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**(54) DETERGENT COMPOSITION CONTAINING GRAFT COPOLYMER**

**PFROPFCOPOLYMERISAT ENTHALTENDE WASCHMITTELZUSAMMENSETZUNG**

**COMPOSITION DETERGENTE CONTENANT UN COPOLYMERE GREFFE**

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**EP 0 745 117 B1**

**Description**TECHNICAL FIELD

5 The present invention relates to particulate detergent compositions containing a defined polymer conferring soil release benefits, for example, a graft copolymer of vinyl acetate units on a polyethylene oxide backbone. The compositions of the invention contain relatively high levels of mobile nonionic surfactants and are of high bulk density.

BACKGROUND AND PRIOR ART

10 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.

EP 358 474A (Unilever) discloses 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.

15 EP 358 473A and EP 358 472A (Unilever) also relate to enhanced antiredeposition properties when the graft copolymer is used in conjunction with, respectively, aluminosilicate builder and acrylic polymer, or dipicolinic acid builder.

20 We have now unexpectedly discovered that incorporation of these graft copolymers in certain particulate detergent compositions can additionally confer another, quite different benefit, unconnected with antiredeposition or soil suspension: when high levels of mobile nonionic surfactants are present in powders of high bulk density, bleeding out of the nonionic surfactant can be substantially reduced. Delivery into the wash may also be improved.

25 EP 358 474A (Unilever) mentioned above discloses compositions containing ethoxylated nonionic surfactants. However, the benefit concerned (enhanced antiredeposition) is obtained only with nonionic surfactants having a low cloud point and a low HLB value. No benefit is observed, for example, with C<sub>12-15</sub> alcohol ethoxylated with an average of 7 or more moles of ethylene oxide per mole of alcohol. Furthermore, the preferred level of nonionic surfactant disclosed is from 3 to 10 wt% based on the whole composition, and the compositions specifically described in the Examples contain only 4 wt% of nonionic surfactant. High bulk density is not disclosed. The specific disclosures of EP 358 473A and EP 358 472A (Unilever) are similar.

30 WO 92 06152A and WO 93 19145A (Procter & Gamble) disclose the use of soil release polymers, including the graft copolymer, in compositions in which the surfactant system includes a polyhydroxy fatty acid amide. Powders of high bulk density are exemplified in WO 92 06152A but these contain only low levels of ethoxylated nonionic surfactant (less than 2.5 wt%).

35 EP 455 468A (Protein Technologies International) discloses a new proteinaceous soil release material and compares it with graft copolymers of the type discussed above. Powder compositions specifically disclosed contain 5 wt% of nonionic surfactant (C<sub>12-15</sub> alcohol, 9EO).

DEFINITION OF THE INVENTION

40 The present invention accordingly provides a particulate detergent composition comprising an organic surfactant system, a detergency builder system and optionally other detergent ingredients, wherein

(a) the organic surfactant system comprises mobile ethoxylated nonionic surfactant in an amount of at least 10 wt% based on the whole composition,

45 (b) the composition also comprises a graft copolymer of

(i) polyethylene, polypropylene or polybutylene oxide with

50 (ii) vinyl acetate (optionally partially saponified),

in a weight ratio of (i) to (ii) of from 1:0.2 to 1:10, and

(c) the composition has a bulk density of at least 650 g/litre.

55 The invention also provides a process for the preparation of a particulate detergent composition as defined above, which comprises preparing a substantially homogeneous granular base by mixing and granulation, then optionally postdosing further ingredients, the graft copolymer being incorporated in aqueous solution form during the mixing and

granulation process.

The invention further provides the use of a copolymer as defined above to reduce or prevent the bleeding out of nonionic surfactant from a particulate detergent composition having a bulk density of at least 650 g/litre and containing at least 10 wt% of mobile ethoxylated nonionic surfactant.

## DETAILED DESCRIPTION OF THE INVENTION

The particulate detergent compositions of the invention contain a graft copolymer as described and claimed in EP 219 048A (BASF).

The compositions also contain a relatively high level of mobile ethoxylated nonionic surfactant. These surfactants give substantial performance benefits, but in such compositions the phenomenon known as "bleeding" of nonionic surfactant can be a major problem. The mobile nonionic surfactant can migrate through the powder, becoming unevenly distributed, leading to loss of performance, loss of powder flow, and caking; where porous (eg cardboard) packaging is used, the nonionic surfactant tends to move to the narrow capillaries of the pack material leading to penetration and external staining. Bleeding is a particular problem with powders of high bulk density and correspondingly low particle porosity.

According to the invention, the presence of a graft copolymer as previously defined, and as discussed in more detail below, can reduce or prevent nonionic surfactant bleeding. The effect is enhanced if a water-soluble salt of citric acid, preferably sodium citrate, is present.

### 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 suitably present in the compositions of the invention in amounts of from 0.1 to 10% by weight, preferably from 0.2 to 5% by weight and more preferably from 0.3 to 2% by weight.

The graft copolymer is available in aqueous solution form, suitable for use in the preparation of detergent compositions in accordance with the present invention, as described in more detail below.

### The surfactant system

In the compositions of the invention, at least 10 wt% of mobile ethoxylated nonionic surfactant is present. Preferred compositions contain at least 12 wt% of mobile ethoxylated nonionic surfactant.

Preferably the ethoxylated alcohol nonionic surfactant has an average alkyl chain length of C<sub>8</sub>-C<sub>18</sub>, preferably C<sub>12</sub>-C<sub>16</sub>. Especially preferred are C<sub>12</sub>-C<sub>15</sub> aliphatic alcohols ethoxylated with from 2.5 to 8.0 moles of ethylene oxide per mole of alcohol. The benefit associated with the present invention is especially marked with C<sub>12</sub>-C<sub>15</sub> alcohols having an average degree of ethoxylation of from 6.5 to 8.0.

A preferred surfactant system for use in the compositions of the invention comprises ethoxylated nonionic surfactant in combination with primary alcohol sulphate (PAS).

In this embodiment, the ethoxylated nonionic surfactant preferably constitutes from 30 to 90 wt% of the surfactant system, more preferably from 40 to 70 wt%; and the PAS preferably constitutes from 10 to 70 wt%, more preferably from 30 to 60 wt%, of the surfactant system. Preferably the whole composition contains at least 5 wt% of PAS.

The compositions of the invention may also advantageously contain fatty acid soap, suitably in an amount of from 1 to 5 wt%. The presence of soap is beneficial because of its behaviour as a powder structurant, giving crisp free-flowing powder. However, the presence of soap in the compositions of the invention is not essential.

Water-soluble salts

According to a preferred embodiment of the invention, the compositions contain at least one water-soluble salt. The presence of a water-soluble salt appears to be highly beneficial with respect to the reduction of nonionic surfactant "bleeding", and may also simultaneously fulfil other functions within the composition.

For example, the compositions may contain sodium carbonate, which in any case is useful for increasing detergency and can ease processing. Sodium carbonate may generally be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%, and most suitably from 2 to 13 wt%. However, compositions free of alkali metal carbonate are also within the scope of the invention.

According to a highly preferred embodiment of the invention, the compositions contain a water-soluble salt of citric acid, more preferably sodium citrate. Citrate is of course valuable as a detergency builder as well as enhancing the anti-"bleeding" effect associated with the present invention.

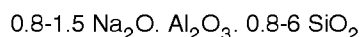
Citrate is suitably present in an amount of from 0.5 to 40 wt% (as sodium citrate dihydrate, based on the whole composition).

Especially preferred is citrate having a Rosin-Rammler particle diameter of less than 800 µm, preferably from 100 to 500 µm, incorporated within the homogeneous base granules of the composition rather than admixed.

Other ingredients

The compositions of the invention contain a detergency builder system, which preferably comprises an alkali metal, preferably sodium, aluminosilicate. Sodium aluminosilicates may suitably be incorporated in amounts of from 10 to 60 wt% (anhydrous basis).

The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula:



These materials 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<sub>2</sub> 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 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

Other builders may also be included in the detergent compositions of the invention as necessary or desired. As mentioned above, citrates are especially preferred.

Another class of builders that may be included is comprised by polycarboxylate polymers, more especially polyacrylates and acrylic/maleic copolymers, which may suitably be used in amounts of from 0.5 to 15 wt%, especially from 1 to 10 wt%.

Other ingredients which may be present include fluorescer; sodium silicate; bleach components such as sodium perborate or percarbonate, bleach activators and bleach stabilisers; proteolytic and lipolytic enzymes; dyes; foam control granules; coloured speckles; perfumes; and fabric softening compounds. This list is not intended to be exhaustive.

Bulk density and powder properties

The invention applies to detergent powders of high bulk density: at least 650 g/l, preferably at least 700 g/l and more preferably at least 800 g/l. Preferred compositions of the invention have a void volume not exceeding 10%, more preferably not exceeding 5%; void volume may be measured by the known technique of mercury intrusion porosimetry.

Advantageously, the content of "fines", that is to say, particles smaller than 180 micrometres, does not exceed 10 wt%, and more preferably it does not exceed 5 wt%.

Preparation of the compositions

The high bulk density powders to which the present invention is applicable are not generally the direct product of spray-drying processes, although they may be prepared by densification of a spray-dried base powder.

A preferred method of preparation, however, involves preparation of a dense, substantially homogeneous granular base by a non-tower (non-spray-drying) process in which liquid and solid ingredients are mixed and granulated together. Other ingredients may subsequently be postdosed if desired.

Of the ingredients listed above, the surfactants, aluminosilicate, fluorescer, sodium carbonate, sodium silicate and other salts may suitably be incorporated in the base, while bleach ingredients, enzymes, perfumes, dyes, foam control granules and fabric softening compounds will generally be postdosed.

According to a preferred process, the preparation of the granular base is carried out in a high-speed mixer/granulator having both a stirring and a cutting action. The high-speed mixer/granulator, also known as a high-speed mixer/densifier, may be a batch machine such as the Fukae (Trade Mark) FS, or a continuous machine such as the Lödige (Trade Mark) Recycler CB30. Suitable processes are described, for example, in EP 544 492A, EP 420 317A and EP 506 184A (Unilever).

Incorporation of sodium citrate

As previously indicated, according to a preferred embodiment of the invention, sodium citrate (or other alkali metal citrate) is incorporated within the granular base, as described and claimed in WO 95 14767A (Unilever).

The citrate in the base powder should desirably amount to at least 0.5 wt%, preferably from 0.5 to 40 wt%, of the total composition; and desirably at least 3 wt%, more preferably at least 5 wt% and most preferably from 3 to 15 wt%, of the total composition.

Sodium citrate incorporated in the base powder is preferably finely divided, having a Rosin-Rammler particle size not exceeding 800 micrometres, preferably not exceeding 500 micrometres, and most preferably from 100 to 500 micrometres.

Generally the inorganic builders and other inorganic materials (for example, zeolite, sodium carbonate) are granulated with the surfactants, which act as binders and granulating or agglomerating agents. The finely divided citrate may suitably be incorporated at this stage. Fatty acid soap may be prepared by in situ neutralisation with sodium hydroxide solution during the mixing and granulation process.

Optionally, the citric acid salt may be incorporated in the form of an intimate mixture with surfactant, more preferably nonionic surfactant. Alternatively it may be added in solid form. Fatty acid may also be added in the form of a premix with surfactant, again preferably nonionic surfactant.

Any optional ingredients as previously mentioned may be incorporated at any suitable stage in the process.

In these processes, any PAS present may be already neutralised, that is to say in salt form, when dosed into the high-speed mixer/granulation, or alternatively may be added in acid form and neutralised in situ. If desired, PAS and nonionic surfactant may be introduced in the form of a homogeneous liquid blend, as described in EP 265 203A and EP 507 402A (Unilever). EP 420 317A and EP 506 184A (Unilever) disclose a different process wherein PAS acid, which is a liquid, is mixed and reacted with a solid inorganic alkaline material, such as sodium carbonate, in a continuous high-speed mixer. The resulting granule or "adjunct" is then dosed into another high-speed mixer with the nonionic surfactants and solid ingredients.

All these processes are suitable for the preparation of compositions of the invention.

In accordance with normal detergent powder manufacturing practice, bleach ingredients (bleaches, bleach precursor, bleach stabilisers), proteolytic and lipolytic enzymes, coloured speckles, perfumes and foam control granules are most suitably postdosed to the base powder after it has left the high-speed mixer/granulator.

Additional citrate may if desired be among the postdosed ingredients. That should not be finely divided, and preferably is of comparable particle size to the rest of the composition.

Incorporation of the graft copolymer

As indicated previously, in the general process outlined above, the preferred route for incorporation of the graft copolymer comprises including a solution (preferably aqueous) of the graft copolymer among the liquid ingredients in the mixing and granulation process used to prepare the base powder.

Thus the preferred process of the invention comprises preparing a substantially homogeneous granular base by mixing and granulation, then optionally postdosing further ingredients, the graft copolymer being incorporated in aqueous solution form during the mixing and granulation process.

Sokalan HP22 is commercially available as a 20 wt% aqueous solution which is highly suitable for incorporation by this route.

EXAMPLES

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

|    |              |   |
|----|--------------|---|
| 5  | CocoPAS      | coconut alcohol sulphate  |
|    | Nonionic 3EO | coconut alcohol ethoxylated with 3 moles of ethylene oxide per mole of alcohol  |
| 10 | Nonionic 7EO | coconut alcohol ethoxylated with 7 moles of ethylene oxide per mole of alcohol  |
|    | Zeolite MAP  | zeolite MAP powder, as described and claimed in EP 384 070A (Unilever), Si:Al ratio 1.00  |
| 15 | Percarbonate | sodium percarbonate having a protective coating of sodium metaborate and sodium metasilicate, as disclosed in GB 2 123 044B (Kao) |
|    | TAED         | tetraacetylene diamine (granules)   |
| 20 | EDTMP        | ethylenediamine tetramethylene phosphonate, Ca salt: Dequest (Trade Mark) ex Monsanto.  |
|    | SCMC         | sodium carboxymethylcellulose   |
|    | Mn catalyst  | bleach catalyst granule as described and claimed in International Patent Application No. PCT/GB94/01904 filed on 2 September 1994 |
| 25 | PVP          | polyvinyl pyrrolidone   |

The following test methods were used to compare nonionic surfactant bleeding and delivery characteristics.

Test for nonionic surfactant bleeding

The test used gives an estimate of the degree of bleeding during a three week storage period at 37°C by measuring the amount of nonionic surfactant absorbed by preweighed filter papers placed near the top and bottom of a powder column.

A 800 g sample of each powder was weighed out. Powder was poured to a depth of 1 cm into the base of a cylindrical container of diameter 15 cm, and an accurately weighed filter paper (Schleicher and Schull No. 589) placed on top of the powder. More powder was added to an approximate depth of 5 cm above the filter paper, and then covered with a second accurately weighed filter paper. The remainder of the powder sample was then used to cover the second filter paper. The container was tightly sealed and stored in a dry atmosphere at 37°C for 3 weeks. After the storage period the filter papers were removed and weighed, the increase in weight of each calculated, and the values for the two increases averaged.

Test 1 for delivery in the wash: cage test

Delivery characteristics of the powders were compared using a model system which simulates the delivery of a powder in an automatic washing machine, under more adverse conditions (low temperature, minimal agitation) than those normally encountered in a real wash situation.

For this test a cylindrical vessel having a diameter of 4 cm and a height of 7 cm, made of 600 micrometre pore size stainless steel mesh, and having a top closure made of Teflon and a bottom closure of the mesh just described, was used.

The top closure had inserted therein a 30 cm metal rod to act as a handle, and this handle was attached to an agitator arm positioned above 1 litre of water at 20°C in an open container. By means of this agitator apparatus the cylindrical vessel, held at 45 degrees, could be rotated through a circle with a 10 cm radius over a period of 2 seconds and allowed to rest for 2 seconds, before the start of the next rotation/rest cycle.

A 50 g powder sample was introduced into the cylindrical vessel which was then closed. The vessel was attached to the agitator arm which was then moved down to a position such that the top of the cylindrical vessel was just below the surface of the water. After a 10 second delay, the apparatus was operated for 15 rotation/rest cycles.

The cylindrical vessel and handle were removed from the water and the vessel detached from the handle.

Surface water was carefully poured off, and any powder residues transferred to a preweighed container and dried for 24 hours at 100°C. The weight of dried residue as a percentage of the initial powder weight (50 g) was then calculated.

#### Test 2 for delivery to the wash: delivery device test

Delivery characteristics of the powders were also compared using a model system which emulates the delivery of a powder in an automatic washing machine from a flexible delivery device of the type supplied with Lever's Persil (Trade Mark) Micro System powder in the UK: a spherical container of flexible plastics material having a diameter of approximately 4 cm and a top opening of diameter approximately 3 cm.

In this test the delivery device was attached in an upright position (opening uppermost) to an agitator arm positioned above water (5 litres at 20°C). By means of this apparatus the device could be moved vertically up and down through a distance of 30 cm, the lowest 5 cm of this travel being under water. Each up or down journey had a duration of 2 seconds, the device being allowed to rest 5 cm under water for 4 seconds at the lowest position, and at the highest position being rotated through 100° and allowed to rest in the resulting tilted orientation for 2 seconds before re-descending.

A preweighed powder sample was introduced into the device in its highest position, and the apparatus then allowed to operate for six cycles and stopped when the device was again in its highest position. Surface water was carefully poured off, and any powder residues transferred to a preweighed container. The container was then dried at 100°C for 24 hours, and the weight of dried residue as a percentage of the initial powder weight calculated.

#### EXAMPLES 1 and 2, COMPARATIVE EXAMPLES A to C

Bleaching detergent powders of high bulk density were prepared to the formulations shown in Table 1. Examples 1 and 2 were in accordance with the invention, while Examples A to C were comparative.

Base powders were prepared using a continuous high-speed mixer/granulator, and other ingredients were post-dosed as shown. The Sokalan HP22 was incorporated as a 20 wt% aqueous solution, but the amounts quoted here are for 100 wt% material. Sodium citrate dihydrate incorporated in the base had a Rosin Rammler particle diameter of 415 micrometres.

Table 2 shows the bleeding and delivery characteristics of the base powders prior to the postdosing of the ingredients in the lower part of Table 1.

Detergencies of all the powders (full compositions) were very similar, but the Sokalan HP22 gave a noticeable boost to oily soil removal from polyester and polyester/cotton fabrics.

#### EXAMPLES 3 to 8

Table 3 shows some examples of non-bleaching formulations in accordance with the invention.

These formulations also contained postdosed sodium citrate dihydrate of larger particle size than the sodium citrate dihydrate incorporated in the base powders.

Examples 1 and 2. Comparative Examples A to CTable 1: formulations

|                     | A     | B     | 1     | C     | 2     |
|---------------------|-------|-------|-------|-------|-------|
| <u>Base</u>         |       |       |       |       |       |
| CocOPAS             | 5.82  | 5.98  | 5.55  | 5.82  | 6.04  |
| Nonionic 3EO        | 5.27  | 5.65  | 5.25  | -     | -     |
| Nonionic 7EO        | 7.91  | 8.38  | 7.78  | 13.18 | 14.16 |
| Sokalan HP22        | -     | -     | 0.74  | -     | 0.79  |
| Soap                | 2.05  | 1.40  | 1.30  | 2.05  | -     |
| Zeolite MAP         | 36.65 | 39.17 | 38.85 | 36.65 | 38.98 |
| Sodium citrate      | -     | 4.25  | 4.18  | -     | 4.85  |
| Sodium carbonate    | 1.16  | 1.20  | 1.11  | 1.16  | 1.20  |
| SCMC                | 0.90  | -     | -     | 0.90  | -     |
| Water/salts         | 5.49  | 0.47  | 0.43  | 5.49  | 0.47  |
| Total               | 65.25 | 66.49 | 65.18 | 65.25 | 66.48 |
| <u>Postdosed</u>    |       |       |       |       |       |
| Sodium carbonate    | 2.23  | -     | 2.30  | 2.23  | -     |
| Antifoam/fluorescer | 3.00  | 4.00  | 3.00  | 3.00  | 4.00  |
| TAED granule        | 4.75  | 4.75  | 4.75  | 4.75  | 4.75  |
| Mn catalyst         | 1.70  | 1.70  | 1.70  | 1.70  | 1.70  |
| Percarbonate        | 20.50 | 20.50 | 20.50 | 20.50 | 20.50 |
| EDTMP               | 0.37  | 0.37  | 0.37  | 0.37  | 0.37  |
| Enzymes             | 1.75  | 1.75  | 1.75  | 1.75  | 1.75  |
| Perfume             | 0.45  | 0.45  | 0.45  | 0.45  | 0.45  |



Examples 1 and 2. Comparative Examples A to C

Table 2: properties and test results

|                               | A    | B    | 1    | C    | 2    |
|-------------------------------|------|------|------|------|------|
| Citrate in base               |      | /    | /    |      | /    |
| Sokalan HP22 solution in base |      |      | /    |      | /    |
| Nonionic 3EO/7EO              | /    | /    | /    |      |      |
| Nonionic 7EO only             |      |      |      | /    | /    |
| Bleeding                      | 36.0 | 35.0 | 0    | 45.0 | 11.0 |
| Cage test residue             | 47.2 | 24.8 | 23.7 | 70.0 | 26.1 |
| Delivery device test          | 62.3 | 0    | 0    | 50.0 | 0    |

Table 3: Examples 3 to 8: non-bleaching formulations

|                  | 3     | 4     | 5     | 6     | 7     | 8     |
|------------------|-------|-------|-------|-------|-------|-------|
| <u>Base</u>      |       |       |       |       |       |       |
| CocOPAS          | 6.16  | 5.84  | 10.66 | 9.44  | 6.46  | 6.46  |
| Nonionic 3EO     | 5.78  | -     | 4.24  | 3.83  | 5.86  | -     |
| Nonionic 7EO     | 5.78  | 13.74 | 6.37  | 5.76  | 8.78  | 14.64 |
| Sokalan HP22     | 0.68  | 0.65  | 0.62  | 0.65  | 0.51  | 0.51  |
| Soap             | 1.84  | 2.03  | 1.85  | 1.64  | 2.25  | 2.25  |
| Zeolite MAP      | 38.66 | 38.49 | 30.91 | 31.52 | 40.15 | 40.15 |
| Sodium citrate   | 4.95  | 4.71  | -     | 4.30  | -     | -     |
| Sodium carbonate | 1.31  | 1.31  | 2.18  | 1.83  | 1.26  | 1.26  |
| SCMC             | -     | -     | -     | -     | 0.72  | 0.72  |
| Water/salts      | 4.72  | 6.03  | 5.32  | 5.92  | 6.22  | 6.22  |
| Total            | 72.80 | 72.80 | 62.15 | 64.89 | 72.22 | 72.22 |
| <u>Postdosed</u> |       |       |       |       |       |       |
| Sodium citrate   | 20.62 | 20.62 | 30.47 | 27.73 | 21.53 | 21.53 |
| Antifoam/PVP     | 3.20  | 3.20  | 4.00  | 4.00  | 3.15  | 3.15  |
| EDTMP            | 1.43  | 1.43  | 1.43  | 1.43  | 1.43  | 1.43  |
| Enzymes          | 1.50  | 1.50  | 1.50  | 1.50  | 1.50  | 1.50  |
| Perfume          | 0.45  | 0.45  | 0.45  | 0.45  | 0.45  | 0.45  |

## Claims

1. A particulate detergent composition comprising an organic surfactant system, a detergency builder system and optionally other detergent ingredients, characterised in that
  - (a) the organic surfactant system comprises mobile ethoxylated nonionic surfactant in an amount of at least 10 wt% based on the whole composition,
  - (b) the composition also comprises 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, and
  - (c) the composition has a bulk density of at least 650 g/litre.
2. A detergent composition as claimed in claim 1, characterised in that it contains at least 12 wt% of mobile ethoxylated nonionic surfactant.
3. A detergent composition as claimed in claim 1, characterised in that the nonionic surfactant consists of one or more C<sub>12-15</sub> aliphatic alcohols ethoxylated with from 2.5 to 8.0 moles of ethylene oxide.
4. A detergent composition as claimed in claim 3, characterised in that the nonionic surfactant consists of one or more C<sub>12-15</sub> aliphatic alcohols ethoxylated with from 6.5 to 8.0 moles of ethylene oxide.
5. A detergent composition as claimed in any preceding claim, characterised in that the organic surfactant system consists essentially of:
  - (i) the ethoxylated nonionic surfactant (60-100 wt% of the surfactant system), and
  - (ii) optionally primary alcohol sulphate (0-40 wt% of the surfactant system).
6. A detergent composition as claimed in claim 5, characterised in that the surfactant system consists essentially of from 30 to 90 wt% (based on the surfactant system) of ethoxylated nonionic surfactant and from 10 to 70 wt% (based on the surfactant system) of primary alcohol sulphate.
7. 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.
8. A detergent composition as claimed in any one of claims 1 to 7, 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.
9. A detergent composition as claimed in any preceding claim, characterised in that the graft copolymer is present in an amount of from 0.1 to 10 wt%.
10. A detergent composition as claimed in any preceding claim, which further comprises a water-soluble salt of citric acid.
11. A detergent composition as claimed in claim 10, characterised in that the composition contains from 0.5 to 40 wt% of sodium citrate.
12. A detergent composition as claimed in claim 11, comprising a substantially homogeneous granular base and optionally postdosed ingredients, characterised in that the granular base contains at least 0.5 wt% (based on the whole composition) of sodium citrate.

13. A detergent composition as claimed in claim 12, characterised in that the substantially homogeneous granular base contains from 3 to 15 wt% (based on the whole composition) of sodium citrate.
14. A detergent composition as claimed in claim 12 or claim 13, characterised in that the sodium citrate in the substantially homogeneous granular base has a Rosin-Rammler particle size not exceeding 800 micrometres.
15. A detergent composition as claimed in any preceding claim, characterised in that the detergency builder system comprises from 10 to 60 wt% (based on the whole composition) of crystalline or amorphous alkali metal aluminosilicate.
16. A detergent composition as claimed in claim 15, characterised in that the alkali metal aluminosilicate is zeolite P having a silicon to aluminium ratio not exceeding 1.33 (zeolite MAP).
17. A detergent composition as claimed in any preceding claim, characterised by a void volume not exceeding 10%.
18. A detergent composition as claimed in claim 17, characterised by a void volume not exceeding 5%.
19. A process for the preparation of a particulate detergent composition as claimed in any preceding claim, characterised in that it comprises preparing a substantially homogeneous granular base by mixing and granulation, then optionally postdosing further ingredients, there is incorporated during the granulation process an aqueous solution of the graft copolymer (b).
20. A process as claimed in claim 19, characterised in that a water-soluble salt of citric acid is also incorporated within the substantially homogeneous granular base.
21. A process as claimed in claim 20, characterised in that the water-soluble salt is sodium citrate and is incorporated in an amount of at least 0.5 wt% based on the whole composition.
22. Use 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, to prevent or reduce the bleeding out of nonionic surfactant from a particulate detergent composition having a bulk density of at least 650 g/litre and comprising an organic surfactant system comprising a mobile ethoxylated nonionic surfactant in an amount of at least 10 wt% based on the whole composition, a detergency builder system and optionally other detergent ingredients.

## Patentansprüche

1. Teilchenförmige Waschmittel-Zusammensetzung umfassend ein organisches Tensidsystem, ein Waschmittel-Buildersystem und gegebenenfalls andere Wasch-Inhaltsstoffe,  
**dadurch gekennzeichnet**, daß
  - (a) das organische Tensidsystem mobiles ethoxyliertes nichtionisches Tensid in einer Menge von mindestens 10 Gew.-%, bezogen auf die gesamte Zusammensetzung, umfaßt,
  - (b) die Zusammensetzung auch ein Pfropf-Copolymer aus
    - (i) Polyethylen-, Polypropylen- oder Polybutylenoxid mit
    - (ii) Vinylacetat (gegebenenfalls teilweise verseift)in einem Gewichtsverhältnis von (i) und (ii) von 1:0,2 bis 1:10 umfaßt und  
(c) die Zusammensetzung eine Schüttdichte von mindestens 650 g/l hat.
2. Waschmittel-Zusammensetzung nach Anspruch 1,

**dadurch gekennzeichnet**, daß sie mindestens 12 Gew.-% mobiles ethoxyliertes nichtionisches Tensid enthält.

3. Waschmittel-Zusammensetzung nach Anspruch 1,  
**dadurch gekennzeichnet**, daß das nichtionische Tensid aus einem oder mehreren aliphatischen C<sub>12</sub>-C<sub>15</sub>-Alkoholen, die mit 2,5 bis 8,0 mol Ethylenoxid ethoxyliert sind, besteht.

4. Waschmittel-Zusammensetzung nach Anspruch 3,  
**dadurch gekennzeichnet**, daß das nichtionische Tensid aus einem oder mehreren aliphatischen C<sub>12</sub>-C<sub>15</sub>-Alkoholen, die mit 6,5 bis 8,0 mol Ethylenoxid ethoxyliert sind, besteht.

5. Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, daß das organische Tensidsystem im wesentlichen aus

(i) dem ethoxylierten nichtionischen Tensid (60 bis 100 Gew.-% des Tensidsystems) und

(ii) gegebenenfalls einem primären Alkoholsulfat (0 bis 40 Gew.-% des Tensidsystems)

besteht.

6. Waschmittel-Zusammensetzung nach Anspruch 5,  
**dadurch gekennzeichnet**, daß das Tensidsystem im wesentlichen aus 30 bis 90 Gew.-% (bezogen auf das Tensidsystem) aus ethoxyliertem nichtionischem Tensid und 10 bis 70 Gew.-% (bezogen auf das Tensidsystem) aus primärem Alkoholsulfat besteht.

7. Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, daß das Pfpf-Copolymer erhältlich ist, indem ein Polyalkylenoxid mit einem (zahlenmittleren) Molekulargewicht von 2.000 bis 100.000 mit Vinylacetat (gegebenenfalls teilweise verseift) in einem Gewichtsverhältnis von Polyalkylenoxid zu Vinylacetat von 1:0,2 bis 1:10 gepfpft wird.

8. Waschmittel-Zusammensetzung nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet**, daß das Pfpf-Copolymer erhältlich ist, indem ein Polyethylenoxid mit einem (zahlenmittleren) Molekulargewicht von 2.000 bis 50.000 mit Vinylacetat (gegebenenfalls teilweise verseift) in einem Gewichtsverhältnis von Polyethylenoxid zu Vinylacetat von 1:0,5 bis 1:6 gepfpft wird.

9. Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, daß das Pfpf-Copolymer in einer Menge von 0,1 bis 10 Gew.-% vorhanden ist.

10. Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, weiter umfassend ein wasserlösliches Salz der Citronensäure.

11. Waschmittel-Zusammensetzung nach Anspruch 10,  
**dadurch gekennzeichnet**, daß die Zusammensetzung 0,5 bis 40 Gew.-% Natriumcitrat enthält.

12. Waschmittel-Zusammensetzung nach Anspruch 11, umfassend einen im wesentlichen homogenen körnigen Grundstoff und gegebenenfalls nachdosierte Inhaltsstoffe,  
**dadurch gekennzeichnet**, daß der körnige Grundstoff mindestens 0,5 Gew.-% (bezogen auf die gesamte Zusammensetzung) Natriumcitrat enthält.

13. Waschmittel-Zusammensetzung nach Anspruch 12,  
**dadurch gekennzeichnet**, daß der im wesentlichen homogene körnige Grundstoff 3 bis 15 Gew.-% (bezogen auf die gesamte Zusammensetzung) Natriumcitrat enthält.

14. Waschmittel-Zusammensetzung nach Anspruch 12 oder Anspruch 13, **dadurch gekennzeichnet**, daß das Natriumcitrat in dem im wesentlichen homogenen körnigen Grundstoff eine Teilchengröße nach Rosin-Rammler von nicht mehr als 800 µm hat.

15. Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, **dadurch gekennzeichnet**, daß das Waschmittel-Buildersystem 10 bis 60 Gew.-% (bezogen auf die gesamte Zusammensetzung) an kristallinem oder amorphem Alkalialuminosilikat enthält.

16. Waschmittel-Zusammensetzung nach Anspruch 15,  
dadurch gekennzeichnet, daß das Alkalialuminosilikat Zeolit P mit einem Verhältnis von Silicium zu Aluminium von nicht mehr als 1,33 ist (Zeolit MAP).

17. Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche gekennzeichnet durch ein Hohlraumvolumen von nicht mehr als 10 %.

18. Waschmittel-Zusammensetzung nach Anspruch 17,  
gekennzeichnet durch ein Hohlraumvolumen von nicht mehr als 5 %.

19. Verfahren zur Herstellung einer teilchenförmigen Waschmittel-Zusammensetzung nach einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß es umfaßt, daß man einen im wesentlichen homogenen körnigen Grundstoff herstellt durch Vermischen und Granulieren, dann gegebenenfalls weitere Inhaltsstoffe nachdosiert und während des Granulierungsverfahrens eine wäßrige Lösung des Pfpf-Copolymers (b) einarbeitet.

20. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß ein wasserlösliches Salz der Citronensäure auch in den im wesentlichen homogenen körnigen Grundstoff eingearbeitet wird.

21. Verfahren nach Anspruch 20, dadurch gekennzeichnet, daß das wasserlösliche Salz Natriumcitrat ist und in einer Menge von mindestens 0,5 Gew.-% bezogen auf die gesamte Zusammensetzung eingearbeitet wird.

22. Verwendung eines Pfpf-Copolymers aus

(i) Polyethylen-, Polypropylen- oder Polybutylenoxid mit

(ii) Vinylacetat (gegebenenfalls teilweise verseift) in einem Gewichtsverhältnis von (i) zu (ii) von 1:0,2 bis 1:10,

um das Ausbluten des nichtionischen Tensids aus einer teilchenförmigen Waschmittel-Zusammensetzung mit einer Schüttdichte von mindestens 650 g/l, die ein organisches Tensidsystem mit einem mobilen ethoxylierten nicht-ionischen Tensid in einer Menge von mindestens 10 Gew.-% bezogen auf die gesamte Zusammensetzung, ein Waschmittel-Buildersystem und gegebenenfalls andere Waschmittel-Inhaltsstoffe enthält, zu verhindern oder zu vermindern.

## Revendications

1. Une composition détergente particulière comprenant un système tensioactif organique, un système d'édificateur de détergence et optionnellement d'autres ingrédients détergents, caractérisée en ce que

(a) le système tensioactif organique comprend un agent tensioactif non ionique éthoxylé mobile dans une quantité au moins égale à 10 % en masse, sur la base de l'ensemble de la composition,

(b) la composition comprend également un copolymère greffé de

(i) oxyde de polyéthylène, polypropylène ou polybutylène avec

(ii) de l'acétate de vinyle (en option partiellement saponifié),

selon un rapport de masse entre (i) et (ii) compris entre 1:0,2 et 1:10, et

(c) la composition présente une masse volumique au moins égale à 650 g/litre.

2. Une composition détergente telle que revendiquée dans la Revendication 1, caractérisée en ce qu'elle contient au moins 12 % en masse d'agent tensioactif non ionique éthoxylé mobile.

3. Une composition détergente telle que revendiquée dans la Revendication 1, caractérisée en ce que l'agent tensioactif non ionique se compose d'un ou de plusieurs alcools aliphatiques en C<sub>12-15</sub> éthoxylés avec 2,5 à 8,0 moles d'oxyde d'éthylène.

4. Une composition détergente telle que revendiquée dans la Revendication 3, caractérisée en ce que l'agent tensioactif non ionique se compose d'un ou de plusieurs alcools aliphatiques en C<sub>12-15</sub> éthoxylés avec 6,5 à 8,0 moles d'oxyde d'éthylène.
- 5 5. Une composition détergente telle que revendiquée dans l'une quelconque des Revendications précédentes, caractérisée en ce que le système tensioactif organique se compose essentiellement de :
  - (i) l'agent tensioactif non ionique éthoxylé (60 à 100% en masse du système tensioactif), et
  - 10 (ii) optionnellement du sulfate d'alcool primaire (0 à 40 % en masse du système tensioactif).
6. Une composition détergente telle que revendiquée dans la Revendication 5, caractérisée en ce que le système tensioactif se compose essentiellement de 30 à 90 % en masse (sur la base du système tensioactif) d'agent tensioactif non ionique éthoxylé et de 10 à 70 % en masse (sur la base du système tensioactif) de sulfate d'alcool primaire.
- 15 7. Une composition détergente telle que revendiquée dans l'une quelconque des Revendications précédentes, caractérisée en ce que le copolymère greffé peut être obtenu par l'étape consistant à greffer un oxyde de polyalkylène de masse moléculaire (pondérée en nombre) comprise entre 2 000 et 100 000 avec de l'acétate de vinyle (en option partiellement saponifié), selon un rapport de masse entre oxyde de polyalkylène et acétate de vinyle compris entre 1:0,2 et 1:10.
- 20 8. Une composition détergente telle que revendiquée dans l'une quelconque des Revendications 1 à 7, caractérisée en ce que le copolymère greffé peut être obtenu par l'étape consistant à greffer un oxyde de polyéthylène de masse moléculaire (pondérée en nombre) comprise entre 2 000 et 50 000 avec de l'acétate de vinyle (en option partiellement saponifié), selon un rapport de masse entre oxyde de polyéthylène et acétate de vinyle compris entre 1:0,5 et 1:6.
- 25 9. Une composition détergente telle que revendiquée dans l'une quelconque des Revendications précédentes, caractérisée en ce que le copolymère greffé est présent dans une quantité comprise entre 0,1 et 10 % en masse.
- 30 10. Une composition détergente telle que revendiquée dans l'une quelconque des Revendications précédentes, qui comprend en outre un sel d'acide citrique soluble dans l'eau.
- 35 11. Une composition détergente telle que revendiquée dans la Revendication 10, caractérisée en ce que la composition contient 0,5 à 40 % en masse de citrate de sodium.
- 40 12. Une composition détergente telle que revendiquée dans la Revendication 11, comprenant une base granulaire substantiellement homogène et optionnellement des ingrédients post-dosés, caractérisée en ce que la base granulaire contient au moins 0,5 % en masse (sur la base de l'ensemble de la composition) de citrate de sodium.
- 45 13. Une composition détergente telle que revendiquée dans la Revendication 12, caractérisée en ce que la base granulaire substantiellement homogène contient 3 à 15% en masse (sur la base de l'ensemble de la composition) de citrate de sodium.
- 50 14. Une composition détergente telle que revendiquée dans la Revendication 12 ou la Revendication 13, caractérisée en ce que le citrate de sodium de la base granulaire substantiellement homogène présente une taille de particules Rosin-Rammler n'excédant pas 800 micromètres.
- 55 15. Une composition détergente telle que revendiquée dans l'une quelconque des Revendications précédentes, caractérisée en ce que le système d'édificateur de détergence comprend 10 à 60 % en masse (sur la base de l'ensemble de la composition) d'aluminosilicate de métal alcalin cristallin ou amorphe.
16. Une composition détergente telle que revendiquée dans la Revendication 15, caractérisée en ce que l'aluminosilicate de métal alcalin est de la zéolite P présentant un rapport entre silicone et aluminium n'excédant pas 1,33 (Zéolite MAP).
17. Une composition détergente telle que revendiquée dans l'une quelconque des Revendications précédentes, ca-

ractérisée par un volume de vide n'excédant pas 10 %.

18. Une composition détergente telle que revendiquée dans la Revendication 17, caractérisée par un volume de vide n'excédant pas 5 %.

19. Un procédé de préparation d'une composition détergente particulière telle que revendiquée dans l'une quelconque des Revendications précédentes, caractérisé en ce qu'il comprend les étapes consistant à préparer une base granulaire substantiellement homogène par mélange et granulation, puis optionnellement à post-doser d'autres ingrédients, et en ce qu'une solution aqueuse du copolymère greffé (b) est incorporée au cours du procédé de granulation.

20. Un procédé tel que revendiqué dans la Revendication 19, caractérisé en ce qu'un sel d'acide citrique soluble dans l'eau est également incorporé à l'intérieur de la base granulaire substantiellement homogène.

21. Un procédé tel que revendiqué dans la Revendication 20, caractérisé en ce que le sel soluble dans l'eau est du citrate de sodium et qu'il est incorporé dans une quantité au moins égale à 0,5 % en masse sur la base de l'ensemble de la composition.

22. Utilisation d'un copolymère greffé de

(i) oxyde de polyéthylène, polypropylène ou polybutylène avec

(ii) de l'acétate de vinyle (en option partiellement saponifié),

selon un rapport de masse entre (i) et (ii) compris entre 1:0,2 et 1:10, afin d'empêcher ou de réduire le ressuage d'un agent tensioactif non ionique depuis une composition détergente particulière présentant une masse volumique au moins égale à 650 g/litre et comprenant un système tensioactif organique comprenant un agent tensioactif non ionique éthoxylé mobile dans une quantité au moins égale à 10% en masse sur la base de l'ensemble de la composition, un système d'édificateur de détergence et en option d'autres ingrédients détergents.