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(54) Detergent compositions.

(57) Detergent compositions having improved antiredeposition properties on polyester and polyester/cotton fabrics contain a polyalkylene oxide/vinyl acetate graft copolymer, and also contain an alkali metal aluminosilicate builder, and a polymer comprising acrylate and/or maleate units. The compositions are preferably free of inorganic phosphate builders.

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Description

DETERGENT COMPOSITIONS

TECHNICAL FIELD

The present invention relates to fabric washing detergent compositions built with zeolite and 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).

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 built predominantly or wholly with zeolite and containing a graft copolymer of this type in conjunction with an acrylic and/or maleic polymer exhibit surprisingly enhanced soil suspension (antiredeposition) properties on polyester and polyester/cotton fabrics. A corresponding improvement is not observed with phosphate-built compositions.

DEFINITION OF THE INVENTION

The present invention provides a detergent composition comprising:

(a) from 2 to 50% by weight of a detergent active system comprising one or more anionic, nonionic, cationic, zwitterionic or amphoteric surfactants;

(b) from 10 to 60% by weight of crystalline or amorphous alkali metal aluminosilicate;

(c) from 0.5 to 5% by weight of a polycarboxylate polymer comprising (meth)acrylate units and/or maleate units; and

(d) 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 four specified ingredients - a surfactant system, an aluminosilicate builder, a polycarboxylate polymer, and a graft copolymer - which may additionally contain any other conventional detergent ingredients, for example, other 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 surfactant system

The total amount of detergent-active material (surfactant) in the compositions of the invention is from 2 to 50% by weight, and is preferably from 5 to 40% by weight.

The compositions of the invention may contain one or more soap or non-soap anionic, nonionic, 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 are soaps and synthetic non-soap anionic surfactants and nonionic 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.

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.

Especially preferred are the primary and secondary alcohol ethoxylates, especially the C_{12-15} primary and secondary alcohols ethoxylated with an average of from 5 to 20 moles of ethylene oxide per mole of alcohol.

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.

The aluminosilicate builder

The detergent compositions of the invention contain from 10 to 60% by weight, preferably from 15 to 50% by weight, of crystalline or amorphous alkali metal aluminosilicate builder.

The alkali metal (preferably sodium) aluminosilicates used in the compositions of the invention may be either crystalline or amorphous or mixtures thereof, and they have the general formula:

$0.8\text{-}1.5\ Na_2O.\ Al_2O_3.\ 0.8\text{-}6\ SiO_2$.

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least about 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply described in the literature.

Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 473 201 (Henkel) and GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof. Especially preferred is zeolite 4A.

Other builders may also be included in the compositions of the invention if necessary or desired: suitable organic or inorganic water-soluble or water-insoluble builders will readily suggest themselves to the skilled detergent formulator. Inorganic builders that may be present include alkali metal (generally sodium) ortho-, pyro- and tripolyphosphate, and carbonate; while organic builders include 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.

The polycarboxylate polymer

The compositions of the invention also contain from 0.5 to 5% by weight, preferably from 1 to 3% by weight, of a polycarboxylate polymer containing (meth)acrylate and/or maleate units. These anionic polymers may be in acid form or in wholly or partially neutralised salt form. Preferred polymers are homopolymers and copolymers of acrylic acid. 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:

Polymer type	Trade name	Supplier	Average m.wt.
Polyacrylate	Versicol* E5	Allied Colloids	3500
Polyacrylate	Versicol* E7	Allied Colloids	27 000
Polyacrylate	Versicol* E9	Allied Colloids	70 000
Polyacrylate	Narlex* LD 30	National Adhesives	5000
Polyacrylate	Narlex* LD 34	National Adhesives	25 000

Polymer type	Trade name	Supplier	Average m.wt.
Polyacrylate	Acrysol* LMW-10	Röhm & Haas	1000
Polyacrylate	Acrysol* LMW-20	Röhm & Haas	2000
Polyacrylate	Acrysol* LMW-45	Röhm & Haas	4500
Polyacrylate	Acrysol* A1-N	Röhm & Haas	60 000
Polyacrylate	Sokalan* PA-20	BASF	2500
Polyacrylate	Sokalan* PA-40	BASF	15 000
Polyacrylate	Sokalan* PA-70	BASF	70 000
Polyacrylate	Sokalan* PA-110	BASF	250 000

Polymer type	Trade name	Supplier
Ethylene/ maleic acid	EMA*	Monsanto
Methyl vinyl ether/maleic acid	Gantrez* AN 119	GAF Corporation
Acrylate/ maleate	Sokalan* CP5, CP7	BASF
Acrylic phosphinate	DKW*	National Adhesives
Acrylic phosphinate	Belsperse*	Ciba-Geigy

*denotes Trade Mark

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 four ingredients - surfactant system, detergency builder, polycarboxylate polymer and graft copolymer - already specified, the compositions of the invention may contain any other non-interfering ingredients known to be suitable for incorporation into detergent compositions.

For example, the detergent compositions according to the invention may 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 the 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.

Similarly, the polycarboxylate polymer can normally be included in the slurry.

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

EXAMPLES

Examples 1 to 3

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 7EO	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
Sodium polyacrylate (see below)	0 or 2.0
Graft copolymer (Sokalan HP22)	0 or 0.5
Water and minor ingredients	to 100.0

The sodium polyacrylate polymers used were Sokalan PA 20, PA 40 and PA 110 (see previously). The polymers present in the various compositions prepared are shown in Table 1 below.

The soil suspension (antiredeposition) properties of the compositions were compared by means of the following procedure. Two new, clean, unwashed polyester 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 Table 1; the lower the reduction in reflectance, the less redeposition had occurred.

It will be seen that Compositions 1 to 3 illustrates the invention while Compositions A to E are comparative. The graft copolymer Sokalan HP22 had little effect on its own on redeposition. The polyacrylates became increasingly effective with increasing molecular weight at reducing redeposition, but for each of them the effect was considerably enhanced by the presence of the graft copolymer.

Table 1

Example		Polymers	Reflectance change (delta R_{460^*})
A	no polymers		-6.0
B	0.5% Sokalan HP22		-7.1
C		2.0% Sokalan PA 20	-6.0
1	0.5% Sokalan HP22 +	2.0% Sokalan PA 20	-4.0
D		2.0% Sokalan PA 40	-4.3
2	0.5% Sokalan HP22 +	2.0% Sokalan PA 40	-2.3
E		2.0% Sokalan PA 110	-2.3
3	0.5% Sokalan HP22 +	2.0% Sokalan PA 110	-1.6

Examples 4 and 5

The procedure of Examples 1 to 3 was repeated using acrylic/maleic copolymers instead of the sodium polyacrylates. These were Sokalan CP5 and Sokalan CP7, which differ in the proportions of acrylic units and maleic units they contain: Sokalan CP5 contains about 70% by weight of acrylic units and 30% by weight of maleic units, while Sokalan CP7 contains about 50% by weight of each.

The compositions prepared, and the results obtained, are shown in Table 2 below, the controls A and B being shown again for comparison. Again, numbered compositions illustrate the invention while those represented by letters are comparative. The two acrylate/maleate copolymers were both quite effective at reducing redeposition, but for each of them the effect was considerably enhanced by the presence of the graft copolymer.

Table 2

Example		Polymers	Reflectance change (delta R_{460^*})
A	no polymers		-6.0
B	0.5% Sokalan HP22		-7.1
F		2.0% Sokalan CP 5	-3.4
4	0.5% Sokalan HP22 +	2.0% Sokalan CP 5	-2.6
G		2.0% Sokalan CP 7	-4.0
5	0.5% Sokalan HP22 +	2.0% Sokalan CP 7	-3.2

Comparative Examples H to V

The procedure of Examples 1 to 5 was repeated using a phosphate-built detergent composition having the following formulation:

	Parts
Sodium linear alkylbenzene sulphonate	9.0
Nonionic surfactant 7EO	4.0
Soap	1.1
Sodium tripolyphosphate	30.0
Sodium alkaline silicate	6.0
Sodium sulphate	12.9
Sodium carbonate	5.0
Sodium carboxymethylcellulose	0.6
Fluorescer	0.3
Sodium perborate tetrahydrate	18.0
Enzyme granules	0.5
Lather control granules	1.3
Polycarboxylate polymer (see below)	0 or 2.0
Graft copolymer (Sokalan HP22)	0 or 0.5
Water and minor ingredients	to 100.0

The compositions prepared, and the reflectance reduction results obtained, are shown in Table 3 below.

Table 3

Example		Polymers	Reflectance change (delta R_{460^*})
H	no polymers		-2.6
J	0.5% Sokalan HP22		-1.5
L		2.0% Sokalan PA 40	-2.0
M	0.5% Sokalan HP22 +	2.0% Sokalan PA 40	-2.0
N		2.0% Sokalan PA 70	-2.8
P	0.5% Sokalan HP22 +	2.0% Sokalan PA 70	-1.8
Q		2.0% Sokalan PA 110	-2.7
R	0.5% Sokalan HP22 +	2.0% Sokalan PA 110	-1.8
S		2.0% Sokalan CP 5	-2.2
T	0.5% Sokalan HP22 +	2.0% Sokalan CP 5	-1.8
U		2.0% Sokalan CP 7	-3.0
V	0.5% Sokalan HP22 +	2.0% Sokalan CP 7	-2.0

In all cases, the combination of polymers was inferior to the graft copolymer alone, showing that the benefit that characterises the present invention is not observed in detergent compositions built with sodium tripolyphosphate.

Examples 6 and 7

The procedure of Examples 1 and 5, with the same zeolite-built detergent composition and the same polymers, was repeated using polyester/cotton test cloths. The results were as shown in Table 4 below.

Table 4

Example		Polymers	Reflectance change (delta R_{460^*})
W	no polymers		-5.6
X	0.5% Sokalan HP22		-7.5
Y		2.0% Sokalan PA 20	-5.1
6	0.5% Sokalan HP22 +	2.0% Sokalan PA 20	-2.4
Z		2.0% Sokalan CP 7	-4.5
7	0.5% Sokalan HP22 +	2.0% Sokalan CP 7	-3.9

It will be seen that combinations of these two representative polycarboxylate polymers with the graft copolymer gave antiredeposition benefits on polyester/cotton fabric.

Claims

1. A detergent composition comprising:
   (a) from 2 to 50% by weight of a detergent active system comprising one or more anionic, nonionic, cationic, zwitterionic or amphoteric surfactants;
   (b) from 10 to 60% by weight of crystalline or amorphous alkali metal aluminosilicate;
   (c) from 0.5 to 5% by weight of a polycarboxylate polymer comprising (meth)acrylate units and/or maleate units;
   characterised in that it further comprises:
   (d) 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 it contains less than 10% by weight of inorganic phosphate builder.

3. A detergent composition as claimed in claim 3, characterised in that it is substantially free of inorganic phosphate builders.

4. A detergent composition as claimed in any preceding claim, characterised in that the polycarboxylate polymer (c) is a homopolymer of copolymer of acrylic acid.

5. A detergent composition as claimed in claim 4, characterised in that the polycarboxylate polymer (c) is a polyacrylate, an acrylate/maleate copolymer, or an acrylic phosphinate.

6. A detergent composition as claimed in any preceding claim, characterised in that the polycarboxylate polymer (c) is present in an amount of from 1 to 3% by weight.

7. A detergent composition as claimed in any preceding claim, characterised in that the graft copolymer (d) 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.

8. A detergent composition as claimed in any preceding claim, characterised in that the graft copolymer (d) 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.

9. A detergent composition as claimed in any one of claims 1 to 7, characterised in that the graft copolymer (d) 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.

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

11. A detergent composition as claimed in any preceding claim, characterised in that the aluminosilicate builder is a zeolite.

12. A detergent composition as claimed in claim 11, characterised in that the aluminosilicate builder is zeolite 4A.

13. A detergent composition as claimed in any preceding claim, characterised in that the aluminosilicate builder is present in an amount of from 15 to 50% by weight.