PHOTOBLEACH SPECKLE AND LAUNDRY DETERGENT COMPOSITIONS CONTAINING IT
PHOTOBLEICHSPRENKEL UND ES ENTHALTENDE WASCHMITTEL
AGENT DE BLANCHIMENT ET COMPOSITIONS DE DETERGENT A LESSIVE RENFERMANT CE DERNIER

Designated Contracting States:
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References cited:
DE-A- 3 430 773 GB-A- 2 199 338
US-A- 4 721 633

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Description

TECHNICAL FIELD

[0001] The present invention relates to a coloured granular composition for use as speckles in a particulate laundry detergent composition comprising photobleach.

BACKGROUND AND PRIOR ART

[0002] Photobleaches are often added to detergent laundry powders to provide bleaching of the washed fabrics to improve their visual appeal. The most common and simplest way of incorporating them into detergent powders is to add them to the slurry prior to spray drying of the base powder. However some of the photobleach may be lost due to degradation and evaporation in the spray drying process. Furthermore, there is a well-known problem of staining of the washed fabric due to the photobleach.

[0003] EP 119 746A (Unilever) discloses spraying a solution or suspension of a Zn or Al phthalocyanine sulphonate photobleach onto a detergent base powder subsequent to the spray drying process.

[0004] WO 99 51714A (Unilever) discloses a coloured photobleach speckle composition giving reduced staining wherein the carrier is an α-hydroxy organic acid, preferably citric acid, with a water-soluble barrier material and a flow aid e.g. silica. The composition is claimed to provide reduced fabric staining.

[0005] GB 2199338A discloses a process for the production of detergent speckles comprising applying a phthalocyanine pigment to a spray dried detergent composition.

[0006] DE 3 430 773A (Ciba Geigy) discloses a washing powder additive in speckle form which contains a photobleach, an inorganic carbonate and an acid. Effervescence action generated by the reaction between the carbonate and the acid is claimed to keep the speckles at the surface of the wash liquor and reduce staining of the washed fabrics.

[0007] US 3 931 037 (Procter & Gamble) discloses a colourless granular composition comprising a pale-coloured photobleach granule made by the dry-mixing of a phthalocyanine photobleach particle and a granular material (e.g. sodium tripolyphosphate or spray-dried detergent base powder) to which a liquid (e.g. water) is added.

[0008] US 4 762 636 (Ciba-Geigy) discloses a process for the preparation of spray-dried floating speckles that contain an active substance.

SUMMARY OF INVENTION

[0009] The present inventors have surprisingly found that a coloured speckle composition comprising photobleach which is carried on a spray-dried detergent base powder is able to float on the surface of the wash liquor due to its natural density and provides an attractively coloured speckle which contrasts with the colour of the majority of the detergent powder and delivers a photobleach to the fabric with little or no staining.

[0010] In a first aspect, the present invention provides a coloured granular composition for use as speckles in a particulate laundry detergent composition comprising a porous granular carrier, which is a spray-dried detergent base powder comprising surfactant and optionally builder, and at least 0.01 wt% photobleach based on the active ingredient, the composition having an average bulk density of at most 600 g/l, and layered with a finely divided high liquid carrying capacity particulate material.

[0011] In a second aspect, the present invention provides a particulate laundry detergent composition which comprises surfactant, optionally builder, and from 0.05 to 10 wt% of speckles which are a coloured granular composition as defined above.

[0012] In a third aspect, the present invention provides a process for making a coloured granular composition for use as speckles in a particulate laundry detergent composition, which comprises the steps of:

(i) mixing an aqueous solution of photobleach with a porous carrier having an average bulk density of no more than 600 g/l; followed by

(ii) layering with a finely divided, high liquid carrying capacity particulate material.

DETAILED DESCRIPTION

The Speckles

[0013] The coloured granular compositions of the present invention are intended to be used as speckles in particulate laundry detergent compositions. It is important that such speckles comprise at least 0.01 wt% of the photobleach active ingredient and that in order to float readily on the surface of the water they should have an average bulk density of at
most 600 g/l. Preferably the average bulk density is at most 500 g/l and more preferably at most 400 g/l.

[0014] As well as providing reduced staining photobleach delivery, the speckles are intended to provide an attractive colouration to the powder which the consumer sees during use. Hence it is preferred that the speckles have a number average particle size of at least 200 microns, preferably at least 400 microns.

[0015] In order that the speckles may provide effective delivery of photobleach for the whole of the detergent powder for which they are intended to be incorporated it is preferred that they comprise at least 0.05 wt% photobleach based on the active ingredient, preferably at least 0.1 wt%.

[0016] The carrier for the speckles is a spray-dried detergent base powder comprising surfactant and optionally builder.

[0017] Commercially available photobleaches often come as an aqueous solution and, to improve the process of adding the photobleach to the carrier, other liquid materials may also be added. An especially useful ingredient is propylene glycol.

[0018] Preferred photobleaches are phthalocyanine sulphonates, especially zinc phthalocyanine sulphonates, aluminium phthalocyanine sulphonates or a mixture of the two.

[0019] Since the speckle composition floats on the surface of the water due to its natural buoyancy, it is unnecessary to include ingredients which may cause effervescence, and hence it is preferred that the speckle is non-effervescent. However, inclusion of effervescence-generating ingredients is within the scope of the invention.

The Process for Making the Speckles

[0020] The process of manufacture of the speckles according to the present invention involves the steps of:

(i) mixing a liquid photobleach with a porous carrier having an average bulk density of no more than 600 g/l; followed by
(ii) layering with a finely divided, high liquid carrying capacity particulate material.

[0021] Preferably the carrier material has an average bulk density of at most 500 g/l, more preferably at most 400 g/l.

[0022] In order to improve the process it is preferred that the process is preceded by the step of blending an aqueous solution of photobleach with propylene glycol.

[0023] Preferred high liquid carrying capacity particulate materials are zeolite and/or silica.

[0024] A particularly advantageous process is wherein step (i) comprises atomising and spraying the liquid photobleach onto the porous carrier.

[0025] The carrier for the speckles may be any material so as to give a speckle with an average bulk density of at most 600 g/l and is compatible with particulate laundry detergent compositions. A preferred material is one that has been spray-dried. Especially preferred is a spray-dried base powder comprising surfactant and optionally builder. An alternative material is granular light sodium carbonate (light soda ash).

The Particulate Laundry Detergent Composition

[0026] Detergent compositions of the present invention comprise surfactant and optionally builder. They also contain from 0.05 to 10 wt%, preferably from 1 to 5 wt%, of speckles as described above. It is preferred that the compositions comprise from 5 to 60 wt% surfactant and from 10 to 80 wt% builder.

[0027] It is preferred that the particulate detergent compositions comprise a spray-dried base powder, and more preferably wherein the composition of the carrier of the speckles is substantially the same as the composition of the base powder. This combination enables the carrier for the speckles to be taken from the stock of base powder of the detergent composition and thus enabling manufacturing simplicity.

[0028] In a particularly advantageous embodiment the whole composition is coloured blue, however the speckles contained within it are a darker shade of blue than the rest of the composition. In another particularly advantageous embodiment the bulk of the powder is coloured white and the speckles are coloured blue.

[0029] To ensure that the speckles do not segregate out from the rest of the composition it is preferred that the average bulk density of the speckles is within 100 g/l, preferably within 50 g/l, of that of the composition as a whole. Additionally it is preferred that the number average particle size of the speckles is within 200 microns, preferably within 100 microns, of that of the composition as a whole.

[0030] Photobleach may be present in both the speckles and the composition as a whole, and preferably at least 50 wt% of the total photobleach present is within the speckles. It is most preferred that the photobleach is entirely contained within the coloured speckles.

Detergent Ingredients

[0031] The particulate laundry detergent compositions of the present invention will also contain conventional detergent
ingredients, notably detergent-active materials (surfactants), and preferably also detergency builders.

**[0032]** Such detergent compositions will contain one or more detergent active compounds (surfactants) which may be chosen from soap and non-soap anionic, cationic, nonionic, amphoteric and zwitterionic detergent active compounds, and mixtures thereof.

**[0033]** 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.

**[0034]** The preferred detergent active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds. Non-soap anionic surfactants are especially preferred.

**[0035]** Non-soap anionic surfactants are well-known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly linear alkylbenzene sulphonates having an alkyl chain length of C₈-C₁₅ primary and secondary alkylsulphates, particularly C₁₂-C₁₅ primary alkyl sulphonates; alkyl ether sulphonates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphasuccinates; and fatty acid ester sulphonates.

**[0036]** Sodium salts are generally preferred. A preferred anionic surfactant is linear alkylbenzene sulphonate.

**[0037]** Nonionic surfactants may optionally be present. These include the primary and secondary alcohol ethoxylates, especially the C₆-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₀-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

**[0038]** Cationic surfactants may optionally be present. These include quaternary ammonium salts of the general formula R₁R₂R₃R₄N⁺X⁻ wherein the R groups are long or short hydrocarbyl chains, typically alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a solubilising anion (for example, compounds in which R₁ is a C₆-C₂₂ alkyl group, preferably a C₉-C₁₀ or C₁₂-C₁₄ alkyl group, R₂ is a methyl group, and R₃ and R₄, which may be the same or different, are methyl or hydroxyethyl groups); and cationic esters (for example, choline esters).

**[0039]** In an especially preferred cationic surfactant of the general formula R₁R₂R₃R₄N⁺X⁻, R₁ represents a C₈-C₁₀ or C₁₂-C₁₄ alkyl group, R₂ and R₃ represent methyl groups, R₄ presents a hydroxyethyl group, and X⁻ represents a halide or methosulphate ion.

**[0040]** Optionally, amphoteric surfactants, for example, amine oxides, and zwitterionic surfactants, for example, betaines, may also be present.

**[0041]** Preferably, the quantity of anionic surfactant is in the range of from 5 to 50% by weight of the total composition. More preferably, the quantity of anionic surfactant is in the range of from 8 to 35 wt%, most preferably from 10 to 30 wt%.

**[0042]** Nonionic surfactant, if present, is preferably used in an amount within the range of from 1 to 20 wt% in addition to that which may be present in the structured emulsion.

**[0043]** The detergent compositions may contain as builder a crystalline aluminosilicate, preferably an alkali metal aluminosilicate, more preferably a sodium aluminosilicate (zeolite).

**[0044]** The zeolite used as a builder may be the commercially available zeolite A (zeolite 4A) now widely used in laundry detergent powders. Alternatively, the zeolite may be maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070B (Unilever), and commercially available as Doucil (Trade Mark) A24 from Crosfield Chemicals Ltd, UK.

**[0045]** Zeolite MAP is defined as an alkali metal aluminosilicate of zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, preferably within the range of from 0.90 to 1.20.

**[0046]** Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The particle size of the zeolite is not critical. Zeolite A or zeolite MAP of any suitable particle size may be used.

**[0047]** This may be used in combination with sodium orthophosphate, and/or sodium pyrophosphate.

**[0048]** Other inorganic builders that may be present additionally or alternatively include sodium carbonate, layered silicate, amorphous aluminosilicates.

**[0049]** Most preferably, the builder is selected from sodium tripolyphosphate, zeolite, sodium carbonate, and combinations thereof.

**[0050]** Organic builders may optionally be present. These include polycarboxylate polymers such as polyacrylates and acrylic/maleic copolymers; polyaspartates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-di- and trisuccinates, carboxymethylxysuccinates, carboxy-methoxyxymalonates, dicopolinates, hydroxyethyl iminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts.

**[0051]** Organic builders may be used in minor amounts as supplements to inorganic builders such as phosphates and zeolites. Especially preferred supplementary organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%.

**[0052]** Builders, both inorganic and organic, are preferably present in alkali metal salt, especially sodium salt, form.

**[0053]** Detergent compositions according to the invention may also suitably contain a bleach system, although non-
bleaching formulations are also within the scope of the invention.

The bleach system is preferably based on peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution. Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate. The peroxy bleach compound is suitably present in an amount of from 5 to 35 wt%, preferably from 10 to 25 wt%.

The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 1 to 8 wt%, preferably from 2 to 5 wt%.

Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and peroxycarboxylic acid precursors; and peroxycarbonic acid precursors. An especially preferred bleach precursor suitable for use in the present invention is N,N,N',N'-tetracetyl ethylenediamine (TAED). A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA) and the polyphosphonates such as Dequest (Trade Mark), EDTMP.

The detergent compositions may also contain one or more enzymes. Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions.

Preferred proteolytic enzymes (proteases) are catalytically active protein materials which degrade or alter protein types of stains when present as in fabric stains in a hydrolysis reaction. They may be of any suitable origin, such as vegetable, animal, bacterial or yeast origin. Proteolytic enzymes or proteases of various qualities and origins and having activity in various pH ranges of from 4-12 are available. Proteases of both high and low isoelectric point are suitable.

Other enzymes that may suitably be present include lipases, amylases, and cellulases including high-activity cellulases such as Carezyme (Trade Mark) ex Novo.

In particulate detergent compositions, detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%. However, any suitable physical form of enzyme may be used in any effective amount.

Antiredeposition agents, for example, cellulose esters and ethers, for example sodium carboxymethyl cellulose, may also be present.

The compositions may also contain soil release polymers, for example sulphonated and unsulphonated PET/POET polymers, both end-capped and non-end-capped, and polyethylene glycol/polyvinyl alcohol graft copolymers such as Sokolan (Trade Mark) HP22.

Especially preferred soil release polymers are the sulphonated non-end-capped polyesters as described and claimed in WO 95 32997A (Rhodia Chimie).

The detergent compositions may also include one or more inorganic salts other than builder salts. These may include, for example, sodium bicarbonate, sodium silicate, sodium sulphate, magnesium sulphate, calcium sulphate, calcium chloride and sodium chloride. Preferred inorganic salts are sodium sulphate, sodium chloride, and combinations thereof.

The detergent compositions may also contain other inorganic materials, for example, calcite, silica or amorphous aluminosilicate, or clays.

Other ingredients that may be present include solvents, hydrotropes, fluorescers, dyes, foam boosters or foam controllers (antifoams) as appropriate, fabric conditioning compounds and perfumes.

Preparation of the Detergent Composition

Powders of low to moderate bulk density may be prepared by spray-drying a slurry, and optionally postdosing (dry-mixing) further ingredients. "Concentrated" or "compact" powders may be prepared by mixing and granulating processes, for example, using a high-speed mixer/granulator, or other non-tower processes. In both types of powder, the speckle composition may be incorporated by postdosing (dry mixing).

The composition of the invention may alternatively be in tablet form. Tablets may be prepared by compacting powders, especially "concentrated" or "compact" powders, prepared as described above. Additionally, the composition may be in the form of a liquid, gel, paste or extrudate.

EXAMPLES

Examples 1 and 2: Photobleach Speckles

Speckle compositions were prepared to the following formulation:
In Example 1, the photobleach used was a mixture of zinc and aluminium phthalocyanine sulphonate.

In Example 2, the photobleach used was an aluminium phthalocyanine sulphonate.

Both photobleaches were obtained from Ciba-Geigy under the “Tinolux” Trade Mark. It will be seen that both compositions contained 0.125 wt% photobleach calculated as 100% active.

Each composition was prepared as follows.

The ingredients except the zeolite, silica, propylene glycol and photobleach were sequentially added to water to form a slurry, which was subsequently spray-dried to form a base-powder with an average bulk density of about 450 g/l and a number average particle size of 648 microns. Meanwhile the liquid propylene glycol was blended with a 10% active solution of the photobleach.

The liquid blend was then sprayed onto the spray-dried base-powder and gently mechanically agitated to ensure good mixing. Finally the zeolite and the silica were added as layering agents and gentle mechanical agitation was resumed to ensure good coverage of the granules. The resultant speckle composition had a bulk density of around 500 g/l, a number average particle size of 709 microns and had an intense blue colouration.

Example 3 and 4 and Comparative Examples A to D: Photobleach Staining

The spray-dried detergent compositions tested for staining had the following formulation:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>wt% of base powder</th>
<th>wt% of total</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spray Dried Base</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium LAS</td>
<td>25.75</td>
<td>22.6</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>11.40</td>
<td>10.0</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>17.21</td>
<td>15.1</td>
</tr>
<tr>
<td>Sodium carboxymethylcellulose</td>
<td>0.72</td>
<td>0.63</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>35.33</td>
<td>31.0</td>
</tr>
<tr>
<td>Fluorescer</td>
<td>0.25</td>
<td>0.22</td>
</tr>
<tr>
<td>Blue colourant</td>
<td>0.021</td>
<td>0.018</td>
</tr>
<tr>
<td>Water</td>
<td>9.32</td>
<td>8.18</td>
</tr>
<tr>
<td><strong>Sub Total</strong></td>
<td>100.0</td>
<td>87.75</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>wt% of base powder</th>
<th>wt% of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Silica</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Propylene glycol</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>Photobleach (as 10% active)</td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>100.0</td>
<td></td>
</tr>
</tbody>
</table>

In Example 1, the photobleach used was a mixture of zinc and aluminium phthalocyanine sulphonate.

In Example 2, the photobleach used was an aluminium phthalocyanine sulphonate.

Both photobleaches were obtained from Ciba-Geigy under the “Tinolux” Trade Mark. It will be seen that both compositions contained 0.125 wt% photobleach calculated as 100% active.

Each composition was prepared as follows.

The ingredients except the zeolite, silica, propylene glycol and photobleach were sequentially added to water to form a slurry, which was subsequently spray-dried to form a base-powder with an average bulk density of about 450 g/l and a number average particle size of 648 microns. Meanwhile the liquid propylene glycol was blended with a 10% active solution of the photobleach.

The liquid blend was then sprayed onto the spray-dried base-powder and gently mechanically agitated to ensure good mixing. Finally the zeolite and the silica were added as layering agents and gentle mechanical agitation was resumed to ensure good coverage of the granules. The resultant speckle composition had a bulk density of around 500 g/l, a number average particle size of 709 microns and had an intense blue colouration.

Example 3 and 4 and Comparative Examples A to D: Photobleach Staining

The spray-dried detergent compositions tested for staining had the following formulation:

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>wt% of base powder</th>
<th>wt% of total</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Spray Dried Base</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaLAS</td>
<td>25.74</td>
<td>18.13</td>
</tr>
<tr>
<td>Sodium silicate</td>
<td>11.40</td>
<td>8.03</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>17.21</td>
<td>12.12</td>
</tr>
<tr>
<td>Sodium carboxymethylcellulose</td>
<td>0.72</td>
<td>0.51</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>35.32</td>
<td>24.88</td>
</tr>
<tr>
<td>Fluorescer</td>
<td>0.25</td>
<td>0.18</td>
</tr>
<tr>
<td>Antifoam granule</td>
<td>0.027</td>
<td>0.019</td>
</tr>
<tr>
<td>Blue colourant</td>
<td>0.021</td>
<td>0.015</td>
</tr>
<tr>
<td>Water</td>
<td>9.31</td>
<td>6.56</td>
</tr>
<tr>
<td><strong>Sub Total</strong></td>
<td>100.0</td>
<td>70.44</td>
</tr>
</tbody>
</table>
Photobleach speckles were added to this detergent base to make compositions either inside or outside the present invention.

Example 3 contained 2 wt% of a speckle composition according to Example 1 where the photobleach was a mixture of zinc and aluminium phthalocyanine sulphonate.

Example 4 contained 2 wt% of a speckle composition according to Example 1 where the photobleach was aluminium phthalocyanine sulphonate.

Comparative Example A contained 2 wt% of an aluminium phthalocyanine sulphonate photobleach speckle of the same concentration as in Example 1 but with dense soda ash as a carrier.

Comparative Example B contained 2 wt% of an aluminium phthalocyanine sulphonate photobleach speckle of the same concentration as in Example 1 but with clay as a carrier.

Comparative Example C contained 2 wt% of a mixture of zinc and aluminium phthalocyanine sulphonate photobleach speckle of the same concentration as in Example 1 but with clay as a carrier.

Comparative Example D contained no photobleach speckle.

Experimental Protocol

Six pieces of white knitted cotton of size 15 cm x 15 cm were used as test cloths. The cloths were placed at the bottom of a bowl containing 1 litre of water, onto which 10 g of the detergent composition was poured. The detergent composition was allowed to settle for 10 minutes, after which the fabric was removed and gently rinsed to remove any detergent residues. The fabrics were subsequently dried in a tumble drier and then assessed for the degree of staining, by an expert panel, on a scale of 1 to 5. A result of 1 means no staining and a result of 5 means full staining. A summary of the experimental conditions and the staining results are shown in table 3.

Examples 5 to 8: Detergent Compositions

The formulations shown in Table 4 represent detergent compositions in accordance with the invention.

Table 3

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Photobleach</th>
<th>Carrier</th>
<th>Bulk Density g/l</th>
<th>Degree of staining</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Zn/Al</td>
<td>As in Example 1</td>
<td>505</td>
<td>1-2</td>
</tr>
<tr>
<td>4</td>
<td>Al</td>
<td>As in Example 2</td>
<td>431</td>
<td>1-2</td>
</tr>
<tr>
<td>A</td>
<td>Al</td>
<td>Dense soda ash</td>
<td>1100</td>
<td>3</td>
</tr>
<tr>
<td>B</td>
<td>Al</td>
<td>Clay</td>
<td>935</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td>Zn/Al</td>
<td>Clay</td>
<td>935</td>
<td>4</td>
</tr>
<tr>
<td>D</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>wt% 5</th>
<th>wt% 6</th>
<th>wt% 7</th>
<th>wt% 8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray Dried Base</td>
<td>17.73</td>
<td>6.59</td>
<td>19.5</td>
<td>12.3</td>
</tr>
</tbody>
</table>
Claims

1. A coloured granular composition for use as speckles in a particulate laundry detergent composition characterised in that it comprises a porous granular carrier, which is a spray-dried detergent base powder comprising surfactant and optionally builder, and at least 0.01 wt% photobleach based on the active ingredient, the composition having an average bulk density of at most 600 g/l, and layered with an finally divided, high liquid carrying capacity particulate material.

2. A coloured granular composition according to claim 1, characterised in that it has an average bulk density of at most 500 g/l.

3. A coloured granular composition according to claim 2, characterised in that it has an average bulk density of at most 400 g/l.

4. A coloured granular composition according to any preceding claim, characterised in that it has a number average particle size of at least 200 microns.

5. A coloured granular composition according to claim 4, characterised in that it has a number average particle size of at least 400 microns.

6. A coloured granular composition according to any preceding claim, characterised in that it comprises at least 0.1 wt% photobleach.

7. A coloured granular composition according to any preceding claim, characterised in that it also comprises propylene glycol.

8. A coloured granular composition according to any preceding claim, characterised in that the photobleach is a zinc and/or aluminium phthalocyanine sulphonate.

9. A coloured granular composition according to claim 8, characterised in that the photobleach is a mixture of zinc and aluminium phthalocyanine sulphonate.

10. A coloured granular composition according to any preceding claim, characterised in that it is non-effervescent.
11. A particulate laundry detergent composition **characterised in that** it comprises surfactant, optionally builder, and from 0.05 to 10 wt% of speckles which are a coloured granular composition according to any preceding claim.

12. A detergent composition according to claim 11, which comprises a spray-dried base powder and wherein the composition of the carrier of the speckles is substantially the same as the composition of the base powder.

13. A detergent composition according to claim 11 or 12, **characterised in that** it comprises from 1 to 5 wt% of speckles.

14. A detergent composition according to any one of claims 11 to 13, **characterised in that** it comprises from 5 to 60 wt% surfactant and from 10 to 80 wt% builder.

15. A detergent composition according to any one of claims 11 to 14, **characterised in that** the bulk of the composition is blue and the speckles are a darker shade of blue than the rest of the composition.

16. A detergent composition according to any one of claims 11 to 14, **characterised in that** the bulk of the composition is white and the speckles are blue.

17. A detergent composition according to any one of claims 11 to 16, **characterised in that** the average bulk density of the speckles is within 100 g/l, preferably within 50 g/l, of that of the composition as a whole.

18. A detergent composition according to any one of claims 11 to 17, **characterised in that** the number average particle size of the speckles is within 200 microns, preferably within 100 microns, of that of the composition as a whole.

19. A detergent composition according to any one of claims 11 to 18, **characterised in that** at least 50 wt% of photobleach present in the composition is contained within the coloured speckles.

20. A detergent composition according to claim 19, **characterised in that** all photobleach in the composition is contained within the coloured speckles.

21. A process for making a coloured granular composition for use as speckles in a particulate laundry detergent composition, **characterised in that** it comprises the steps of :

   (i) mixing a liquid photobleach with a porous carrier having an average bulk density of no more than 600 g/l; followed by
   (ii) layering with a finely divided, high liquid carrying capacity particulate material.

22. A process according to claim 21, **characterised in that** the porous carrier has an average bulk density of no more than 500 g/l.

23. A process according to claim 22, **characterised in that** the porous carrier has an average bulk density of no more than 400 g/l.

24. A process according to any one of claims 21 to 23, **characterised in that** it is preceded by the step of blending an aqueous solution of photobleach with propylene glycol.

25. A process according to any one of claims 21 to 24, **characterised in that** the high liquid carrying capacity material is zeolite and/or silica.

26. A process according to any one of claims 21 to 25, **characterised in that** step (i) comprises atomising and spraying the liquid photobleach onto the porous carrier.

27. A process according to any one of claims 21 to 26, **characterised in that** the porous carrier is a spray-dried detergent base powder.

**Patentansprüche**

1. Gefärbte granuläre Zusammensetzung zur Verwendung als Sprenkel in einer teilchenförmigen Wäschewaschmit-
telzusammensetzung, **dadurch gekennzeichnet, dass** sie einen porösen granulären Träger umfasst, der ein sprühgetrocknetes Waschmittelgrundpulver, umfassend Tensid und gegebenenfalls Builder darstellt, und mindestens 0,01 Gewichtsprozent Photobleichmittel, bezogen auf den aktiven Bestandteil, wobei die Zusammensetzung eine mittlere Schüttichte von maximal 600 g/l aufweist und beschichtet mit einem fein verteilten, teilenförmigen Material, das viel Flüssigkeit aufnehmen kann.

2. Gefärbte granuläre Zusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** sie eine mittlere Schüttichte von maximal 500 g/l aufweist.

3. Gefärbte granuläre Zusammensetzung nach Anspruch 2, **dadurch gekennzeichnet, dass** sie eine mittlere Schüttichte von maximal 400 g/l aufweist.

4. Gefärbte granuläre Zusammensetzung nach einem vorangehenden Anspruch, **dadurch gekennzeichnet, dass** sie eine zahlenmittlere Teilchengröße von mindestens 200 µm aufweist.

5. Gefärbte granuläre Zusammensetzung nach Anspruch 4, **dadurch gekennzeichnet, dass** sie eine zahlenmittlere Teilchengröße von mindestens 400 µm aufweist.

6. Gefärbte granuläre Zusammensetzung nach einem vorangehenden Anspruch, **dadurch gekennzeichnet, dass** sie mindestens 0,1 Gewichtsprozent Photobleichmittel umfasst.

7. Gefärbte granuläre Zusammensetzung nach einem vorangehenden Anspruch, **dadurch gekennzeichnet, dass** sie auch Propylenglycol umfasst.

8. Gefärbte granuläre Zusammensetzung nach einem vorangehenden Anspruch, **dadurch gekennzeichnet, dass** das Photobleichmittel ein Zink- und/oder Aluminiumphthalocyaninsulfonat darstellt.

9. Gefärbte granuläre Zusammensetzung nach Anspruch 8, **dadurch gekennzeichnet, dass** das Photobleichmittel ein Gemisch von Zink- und Aluminiumphthalocyaninsulfonat ist.

10. Gefärbte granuläre Zusammensetzung nach einem vorangehenden Anspruch, **dadurch gekennzeichnet, dass** sie nicht aufschäumend ist.

11. Teilchenförmige Wäschewaschmittelzusammensetzung, **dadurch gekennzeichnet, dass** sie Tensid, gegebenenfalls Builder, und 0,05 bis 10 Gewichtsprozent Sprengel umfasst, die eine gefärbte granuläre Zusammensetzung nach einem vorangehenden Anspruch darstellen.

12. Waschmittelzusammensetzung nach Anspruch 11, die ein sprühgetrocknetes Grundpulver umfasst und worin die Zusammensetzung des Trägers der Sprengel im Wesentlichen die gleiche wie die Zusammensetzung des Grundpulvers ist.

13. Waschmittelzusammensetzung nach Anspruch 11 oder 12, **dadurch gekennzeichnet, dass** sie 1 bis 5 Gewichtsprozent Sprengel umfasst.

14. Waschmittelzusammensetzung nach einem der Ansprüche 11 bis 13, **dadurch gekennzeichnet, dass** sie 5 bis 60 Gewichtsprozent Tensid und 10 bis 80 Gewichtsprozent Builder umfasst.

15. Waschmittelzusammensetzung nach einem der Ansprüche 11 bis 14, **dadurch gekennzeichnet, dass** die Masse der Zusammensetzung blau ist und die Sprengel einen dunkleren Blauton haben als der Rest der Zusammensetzung.

16. Waschmittelzusammensetzung nach einem der Ansprüche 11 bis 14, **dadurch gekennzeichnet, dass** die Masse der Zusammensetzung weiß ist und die Sprengel blau sind.

17. Waschmittelzusammensetzung nach einem der Ansprüche 11 bis 16, **dadurch gekennzeichnet, dass** die mittlere Schüttichte der Sprengel innerhalb 100 g/l, vorzugsweise innerhalb 50 g/l, von jener der Zusammensetzung als Ganzes ist.

18. Waschmittelzusammensetzung nach einem der Ansprüche 11 bis 17, **dadurch gekennzeichnet, dass** die zah-
lenmittlere Teilchengröße der Sprenkel innerhalb 200 µm, vorzugsweise innerhalb 100 µm, von jener der Zusammensetzung als Ganzes ist.


21. Verfahren zur Herstellung einer gefärbten granulären Zusammensetzung zur Verwendung als Sprenkel in einer teilchenförmigen Wäschewaschmittelzusammensetzung, dadurch gekennzeichnet, dass es die Schritte umfasst von:

(i) Vermischen eines flüssigen Photobleichmittels mit einem porösen Träger mit einer mittleren Schüttdichte von nicht mehr als 600 g/l; gefolgt von
(ii) Beschichten mit einem fein verteilten, teilchenförmigen Material, das viel Flüssigkeit aufnehmen kann.

22. Verfahren nach Anspruch 21, dadurch gekennzeichnet, dass der poröse Träger eine mittlere Schüttdichte von nicht mehr als 500 g/l aufweist.

23. Verfahren nach Anspruch 22, dadurch gekennzeichnet, dass der poröse Träger eine mittlere Schüttdichte von nicht mehr als 400 g/l aufweist.


25. Verfahren nach einem der Ansprüche 21 bis 24, dadurch gekennzeichnet, dass das Material, das viel Flüssigkeit aufnehmen kann, Zeolith und/oder Siliziumdioxid ist.


27. Verfahren nach einem der Ansprüche 21 bis 26, dadurch gekennzeichnet, dass der poröse Träger ein sprühgetrocknetes Waschmittelgrundpulver ist.

Revendications

1. Composition granulaire colorée destinée à servir de paillettes dans une composition de particules de détergent à lessive caractérisée en ce qu’elle comprend un agent de transport granulaire poreux, qui est une poudre de base détergente séchée par atomisation comprenant un agent tensioactif et éventuellement un adjuvant, et au moins 0,01 % en poids d’un agent de blanchiment par rapport à l’ingrédient actif, la composition ayant une densité apparente moyenne au plus égale à 600 g/l, et étant recouverte de particules finement divisées à haute capacité de transport de liquide.

2. Composition granulaire colorée selon la revendication 1, caractérisée en ce qu’elle a une densité apparente moyenne au plus égale à 500 g/l.

3. Composition granulaire colorée selon la revendication 2, caractérisée en ce qu’elle a une densité apparente moyenne au plus égale à 400 g/l.

4. Composition granulaire colorée selon l’une quelconque des revendications précédentes, caractérisée en ce qu’elle a une taille moyenne de particule au moins égale à 200 microns.

5. Composition granulaire colorée selon la revendication 4, caractérisée en ce qu’elle a une taille moyenne de particule au moins égale à 400 microns.
6. Composition granulaire colorée selon l’une quelconque des revendications précédentes, caractérisée en ce qu’elle comprend au moins 0,1 % en poids d’un agent de blanchiment.

7. Composition granulaire colorée selon l’une quelconque des revendications précédentes, caractérisée en ce qu’elle comprend également du propylène glycol.

8. Composition granulaire colorée selon l’une quelconque des revendications précédentes, caractérisée en ce que l’agent de blanchiment est un sulfonate de phthalocyanine de zinc et/ou d’aluminium.

9. Composition granulaire colorée selon la revendication 8, caractérisée en ce que l’agent de blanchiment est un mélange de sulfonate de phthalocyanine de zinc et d’aluminium.

10. Composition granulaire colorée selon l’une quelconque des revendications précédentes, caractérisée en ce qu’elle est non effervescente.

11. Composition de particules de détergent à lessive caractérisée en ce qu’elle comprend un agent tensioactif, éventuellement un adjuvant, et de 0,05 à 10 % en poids de paillettes qui sont une composition granulaire colorée selon l’une quelconque des revendications précédentes.

12. Composition détergente selon la revendication 11, qui comprend une poudre de base séchée par atomisation et dans laquelle la composition de l’agent de transport des paillettes est sensiblement identique à la composition de la poudre de base.

13. Composition détergente selon la revendication 11 ou 12, caractérisée en ce qu’elle comprend de 1 à 5 % en poids de paillettes.

14. Composition détergente selon l’une quelconque des revendications 11 à 13, caractérisée en ce qu’elle comprend de 5 à 60 % en poids d’un agent tensioactif et de 10 à 80 % en poids d’un adjuvant.

15. Composition détergente selon l’une quelconque des revendications 11 à 14, caractérisée en ce que la masse de la composition est de couleur bleue et en ce que les paillettes sont d’un bleu plus foncé que le reste de la composition.

16. Composition détergente selon l’une quelconque des revendications 11 à 14, caractérisée en ce que la masse de la composition est de couleur blanche et en ce que les paillettes sont de couleur bleue.

17. Composition détergente selon l’une quelconque des revendications 11 à 16, caractérisée en ce que la densité apparente moyenne des paillettes se situe à moins de 100 g/l, et de préférence à moins de 50 g/l, de celle de l’ensemble de la composition.

18. Composition détergente selon l’une quelconque des revendications 11 à 17, caractérisée en ce que la taille moyenne de particule des paillettes se situe à moins de 200 microns, et de préférence à moins de 100 microns, de celle de l’ensemble de la composition.

19. Composition détergente selon l’une quelconque des revendications 11 à 18, caractérisée en ce qu’au moins la moitié en poids de l’agent de blanchiment présent dans la composition se trouve dans les paillettes colorées.

20. Composition détergente selon la revendication 19, caractérisée en ce que la totalité de l’agent de blanchiment présent dans la composition se trouve dans les paillettes colorées.

21. Procédé pour fabriquer une composition granulaire colorée destinée à servir de paillettes dans une composition de particules de détergent à lessive, caractérisée en ce qu’il comprend les étapes consistant à :

(i) mélanger un agent de blanchiment liquide à un agent de transport poreux ayant une densité apparente moyenne au plus égale à 600 g/l ; puis à

(ii) recouvrir le mélange de particules finement divisées à haute capacité de transport de liquide.

22. Procédé selon la revendication 21, caractérisé en ce que l’agent de transport poreux a une densité apparente moyenne au plus égale à 500 g/l.
23. Procédé selon la revendication 22, caractérisé en ce que l’agent de transport poreux a une densité apparente moyenne au plus égale à 400 g/l.

24. Procédé selon l’une quelconque des revendications 21 à 23, caractérisé en ce qu’il est précédé de l’étape consistant à mélanger une solution aqueuse d’un agent de blanchiment avec du propylène glycol.

25. Procédé selon l’une quelconque des revendications 21 à 24, caractérisé en ce que le matériau à haute capacité de transport de liquide est une zéolithe et/ou une silice.


27. Procédé selon l’une quelconque des revendications 21 à 26, caractérisé en ce que l’agent de transport poreux est une poudre de base détergente séchée par atomisation.