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(54) **Detergent compositions.**

(57) A detergent composition having improved antiredeposition properties on polyester/cotton fabrics contains a polyalkylene oxide/vinyl acetate graft copolymer, and includes in its surfactant system one or more nonionic surfactants of low cloud point.

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**Description**

# DETERGENT COMPOSITIONS

## TECHNICAL FIELD

The present invention relates to fabric washing detergent compositions having improved antiredeposition properties.

## BACKGROUND AND PRIOR ART

Redeposition of soil removed from washed articles back onto the articles themselves is a well-known problem which is of particular significance with textile fabrics, and many solutions to this problem have been suggested. Classically, sodium carboxymethyl cellulose was incorporated into fabric washing compositions, and that compound is still used today. More recently, copolymers of ethylene or vinyl methyl ether and maleic anhydride, copolymers of acrylic acid and maleic anhydride, and homopolymers of acrylic acid have been suggested in the patent literature; see, for example, GB 1 269 848 (Procter & Gamble) and GB 1 460 893 (Unilever).

Another polymeric material that has been suggested for improving soil suspension is polyvinylpyrrolidone. EP 262 897A (Unilever) discloses detergent compositions containing polyvinylpyrrolidone, an anionic surfactant, and a nonionic surfactant system having a hydrophilic-lipophilic balance (HLB) of not more than 10.5.

EP 219 048A (BASF) discloses the use of graft copolymers of polyalkylene oxide with vinyl acetate as greying inhibitors in the washing and post-wash treatment of synthetic textile fabrics.

We have now discovered that detergent compositions containing a graft copolymer of this type in conjunction with a low-HLB nonionic surfactant system exhibit surprisingly enhanced soil suspension (antiredeposition) properties on polyester/cotton fabrics.

## DEFINITION OF THE INVENTION

The present invention provides a detergent composition comprising:

(a) from 2 to 50% by weight of a detergent active system which amount includes a nonionic surfactant system consisting of one or more nonionic surfactants, the nonionic surfactant system having a cloud point (as hereinafter defined) not higher than 40°C; and

(b) from 0.1 to 3% by weight of a graft copolymer of (i) polyethylene, polypropylene or polybutylene oxide with (ii) vinyl acetate (optionally partially saponified) in a weight ratio of (i) to (ii) of from 1:0.2 to 1:10.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to detergent compositions containing two specified ingredients - a nonionic surfactant system, and a graft copolymer -which may additionally contain any other conventional detergent ingredients, for example, other surfactants, builders, bleach systems, antifoam systems, fluorescers, inorganic salts, and other materials well known to those skilled in formulating detergents. The compositions of the invention may take any suitable form, for example, powders, liquids or bars.

### The nonionic surfactant system

The nonionic surfactant system of the present invention exists as a cloudy phase somewhere in the temperature range of 0°C to 40°C, preferably 0°C to 15°C, in distilled water at a concentration of 1%. In practice this means that the system has a cloud point of not more than 40°C, preferably not more than 15°C. Cloud point is a term well known in the art, for example, from "Surface Active Ethylene Oxide Adducts" by N Schonfeldt, Pergamon Press 1969, pages 145 to 154. In general terms the cloud point of a surfactant material is the temperature at which association between the surfactant molecules and water molecules through hydrogen bonding breaks down, leading to the separation of surfactant-rich and water-rich phases and a consequent increase in turbidity or cloudiness.

The cloud point correlates approximately to the hydrophilic-lipophilic balance (HLB) of the surfactant system and it is therefore preferred that the HLB should be not higher than 10.5 and more preferably not higher than 9.5. The HLB should however preferably be above 6.0, more preferably above 8.0, in order to provide sufficient detergency.

Suitable nonionic detergent compounds which may be used include in particular 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 nonionic detergent compounds are alkyl ($C_{6-22}$) phenol-ethylene oxide condensates, the condensation products of linear or branched aliphatic $C_{8-20}$ primary or secondary alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylenediamine. Other so-called nonionic detergent compounds include long-chain tertiary amine oxides, tertiary phosphine oxides, and dialkyl sulphoxides.

Where, for example, alkylene oxide adducts of fatty materials (aliphatic alcohols, acids or amides) are used as the nonionic detergent compounds, the number of alkylene oxide groups per molecule has a

considerable effect upon the cloud point as indicated by the Schonfeldt reference mentioned above. The chain length and nature of the fatty material is also influential, and thus the preferred number of alkylene oxide groups per molecule depends on the the nature and chain length of the fatty material. We have found, for example, that where the fatty material is an alcohol having about 12 to 15 carbon atoms, the adducts having 3 and 4 ethylene oxide groups per molecule (hereinafter the 3EO and 4EO materials) both have cloud points of less than 0°C and are therefore suitable for use in the present invention. The corresponding 5EO and 6EO surfactants have cloud points of about 12°C and about 30°C respectively; both are therefore suitable for use in the present invention, but the 5EO is preferred to the 6EO.

The corresponding 7EO surfactant has a cloud point of about 48°C and is therefore unsuitable for use in the present invention, unless in admixture with another surfactant of lower cloud point: for example, a mixture of 1 part by weight of the 7EO material with 3 parts by weight of the 3EO material has a sufficiently low cloud point to be useful in the present invention. Further ethoxylation raises the cloud point still higher: thus the corresponding 11EO material has a cloud point higher than 80°C and is unsuitable for use in the present invention.

Thus preferred nonionic surfactants for use in the compositions of the invention are $C_{12-15}$ aliphatic alcohols having a degree of ethoxylation not exceeding 6, preferably 3 to 5.

The nonionic surfactant system of the compositions of the invention may consist of a single nonionic surfactant of appropriate cloud point, although it must be remembered that even a single commercial nonionic surfactant is a mixture of materials of different chain lengths and degrees of ethoxylation: the chain lengths and degrees of ethoxylation quoted in this specification are average values. Alternatively, a nonionic surfactant system of suitable cloud point and HLB value may be obtained by blending two or more nonionic surfactants, as exemplified by the 7EO/3EO mixture mentioned in the previous paragraph.

The nonionic surfactant system is preferably present in an amount of from 2 to 20% by weight, more preferably from 3 to 10% by weight, based on the total composition. As indicated below under "Optional Ingredients", other surfactants, of other ionic types, may also be present if desired, the total amount of surfactant of all ionic types present being within the range of from 2 to 50% by weight, preferably from 5 to 40% by weight, of the final composition.

The graft copolymer

The graft copolymers used in the compositions of the present invention are described and claimed in EP 219 048A (BASF). They are obtainable by grafting a polyalkylene oxide of molecular weight (number average) 2000 - 100 000 with vinyl acetate, which may be partially saponified, in a weight ratio of polyalkylene oxide to vinyl acetate of 1:0.2 to 1:10. The vinyl acetate may, for example, be saponified to an extent of up to 15%. The polyalkylene oxide may contain units of ethylene oxide, propylene oxide and/or butylene oxide; polyethylene oxide is preferred.

Preferably the polyalkylene oxide has a number-average molecular weight of from 4000 to 50 000, and the weight ratio of polyalkylene oxide to vinyl acetate is from 1:0.5 to 1:6. Especially preferred are polymers derived from polyethylene oxide of molecular weight 2000-50 000 and having a weight ratio of polyethylene oxide to vinyl acetate of from 1:0.5 to 1:6.

A material within this definition, based on polyethylene oxide of molecular weight 6000 (equivalent to 136 ethylene oxide units), containing approximately 3 parts by weight of vinyl acetate units per 1 part by weight of polyethylene oxide, and having itself a molecular weight of 24 000, is commercially available from BASF as Sokalan (Trade Mark) HP22.

The polymers are present in the compositions of the invention in amounts of from 0.1 to 3% by weight, preferably from 0.3 to 1% by weight.

Optional ingredients

As well as the specified nonionic surfactant system and graft copolymer, the compositions of the invention may contain any other non-interfering ingredients known to be suitable for incorporation into detergent compositions.

The compositions may usefully contain one or more soap or non-soap anionic, cationic, amphoteric or zwitterionic surfactants, or combinations of these. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred detergent-active compounds that can be used, in addition to the specified nonionic surfactant system, are soaps and synthetic non-soap anionic surfactants.

Synthetic anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of $C_8$-$C_{15}$; primary and secondary alkyl sulphates, particularly sodium $C_{12}$-$C_{15}$ primary alcohol sulphates; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

It may also be desirable to include one or more soaps of fatty acids. These are preferably sodium soaps derived from naturally occurring fatty acids, for example, the fatty acids from coconut oil, beef tallow, sunflower or hardened rape seed oil.

A preferred type of detergent composition suitable for use in most automatic fabric washing machines contains anionic and nonionic surfactant together in a weight ratio of at least 0.67:1, preferably at least

1:1, and more preferably within the range of from 1:1 to 10:1. Soap may also be present if desired.

As previously indicated, the total amount of surfactant in the compositions of the invention is from 2 to 50% by weight, and is preferably from 5 to 40% by weight.

Compositions of the invention will also generally contain one or more detergency builders. These are as well known to the skilled formulator as are the surfactants listed above. Inorganic builders that may be present include alkali metal (generally sodium) ortho-, pyro- and tripolyphosphate, carbonate, and crystalline and amorphous aluminosilicates; while organic builders include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and polyacetal carboxylates, and monomeric polycarboxylates such as nitrilotriacetates, citrates and carboxymethyloxysuccinates. This list is not intended to be exhaustive. The total level of detergency builder is generally within the range of from 20 to 80% by weight.

According to a preferred embodiment of the invention, the compositions contain less than 10% by weight of inorganic phosphate builders, and are more preferably substantially free of inorganic phosphate.

In this preferred embodiment, the builder system preferably comprises crystalline or amorphous alkali metal aluminosilicate, optionally in conjunction with a supplementary builder. The aluminosilicate is suitably present in an amount of from 10 to 60% by weight.

Detergent compositions according to the invention may also suitably contain a bleach system. Preferred are 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. The skilled detergent worker will have no difficulty in applying the normal principles to choose a suitable bleach system.

Other materials that may be present in detergent compositions of the invention include sodium silicate, fluorescers, inorganic salts such as sodium sulphate, enzymes, lather control agents or lather boosters as appropriate, pigments, and perfumes. Again, this list is not intended to be exhaustive.

Preparation of detergent compositions

Detergent compositions of the invention may be prepared by any suitable method. Detergent powders are suitably prepared by spray-drying a slurry of compatible heat-insensitive components, and then spraying on or postdosing those ingredients unsuitable for processing via the slurry. The skilled detergent formulator will generally have no difficulty in deciding which components should be included in the slurry and which should be postdosed or sprayed on.

The graft copolymer is available as a solution having a solids content of 20% which is stable at slurry processing temperatures and can be incorporated in the slurry without problems, provided that the pH is maintained below 12.

The nonionic surfactant system is preferably not incorporated via the slurry. If, however, a mixed system is used which includes a relatively highly ethoxylated component, that component may if desired be processed via the slurry while material of lower ethoxylation is sprayed on or postdosed on a solid carrier.

The invention is further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated.

## EXAMPLES

### Example 1

Four detergent compositions were prepared to the following formulation by conventional slurry-making, spray-drying and postdosing techniques:

| | % |
|---|---|
| Sodium linear alkylbenzene sulphonate | 9.0 |
| Nonionic surfactant (see below) | 4.0 |
| Zeolite 4A (hydrated basis) | 24.0 |
| Sodium alkaline silicate | 5.0 |
| Sodium sulphate | 19.3 |
| Sodium carbonate | 7.0 |
| Sodium carboxymethylcellulose | 0.5 |
| Fluorescer | 0.7 |
| Sodium perborate monohydrate | 8.0 |
| Tetraacetylethylene-diamine (76% granules) | 3.0 |
| Enzyme granules | 0.5 |
| Graft copolymer (Sokalan HP22) | 0 or 0.5 |
| Water and minor ingredients | to 100.0 |

&

The compositions prepared contained the following amounts of nonionic surfactants and Sokalan HP22:

| Example | 1 | A | B | C |
|---|---|---|---|---|
| Nonionic surfactant 7EO[1] | 1.0 | 4.0 | 4.0 | 1.0 |
| Nonionic surfactant 3EO[2] | 3.0 | - | - | 3.0 |
| Sokalan HP22 | 0.5 | - | 0.5 | |

[1] Synperonic (Trade Mark) A7 ex ICI, $C_{12-15}$ linear primary alcohol 7EO
[2] Synperonic (Trade Mark) A3 ex ICI, $C_{12-15}$ linear primary alcohol 3EO

It will be seen that Composition 1 illustrates the invention while Compositions A to C are comparative.

The soil suspension (antiredeposition) properties of the four compositions were compared by means of the following procedure. Two new, clean, unwashed polyester/cotton test cloths were washed together with five soiled cloths in a tergotometer at 60° C in 50° (French) hard water (Ca:Mg ratio 4:1) at a liquor to cloth ratio of about 50:1, the wash liquor containing 4 g/l of the detergent composition under test. The soiled cloths carried a range of different soils such as clay, oil, fat, proteinaceous, and ink. The wash cycle was repeated a further nine times, the soiled cloths being replaced by new soiled cloths (with the same range of soils) for each wash cycle.

The reflectance of the two new cloths was measured before washing, and after the tenth wash cycle. The reduction in reflectance of the washed fabrics after ten washes is shown in the following table; the lower the reduction in reflectance, the less redeposition had occurred.

| Example | 1 | A | B | C |
|---|---|---|---|---|
| Delta $R_{460}$ | -2.4 | -5.6 | -7.5 | -4.7 |

**Claims**

1. A detergent composition comprising:
(a) from 2 to 50% by weight of a detergent active system which amount includes a nonionic surfactant system consisting of one or more nonionic surfactants, the nonionic surfactant system

having a cloud point (as hereinbefore defined) not higher than 40° C;characterised in that it further comprises:

(b) from 0.1 to 3% by weight of a graft copolymer of (i) polyethylene, polypropylene or polybutylene oxide with (ii) vinyl acetate (optionally partially saponified) in a weight ratio of (i) to (ii) of from 1:0.2 to 1:10.

2. A detergent composition as claimed in claim 1, characterised in that the nonionic surfactant system has a cloud point not higher than 15° C.

3. A detergent composition as claimed in claim 1 or claim 2, characterised in that the nonionic surfactant system has an HLB value not greater than 10.5.

4. A detergent composition as claimed in claim 1 or claim 3, characterised in that the nonionic surfactant system has an HLB value not greater than 9.5.

5. A detergent composition as claimed in any preceding claim, characterised in that the nonionic surfactant system consists of one or more $C_{12-15}$ aliphatic alcohols ethoxylated with an average of not more than 5 moles of ethylene oxide.

6. A detergent composition as claimed in claim 5, characterised in that the nonionic surfactant system consists of one or more $C_{12-15}$ aliphatic alcohols ethoxylated with an average of 3-4 moles of ethylene oxide.

7. A detergent composition as claimed in any preceding claim, characterised in that the nonionic surfactant system is present in an amount of from 2 to 20% by weight.

8. A detergent composition as claimed in claim 7, characterised in that the nonionic surfactant system is present in an amount of from 3 to 10% by weight.

9. A detergent composition as claimed in any preceding claim, characterised in that the graft copolymer is obtainable by grafting a polyalkylene oxide of molecular weight (number average) 2000 - 100 000 with vinyl acetate (optionally partially saponified) in a weight ratio of polyalkylene oxide to vinyl acetate of 1:0.2 to 1:10.

10. A detergent composition as claimed in any preceding claim, characterised in that the graft copolymer is obtainable by grafting a polyalkylene oxide of molecular weight (number average) 4000 - 50 000 with vinyl acetate (optionally partially saponified) in a weight ratio of polyalkylene oxide to vinyl acetate of 1:0.5 to 1:6.

11. A detergent composition as claimed in any one of claims 1 to 9, characterised in that the graft copolymer is obtainable by grafting a polyethylene oxide of molecular weight (number average) 2000 - 50 000 with vinyl acetate (optionally partially saponified) in a weight ratio of polyethylene oxide to vinyl acetate of 1:0.5 to 1:6.

12. A detergent composition as claimed in any preceding claim, characterised in that the graft copolymer is present in an amount of from 0.3 to 1.0% by weight.

13. A detergent composition as claimed in any preceding claim, characterised in that it further comprises from 10 to 60% by weight of crystalline or amorphous alkali metal aluminosilicate.

14. A detergent composition as claimed in any preceding claim, characterised in that it further comprises one or more anionic surfactants.

15. A detergent composition as claimed in any preceding claim, characterised in that it contains less than 10% by weight of inorganic phosphate builder.

16. A detergent composition as claimed in claim 15, characterised in that it is substantially free of inorganic phosphate builders.