effect upon the HLB of the nonionic surfactant. The chain length and nature of the fatty material is also influential, and thus the preferred number of alkylene oxide groups per molecule depends upon the nature and chain length of the fatty material.

As indicated above, the nonionic surfactant has an HLB value not above 10.5. It is preferred that the nonionic surfactant has an HLB value below 10, preferably below 9.

The surfactant system may include other surfactant materials in addition to the specified dialkylsul-phosuccinate and nonionic materials. These other surfactant materials may be selected from anionic detergent active materials, zwitterionic or amphoteric detergent active materials or mixtures thereof.

Preferably, any such further surfactant materials are present at a level which is no more than a minor

amount of the total amount of surfactant in the composition.

For compositions in which the dialkylsulphosuccinate has alkyl groups with a total of 14 carbon atoms or less, it is possible to have electrolyte present in the wash liquor, without detriment to detergency. There may well be enough electrolyte to give a concentration of at least 0.05 molar, preferably at least 0.1 molar when the composition is used at a concentration of 1 g/litre.

If more than half of the sulphosuccinate has alkyl groups with a total of 16 carbon atoms, or more, it is very desirable to restrict the concentration of electrolyte in the wash liquor to not over 0.05 molar, preferably 0.035 molar. (The concentration of surfactant in the wash liquor is likely to be from 0.05 to 2.0 g/litre, preferably 0.1 to 1.0 g/litre.

More specifically, if more than half of the sulphosuccinate has alkyl groups with a total of 16 or more carbon atoms, it is desirable that the ionic strength of the wash liquor should not exceed 0.05 moles/litre preferably 0.035 moles/litre.

lonic strength is related to concentration but takes account of the numbers of ions in a molecule and multiple charged ions.

lonic strength is calculated from the molarity (m) of each ionic species present in solution and the charge (z) carried by each ionic species. Ionic strength (I) is one half the summation of m.z2 for all ionic species present i.e.

 $I = \frac{1}{2} \Sigma \text{ m.z}^2$ 

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For a salt whose ions are both univalent, ionic strength is the same as the molar concentration. This is 20 not so where more than two ions or multiple charges are involved. For instance a 1 molar solution of sodium carbonate contains 2 moles/litre of sodium ions and 1 mole/litre of carbonate ions carrying a double charge. Ionic strength is given by:

 $I = \frac{1}{2} [2(1^2) + 1 \times (2^2)] = 3$  moles/litre

A description of ionic strength is given in "Physical Chemistry" by Walter J. Moore, 4th Ed. 1963.

The level of electrolyte in the wash liquor is not, in practice, a parameter over which the domestic user of a fabric washing product exercises direct control. It is determined, inter alia by the level of water-soluble salts present in the product and the recommended dosage for that product. Thus forms of the present invention using alkyl groups with a total of 16 or more carbon atoms are of particular value in two circumstances, i.e. i) where recommended dosage levels are low, as for example in North America, and ii) where the product contains high levels of water-insoluble material, as for example where the product contains a water-insoluble detergency builder material. The only water-insoluble detergency builder material which has been used extensively is zeolite, a crystalline aluminosilicate ion-exchange material, but the invention would also be of value to products containing any other water-insoluble builder material. Detergent compositions are generally used in amounts greater than 1 gram/litre, usually in the range from 4 g/litre to 10 g/litre.

The detergent composition of this invention may comprise from 1% to 50% by weight of the surfactant system. Preferred is that the amount of the surfactant system should range from 2% better 4 or even 6% by weight up to 30 or 35%.

Any electrolyte which is present will generally be a water-soluble salt. This may be such a salt as will provide a benefit in terms of the fabric washing process such as a water-soluble detergency builder salt or a water-soluble alkaline salt. Alternatively the electrolyte may be constituted by a water-soluble filler salt such as sodium sulphate or sodium chloride. Salts from all three classes may be present.

Generally, compositions according to the invention will contain some electrolyte, for example ranging from 10% up to 90% by weight of the composition, so as to give an ionic strength of at least  $5 \times 10^{-3}$ moles/litre, more likely at least 0.01 moles/litre in a wash liquor. A wash liquor may have an electrolyte concentration of at least 0.01 molar.

When a low level of electrolyte is required the composition may comprise not more than 60% by weight, preferably not more than 40% by weight of water-soluble alkali metal salts, and may also contain from 10% to 60% by weight, preferably from 20% to 50% by weight, of a water-insoluble detergency builder material.

It is desirable that the compositions according to the invention be approximately neutral or preferably alkaline, that is when the composition is dissolved in an amount to give surfactant concentration of 1 g/l in distilled water at 25°C the pH should desirably be at least 6, preferably at least 8 and yet more preferably at least 10. To this end the compositions may include a water-soluble alkaline salt. This salt may be a detergency builder (as described in more detail below) or a non-building alkaline material.

The amount of detergency builder can range from 5 to 60% by weight. It may be preferred to use from at least 10% by weight to 50% by weight. The detergency builder may be any material capable of reducing the level of free calcium ions in the wash liquor and will preferably provide the compositions with other

beneficial properties such as the generation of an alkaline pH and the suspension of soil removed from the fabric.

Examples of phosphorus-containing inorganic detergency builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, orthophosphates and hexametaphosphates.

Examples of non-phosphorus-containing inorganic detergency builders, when present, include water-soluble alkali metal carbonates, bicarbonates, silicates and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate (with or without calcite seeds), sodium and potassium bicarbonates and silicates.

Examples of organic detergency builders, when present, include the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, polyacetyl carboxylates and polyhydroxsulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid.

Apart from the ingredients already mentioned, a number of optional ingredients may also be present. Examples of other ingredients which may be present in the composition are polymers containing carboxylic or sulphonic acid groups in acid form or wholly or partially neutralised to sodium or potassium salts, the sodium salts being preferred. Preferred polymers are homopolymers and copolymers of acrylic acid and/or maleic acid or maleic anhydride. Of especial interest are polyacrylates, acrylic/maleic acid copolymers, and acrylic phosphinates.

Suitable polymers, which may be used alone or in combination, include the following: polyacrylic acids, for example Versicol (Trade Mark) E5, E7 and E9 ex Allied Colloids, Narlex (Trade Mark) LD 30 and LD 34 ex National Adhesives and Resins Ltd, Acrysol (Trade Mark) LMW-10, LMW-20, LMW-45 and A1-N ex Röhm & Haas, and Sokalan (Trade Mark) PA-20, PA-40, PA-70 and PA-110 ex BASF; ethylene/maleic acid copolymers, for example the EMA (Trade Mark) series ex Monsanto;

methyl vinyl ether/maleic acid copolymers, for example, Gantrez (Trade Mark) AN 119 and AN 149 ex GAF Corporation;

acrylic acid/maleic acid copolymers, for example, Sokalan (Trade Mark) CP4, CP5 and CP7 ex BASF, and the Alcosperse (Trade Mark) series ex Alco;

acrylic phosphinates, for example, DKW (Trade Mark) 125 ex National Adhesives and Resins Ltd, and the Belsperse (Trade Mark) series ex Ciba-Geigy.

The molecular weights of homopolymers and copolymers are generally 1000 to 150,000, preferably 1500 to 100,000. The amount of any polymer may lie in the range from 0.5 to 5% by weight of the composition. Other suitable polymeric materials are cellulose ethers such as carboxy methyl cellulose, methyl cellulose, hydroxy alkyl celluloses, and mixed ethers, such as methyl hydroxy ethyl cellulose, methyl hydroxy propyl cellulose, and methyl carboxy methyl cellulose. Mixtures of different cellulose ethers, particularly mixtures of carboxy methyl cellulose and methyl cellulose, are suitable. Polyethylene glycol of molecular weight from 400 to 50,000, preferably from 1000 to 10,000, and copolymers of polyethylene oxide with polypropylene oxide are suitable as also are copolymers of polyacrylate with polyethylene glycol. Polyvinyl pyrrolidone of molecular weight of 10,000 to 60,000 preferably of 30,000 to 50,000 and copolymers of polyvinyl pyrrolidone with other poly pyrrolidones are suitable. Polyacrylic phosphonates and related copolymers of molecular weight 1000 to 100,000, in particular 3000 to 30,000 are also suitable.

Further examples of other ingredients which may be present in the composition include fabric softening agents such as fatty amines, fabric softening clay materials, lather boosters such as alkanolamides, particularly the monoethanolamides derived from palm kernel fatty acids and coconut fatty acids, lather depressants, oxygen-releasing bleaching agents such as sodium perborate and sodium percarbonate, peracid bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid, inorganic salts such as sodium sulphate, and, usually present in very minor amounts, fluorescent agents, perfumes including deodorant perfumes, enzymes such as cellulases, proteases and amylases, germicides and colourants

The detergent compositions according to the invention may be in any suitable form including powders, bars, liquids and pastes. For example suitable liquid compositions may be non-aqueous or aqueous, the latter being either isotropic or lamellar structured. The compositions may be prepared by a number of different methods according to their physical form. In the case of granular products they may be prepared by dry-mixing or coagglomeration. Dialkylsulphosuccinate is preferably not subjected to conventional spraydrying, because it is hydrolytically unstable. The specified nonionic surfactants can be liquified by melting or solvent dissolution and sprayed onto preformed base powder granules.

An example of a granular detergent composition which can be used at a dosage of 6 g/litre to yield an ionic strength of 0.023 mole/litre is:

|    |   | % by weight     |
|----|---|-----------------|
| 5  | Dialkylsulphosuccinate                                  | 15              |
|    | Nonionic surfactant                                     | 6               |
| 10 | Zeolite   | 40              |
|    | Alkaline silicate                                       | 3               |
|    | Polyacrylate  | 4               |
| 15 | Sodium carbonate  | 6               |
|    | Sodium sulphate   | 10              |
| 20 | Water and minor constituents which are not electrolytes | balance to 100% |

The invention will now be described in more detail in the following non-limiting examples.

## **EXAMPLES**

A number of examples and comparative examples were carried out. These examples compared the soil removal (specifically triolein removal) from fabrics using various compositions.

The experimental conditions were the same in each case. Wash liquors were used to wash a fabric load in a Tergotometer at a liquor to cloth ratio of 40:1. Washing was carried out at 40° C for 20 minutes, with agitation at 70rpm. The load consisted of a number of polyester test cloths to which had previously been applied an amount of C<sup>14</sup> labelled triolein. Measurement of the level of labelled triolein after washing, using radiotracer techniques gave an indication of the degree of detergency (soil removal).

Various dialkylsulphosuccinate compounds were used. All had straight alkyl chains. The material indicated below as  $C_6/C_8$  was a mixture consisting of molecules with one  $C_6$  and one  $C_8$  alkyl group, molecules with two  $C_6$  alkyl groups and molecules with two  $C_7$  alkyl groups, in a 2:1:1 ratio.

Nonionic surfactants were  $C_{12}$  alcohol ethoxylated with differing average amounts of ethylene oxide, as stated below.

In a first series of experiments, for each tested composition, wash liquors were made up containing 1 g/l of the surfactant mixture and 0.1 molar sodium chloride (to represent the electrolyte level which would derive from other components of the composition in practice) at a pH of 6.5. For sodium chloride electrolyte concentration and ionic strength are the same.

In a second series of experiments wash liquors again contained 1 g/l of the surfactant mixture and had an ionic strength of 0.1 mole/litre but the electrolyte was 1.8 g/l sodium tripolyphosphate, 0.48 g/l sodium silicate and 3.9 g/l sodium chloride, giving a pH of 10.

Results of both series of experiments are given in Table 1 below.

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TABLE 1

|    | Example No  | 1                                     | 2                                    | 3                            | 4                                    |
|----|---|---------------------------------------|--------------------------------------|------------------------------|--------------------------------------|
| 5  | pH Alkyl groups on sulphosuccinate Ethylene oxide residues on C <sub>12</sub> alcohol | 6.5<br>diC <sub>7</sub> straight<br>3 | 10<br>diC <sub>7</sub> straight<br>3 | $6.5$ $C_6/C_8$ straight $3$ | 10<br>diC <sub>8</sub> straight<br>3 |
|    | Sulphosuccinate:  |                                       |                                      |                              |                                      |
| 10 | Nonionic ratio  | % triolein removal                    |                                      |                              |                                      |
|    | 100:0   | 18.2                                  | 62.0                                 | 11.0                         | 28.8                                 |
|    | 87.5:12.5   | -                                     | -                                    | 11.9                         | 28.8                                 |
|    | 75:25   | 27.4                                  | 69.9                                 | 13.1                         | 25.9                                 |
|    | 62.5:37.5   | 18.6                                  | 71.3                                 | 6.9                          | 21.7                                 |
| 15 | 50:50   | 6.7                                   | 68.8                                 | 5.9                          | 12.5                                 |
|    | 37.5:62.5   | -                                     | 39.0                                 | 5.0                          | -                                    |
|    | 25:75   | 4.3                                   | 4.8                                  | -                            | 4.0                                  |
|    | 0:100   | 0.5                                   | 1.0                                  | •                            | -                                    |

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A further series of experiments was carried out at a lower ionic strength of 0.02 mole/litre. Results are set out in Table 2 below.

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TABLE 2

|    | Example No  | 5                        | 6                        | 7                           | 8                       | 9                                    |
|----|---|--------------------------|--------------------------|-----------------------------|-------------------------|--------------------------------------|
| 30 | pH Alkyl groups on sulphosuccinate Ethylene oxide residues on C <sub>12</sub> | $6.5$ $C_6/C_8$ straight | $6.5$ $C_6/C_8$ straight | $10$ $C_6/C_8$ straight $3$ | $10$ $C_6/C_8$ straight | 10<br>diC <sub>8</sub> straight<br>3 |
| 35 | alcohol   |                          |                          |                             |                         |                                      |
|    | Sulphosuccinate:  |                          |                          |                             |                         |                                      |
|    | Nonionic ratio  | % triolein removal       |                          |                             |                         |                                      |
|    | 100:0   | 6.8                      | 6.8                      | 11.0                        | 11.0                    | 31.9                                 |
|    | 80:20   | 7.3                      | 4.8                      | 21.3                        | 10.1                    | 34.4                                 |
| 40 | 60:40   | 10.1                     | 4.5                      | 38.3                        | 14.9                    | 42.4                                 |
|    | 50:50   | 8.7                      | 5.5                      | -                           | -                       | •                                    |
|    | 40:60   | 5.3                      | 8.5                      | 44.8                        | 27.5                    | 35.4                                 |
|    | 20:80   | 4.6                      | 30.6                     | 15.8                        | 53.1                    | 17.6                                 |
| 45 | 0:100   | -                        | 59.9                     | -                           | 77.5                    | -                                    |

Comparison of Examples 5 and 6 and comparison of Examples 7 and 8, all in Table 2, shows that greater detergency occurs with a mixture of the low HLB nonionic and dialkylsulphosuccinate than with either of these components alone. This synergistic effect is not observed with the higher HLB nonionic. The same synergistic effect is observed with Examples 1 to 3 in Table 1.

It can be seen from the Examples that the synergistic effect is obtained both at approximately neutral pH and at alkaline pH, and under both low electrolyte (0.02 mole/litre) and higher electrolyte (0.1 mole/litre) conditions, except however in the case of diC<sub>8</sub> alkylsulphosuccinate for which synergy is observed at low electrolyte only (Example 9).

It can be seen also that synergy generally occurs at sulphosuccinate:nonionic ratios between 1:4 and 4:1, and that diC<sub>7</sub> alkyl sulphosuccinate gives best performance.

Further examples demonstrate liquid compositions built with sodium citrate, as set out in Table 3 below.

The compositions were added to water in an amount of 12 g/l, to provide wash liquors containing 1.7 g/l surfactant, an electrolyte concentration of  $1.18 \times 10^{-2}$  molar and anionic strength of  $3.42 \times 10^{-2}$  moles/litre. The removal of labelled triolein was measured as set out above and the result is included in Table 3. The sulphosuccinate used had  $C_7$  straight alkyl groups, the nonionic surfactant was  $C_{12}$  alcohol ethoxylated with an average of 3 ethylene oxide residues.

TABLE 3

| 1 | n |  |
|---|---|--|
| f | v |  |

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| Example No  | 10                                   | 11                                      | 12                              |  |
|---|--------------------------------------|---|---------------------------------|--|
| Constituent   | %                                    |   |                                 |  |
| DiC <sub>7</sub> alkylsulphosuccinate C <sub>12</sub> 3EO Glycerol Borax Sodium citrate Sodium chloride Ethanol Water | 13<br>-<br>4<br>1.3<br>10<br>3<br>30 | 6.5<br>6.5<br>4<br>1.3<br>10<br>3<br>30 | 13<br>4<br>1.3<br>10<br>3<br>30 |  |
| Triolein removal was:   |                                      |   |                                 |  |
| Example 10  | sulphosuccinate only                 |   | 11.0                            |  |
| Example 11  | sulphosuccinate + nonionic           |   | 71.2                            |  |
| Example 12  | nonionic only                        |   | 1.1                             |  |

Similar examples were carried out using slightly different liquid formations as detailed in Table 4 below, using 6 g/l to make up wash liquors containing 0.85 g/l surfactant, with an electrolyte concentration of 6.26 x  $10^{-3}$  mole/litre and an ionic strength of 1.16 x  $10^{-2}$  mole/litre.

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TABLE 4

| 40 |  |
|----|--|
| 45 |  |
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| Example No  | 13                                  | 14                                     | 15                                  |  |
|---|-------------------------------------|--|-------------------------------------|--|
| Constituent   | % by weight                         |  |                                     |  |
| DiC <sub>7</sub> alkylsulphosuccinate C <sub>12</sub> 3EO Glycerol Borax Sodium citrate Sodium chloride Ethanol | 13<br>-<br>1.3<br>4<br>7<br>4<br>30 | 6.5<br>6.5<br>1.3<br>4<br>7<br>4<br>30 | -<br>13<br>1.3<br>4<br>7<br>4<br>30 |  |
| Water   | balance to 100%                     |  |                                     |  |
| Triolein removal was:   |                                     |  |                                     |  |
| Example 13  | sulphosuccinate only                |  | 2.1                                 |  |
| Example 14  | sulphosuccinate + nonionic          |  | 45.7                                |  |
| Example 15  | nonionic only                       |  | 3.1                                 |  |

The synergy between the dialkylsulphosuccinate and the nonionic surfactant is apparent.

### 5 Claims

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- 1. A detergent composition comprising:
- 1 to 50% by weight of a surfactant system which is a mixture of:
- i) dialkylsulphosuccinate, the alkyl substituent groups of which contain at least 4 carbon atoms each and contain 12 to carbon atoms in total; and
- ii) an alkoxylated nonionic surfactant which has an HLB value not above 10.5;

the ratio of i) to ii) lying between 7:1 and 1:7, and

- 5 to 60% by weight of detergency builder.
  - 2. A composition according to claim 1 wherein the ratio of i) to ii) lies between 4:1 and 1:4.
- 3. A composition according to claim 1 or claim 2 wherein at least half of the sulphosuccinate has alkyl groups with a total of 12 to 16 carbon atoms.
- 4. A composition according to claim 3 wherein at least half of the sulphosuccinate has alkyl groups containing 7 carbon atoms in straight chain formations.
- 5. A composition according to any one of the preceding claims containing at least 10% by weight of detergency builder.
- 6. A composition according to any one of the preceding claims containing at least 10% by weight of water-soluble electrolyte.
  - 7. A composition according to any one of the preceding claims which contains at least one of:

fabric softening agents

5 fabric softening clay

lather booster

lather depressant

bleaching agent

fluorescent agent

o perfume, and

enzyme.

- 8. A method of washing which comprises contacting soiled material with a built aqueous wash liquor which is a solution of surfactant system comprising a mixture of:
- i) dialkylsulphosuccinate, the alkyl substituent groups of which contain at least 4 carbon atoms each and contain 12 to carbon atoms in total; and
  - ii) an alkoxylated nonionic surfactant which has an HLB value not above 10.5;

the ratio of i) to ii) lying between 7:1 and 1:7.

- 9. A method according to claim 8 wherein the wash liquor contains electrolyte to give an electrolyte concentration of at least 0.01 molar.
  - 10. A method according to claim 8 or claim 9 wherein the wash liquor has a pH of at least 6.

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