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(54) **Detergent powders**

Waschpulver

Poudres détergentes

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• **Detergent Manufacture Including Zeolite Builders and Other New Materials, 1979, pp. 445-446**

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Description

5 **[0001]** The present invention relates to detergent powders intended for use in drum-type fabric washing machines. The invention is of especial applicability to powders containing no, or reduced levels of, phosphate builders and to powders of high bulk density, which have a tendency to dispense poorly.

10 **[0002]** In recent years the trend in detergent compositions has been towards reducing or eliminating phosphate builders. The replacement of sodium tripolyphosphate as a builder in detergent powders by its most popular zero-phosphate substitute, crystalline sodium aluminosilicate (zeolite), has led to a number of difficulties with the structure and physical properties of the powder. One such problem that has been encountered is the tendency of zeolite-built powders to disperse less well in automatic washing machines than do their phosphate-built counterparts; a higher proportion of the powder dosed into the machine is left behind in the dispenser, leading to product wastage and clogging. This problem is especially marked at low water inlet temperatures.

15 **[0003]** The tendency towards poor dispensing has been exacerbated by the recent trend in the detergents industry towards higher bulk density powders.

[0004] We have now found that the dispensing behaviour of those powders that are especially prone to this problem may be substantially improved by including in the powders a small amount of an additive, said additive being a polyol which is completely esterified with fatty acids, the mean number of carbon atoms per fatty acid residue being at least 14.

[0005] Surprisingly, the incorporation of these compounds via the slurry also improves powder structure and, when anionic surfactant is present, raises the bulk density.

20 **[0006]** In a first aspect, the invention comprises a granular detergent composition comprising one or more surfactants and an additive, said additive being a polyol which is completely esterified with fatty acids, the mean number of carbon atoms per fatty acid residue being at least 14, which composition comprises a crystalline or amorphous aluminosilicate detergency builder and is substantially free from inorganic phosphate. Preferably, the polyol is a glycerol.

25 **[0007]** In a second aspect, the invention relates to the use of a polyol which is completely esterified with fatty acids, the mean number of carbon atoms per fatty acid residue being at least 14, as an additive for improving the dispensing behaviour of a granular detergent composition.

PRIOR ART

30 **[0008]** EP-A-337,523 (Unilever) discloses that the dispensing properties of certain spray-dried detergent powder may be improved by the incorporation of 0.1 to 6.0% by weight of certain hydrophobic additives such as paraffin wax.

35 **[0009]** EP-A-344,629 (Henkel) relates to a spray-dried granular detergent composition comprising 45 to 75% zeolite, 1 to 6% water-soluble soap, 1 to 12% of a polymer and 10 to 22% water, the granules having a mean particle size of 0.2 to 1.2 mm and a bulk density of 350 to 680 g/l. The granules have a high absorption capacity for liquid or pasty detergent components such as nonionic surfactants, and are used to manufacture a detergent powder having improved dispensing properties. It is mentioned that the dispensing properties may be further improved if the nonionic surfactant contains a polar compound which is sparingly or not soluble in water, but may be dispersed therein, which compound further comprises hydrophobic moieties. Partially esterified polyols such as partially esterified glycerols are mentioned as examples.

40 **[0010]** The first aspect of the invention is a granular detergent composition. The composition of the invention may be a fully formulated detergent composition prepared wholly by spray-drying or dry-mixing. It may also be a spray-dried base to which other ingredients may be admixed to form a finished product or a finished product of that type, comprising a spray-dried base in admixture with other ingredients.

45 **[0011]** As essential ingredients, the detergent powder of the invention contains one or more surfactants, preferably anionic and/or nonionic surfactants, a fully esterified polyol (hereafter also referred to as the additive), which influences its dispensing behaviour in a particular manner, and a crystalline or amorphous aluminosilicate detergency builder.

[0012] The composition of the invention may also contain any of the materials conventionally included in detergent compositions, which are described in more detail below. However, it is substantially free from inorganic phosphate.

50 **[0013]** The total amount of surfactant present in the composition of the invention will generally range from 5 to 40% by weight, more preferably from 10 to 30% by weight and especially from 12 to 20% by weight. These figures are typical for fully formulated detergent compositions, and where a spray-dried base forms only part of such a composition the surfactant content of that base, as a percentage, may of course be higher.

55 **[0014]** The invention is of especial applicability to compositions containing anionic surfactant. When such powders are prepared by spray-drying, the high-foaming anionic surfactant tends to cause "puffing" (entrainment of air) in the slurry, so that highly porous particles are formed in the spray-drying tower. These particles may be very crisp and free-flowing, but may be of lower bulk density than desired. Surprisingly, the incorporation into the slurry of the additive in accordance with the present invention results in a bulk density increase.

[0015] The amount of anionic surfactant present is desirably at least 5% by weight, and may suitably be in the range

of from 5 to 30% by weight, preferably from 5 to 10% by weight, these figures again being based on a fully formulated detergent composition.

[0016] 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 C₈-C₁₅; primary and secondary alkyl sulphates, particularly sodium C₁₂-C₁₅ primary alcohol sulphates; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

[0017] Preferably, the composition of the invention also contains one or more nonionic surfactants. Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₁₂-C₁₅ primary and secondary alcohols ethoxylated with an average of from 3 to 20 moles of ethylene oxide per mole of alcohol.

[0018] The weight ratio of anionic surfactant to nonionic surfactant is preferably at least 0.67:1, more preferably at least 1:1, and most preferably within the range of from 1:1 to 0:1, in order to obtain the optimum detergency and foaming properties appropriate for front-loading automatic washing machines. These ratios of course apply to fully formulated products. A spray-dried base that is to form only part of a product may contain a lower proportion of, or no, nonionic surfactant, the balance of the nonionic surfactant being added after the spray-drying tower.

The additive

[0019] The characterizing feature of the composition of the present invention is the presence of a low level (0.1-6.0% by weight) of an additive, a polyol which is completely esterified with fatty acids, whereby the mean number of carbon atoms per fatty acid residue is at least 14. Preferably, a triglyceride is used.

[0020] The additive may be a single type of triglyceride whereby the fatty acid residues are derived from one single type of fatty acid such as stearic acid or palmitic acid, but also mixtures of fatty acids can be employed. The fatty acids may be saturated or unsaturated and can be of natural or synthetic origin. The only prerequisite appears to be that the mean number of carbon atoms per fatty acid residue in the triglyceride is at least 14, preferably at least 16 and more preferably at least 18.

[0021] Instead of one single type of triglyceride one can also use mixtures of triglycerides such as they occur naturally in fats from animal or plant origin. An example of a much preferred material is tallow fat because it is easily available and attractive from an economic point of view. Mixtures of fats can obviously also be used.

[0022] The additive is preferably present in an amount of from 0.2 to 4% by weight. In a fully formulated product the optimum level for triglycerides appears to be from 0.3 to 2% by weight.

[0023] The composition of the invention can be prepared by a process which includes the step of spray-drying an aqueous crutcher slurry. This slurry will normally contain all those desired ingredients sufficiently heat-stable to survive the spray-drying process, notably anionic surfactants, builders, inorganic salts, sodium silicate, polymers and fluorescers. More heat-sensitive ingredients can be postdosed to, or sprayed onto, the spray-dried base. Alternatively, the composition may be prepared by a process which involves the in-situ neutralization of an acid anionic surfactant precursor by a solid alkaline component.

[0024] There are various methods by means of which the additive characteristic of the invention may be incorporated. It may be included in the slurry, in which case it is preferably used in an amount of from 0.2 to 4.0% by weight, more preferably from 0.3 to 2.0% by weight, based on the final powder including any postdosed ingredients. It may be advantageous to premix the additive with surfactant, especially nonionic surfactant, before admixture with other slurry ingredients.

[0025] It has surprisingly been found that incorporation of the additive via the slurry not only improves dispensing behaviour, but also improves powder structure and, when anionic surfactant is present, also raises the bulk density. Flow properties are not detrimentally affected.

[0026] A second method by which the additive may be incorporated in a detergent composition of the invention is by spraying it in liquefied form onto the spray-dried powder, for example when the powder is transported on a conveyor belt.

[0027] If necessary, the additive may be melted and sprayed directly onto the powder. It is then preferably used in an amount of from 2.0 to 6.0% by weight, more preferably from 3.0 to 4.0% by weight.

[0028] According to a preferred embodiment of the invention, however, the additive is premixed with nonionic surfactant to form a coating composition which may then be sprayed onto the detergent powder. Lower levels of the additive, for example, 0.2 to 4.0%, preferably 0.3 to 2.0%, are then found to be effective. The coating composition consists essentially of 2-50% by weight of the additive and 50-98% by weight of nonionic surfactant. In the preferred embodiment of the invention in which the additive is tallow, the coating composition desirably contains 5-25% by weight of tallow fat and 75-95% by weight of nonionic surfactant. The tallow, and if necessary the nonionic surfactant, are mixed to form the coating composition, which is applied as a liquid, suitably at a temperature of 20-60°C.

[0029] The coating composition should be substantially free of other ingredients that might interfere with the beneficial effect of the additive on dispensing.

Dispensing behaviour

5 **[0030]** It is an essential feature of the detergent powder of the invention that the incorporation as specified above of an additive should bring about an improvement in dispensing behaviour. Dispensing is assessed by means of a standard test using a Philips (Trade Mark) AWB 126/7 washing machine using a 100 g powder dose and a water fill of 5 liters at 20°C flowing in over a period of 1 minute. The dry weight of powder remaining in the dispenser, in grams, then represents the weight percentage of powder not dispensed into the machine (the residue). It will be appreciated that this test is stringent, using a low water inlet temperature and flow rate, and a machine with a drawer-type dispenser which is particularly vulnerable to high residues and clogging. According to the invention, the incorporation of the completely esterified polyol or triglyceride material should effect a reduction in the residue of at least 10 percentage points, preferably at least 20 percentage points.

10 **[0031]** Clearly an improvement of this magnitude can only be observed if the control powder exhibits poor dispensing properties. The present invention is therefore especially applicable to powders which, without the additive, give dispenser residues of at least 10%, more especially at least 20%, by weight. That is especially likely to be the case if the powder is a zero-phosphate composition built with crystalline (zeolite) or amorphous sodium aluminosilicate; if it contains less than 10% sodium silicate; or if it has a bulk density of 600, preferably of 700 g/litre or more.

Optional components

20 **[0032]** As indicated previously, the detergent powder of the invention can contain any of the ingredients conventionally present in compositions intended for the washing of fabrics in automatic washing machines. Examples of such components include inorganic and organic detergency builders, other inorganic salts, sodium silicate, bleaches, fluorescers, polymers, lather control agents, enzymes and perfumes.

25 **[0033]** If desired, the powder of the invention may contain one or more soaps of fatty acids, in addition to the non-soap anionic surfactant mentioned above.

30 **[0034]** The powder will also contain one or more detergency builders. The invention is of especial applicability, as previously mentioned, to low- or zero-phosphate powders containing crystalline (zeolite) or amorphous aluminosilicate. Zeolite may suitably be present in an amount of from 20 to 80% by weight. Other, supplementary, builders may also be present, for example, polycarboxylate polymers such as polyacrylates, acrylic-maleic copolymers, or acrylic phosphinates; monomeric polycarboxylates such as nitrilotriacetates and ethylene diamine tetraacetates; inorganic salts such as sodium carbonate; and many other builder materials familiar to the skilled detergent formulator.

35 **[0035]** If desired, the powder of the invention may contain sodium silicate. High levels of silicate can in themselves have a beneficial effect on dispensing, as well as on powder structure and prevention of machine corrosion, but are undesirable in powders containing aluminosilicate because the two components react together to form insoluble siliceous species. The present invention enables the dispensing behaviour of zeolite-built powders to be improved without a corresponding increase in the level of insoluble material. Accordingly, the invention is of especial applicability to powders containing less than 10% by weight, more especially less than 5% by weight, of sodium silicate.

40 **[0036]** Other materials that may be present in the powder of the invention include fluorescers, antiredeposition agents, inorganic salts such as sodium sulphate, enzymes, lather control agents, bleaches, bleach activators, and bleach stabilizers. These may be included in the spray-dried base powder or postdosed according to their known suitability for undergoing spray-drying processes and their compatibility with other slurry ingredients.

[0037] The invention is further illustrated by the following nonlimiting Examples, in which parts and percentages are by weight unless otherwise stated. In the Examples the following abbreviations are used:

45 ABS : C₁₂-C₁₅ alkyl benzene sulphonate
 Nonionic : Nonionic surfactant (ethoxylated alcohol), Synperonic A3 or A7 (3 or 7 EO groups, respectively) ex ICI
 Carbonate : Sodium carbonate
 Zeolite : Zeolite 4A (Wessalith [Trade Mark] ex Degussa)
 Copolymer : Copolymer of maleic and acrylic acid having a molecular weight of 70,000, CP5 ex BASF

EXAMPLES 1-4

50 **[0038]** A phosphate-free detergent base powder was prepared, by slurry-making and spray-drying, to form the following nominal composition:

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	Parts
ABS	9.23
Nonionic 7EO	2.75
Zeolite (anhydrous)	26.00
Carbonate	3.00
Copolymer	3.00
Minor ingredients	0.99
Moisture	11.24
Total:	56.21

[0039] To this base powder, 6.0 parts of sodium carbonate were postdosed.

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[0040] Subsequently, 0.47 parts of the triglycerides trilaurate, trimyristate tripalmitate and tristearate were each melted and dispersed in 4.7 parts liquid nonionic 3EO surfactant. These coating compositions thus consisted of 90.9% by weight of liquid nonionic surfactant and 9.1% by weight of triglyceride. The liquid triglyceride mixtures were sprayed onto the above described base powder/carbonate mixture. A comparative example A was prepared by spaying only 4.7 parts of nonionic surfactant onto the base powder. The following Table 1 shows the dispenser residue of the obtained five compositions, when measured in a Philips (Trade Mark) AWB 126/7 washing machine using 100 g powder, and 5

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TABLE 1

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	1	2	3	4	A
Type of Triglyceride	trilaurate	trimyristate	tripalmitate	tristearate	-
Number of C-atoms	12	14	16	18	-
Triglyceride level, parts	0.47	0.47	0.47	0.47	-
%	0.70	0.70	0.70	0.70	-
Dispenser Residue (%)	49	52	41	26	58

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The incorporation of triglycerides having 16 C-atoms or more in the fatty acid residue results in a significant improvement of the dispensing behaviour.

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EXAMPLES 5-7

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[0041] The Examples 1-4 were repeated using tallow fat/nonionic mixtures in various amounts. The coating compositions were as follows (amounts given in parts):

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	5	6	7
Tallow fat	0.25	0.50	1.00
Nonionic 3EO	4.70	4.70	4.70

55 The following Table 2 shows the dispenser residue of the obtained compositions, when measured as described above.

TABLE 2

	5	6	7	A
Additive level, parts	4.95	5.20	5.70	-
%	7.40	7.90	8.70	-
Dispenser Residue (%)	1	1	1	58

It can be seen that even at the low level of 0.25 parts or 0.4% by weight of tallow fat, negligible values were found for the dispenser residue.

EXAMPLE 8

Complete fabric washing powders were prepared by post-dozing the ingredients mentioned below to the base powders of Comparative Example A and Example 6, to give the compositions of Comparative Example B and Example 8, respectively.

Base powder	72.3
Sodium perborate monohydrate	19.6
TAED granules	4.5
Enzyme granules	0.6
Anti-foam granules	3.0
Total	100.0

The dispensing properties of the obtained washing powders are given in the following Table 3.

TABLE 2

Example	8	B
Dispenser Residue (%)	0	51

Claims

1. A granular detergent composition comprising one or more surfactants and an additive, said additive being a polyol which is completely esterified with fatty acids, the mean number of carbon atoms per fatty acid residue being at least 14, which composition comprises a crystalline or amorphous aluminosilicate detergency builder and is substantially free from inorganic phosphate.
2. A composition according to claim 1, comprising from 0.1 to 6.0% by weight of the additive.
3. A composition according to any one of the preceding claims, comprising from 0.2 to 4.0% by weight of the additive.
4. A composition according to any one of the preceding claims, wherein the additive is a triglyceride.
5. A composition according to any one of the preceding claims, wherein the mean number of carbon atoms per fatty acid residue in the triglyceride is at least 16, preferably at least 18.
6. A composition according to any one of the preceding claims, wherein the additive is tallow fat.
7. A composition according to any one of the preceding claims, characterised in that a comparative composition with-

out the additive gives a dispenser residue of at least 10%, preferably at least 20% by weight in the defined test.

8. A composition according to any one of the preceding claims, characterised in that a comparative composition without the additive gives a dispenser residue of at least 30% by weight in the defined test.

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9. A composition according to any one of the preceding claims, containing at least 5% by weight of one or more anionic surfactants.

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10. A composition according to any one of the preceding claims, comprising from 20 to 80% by weight of crystalline or amorphous aluminosilicate detergency builder.

11. A composition according to any one of the preceding claims, containing no more than 10% by weight of alkali metal silicate.

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12. A composition according to any one of the preceding claims, having a bulk density of at least 600 g/l, preferably at least 700 g/l.

13. Use of a polyol which is completely esterified with fatty acids, the mean number of carbon atoms per fatty acid residue being at least 14, for improving the dispensing properties of a detergent composition.

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Patentansprüche

1. Gekörntes Waschmittel, umfassend ein oder mehrere Tenside und ein Additiv, wobei das Additiv ein Polyol darstellt, das vollständig mit Fettsäuren verestert ist, die mittlere Zahl an Kohlenstoffatomen pro Fettsäurerest mindestens 14 ist, und das Mittel einen kristallinen oder amorphen Aluminosilicat-Waschmittelbuilder umfaßt und im wesentlichen frei von anorganischem Phosphat ist.

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2. Mittel nach Anspruch 1, umfassend 0,1 bis 6,0 Gew.-% des Additivs.

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3. Mittel nach einem der vorangehenden Ansprüche, umfassend 0,2 bis 4,0 Gew.-% des Additivs.

4. Mittel nach einem der vorangehenden Ansprüche, wobei das Additiv ein Triglycerid ist.

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5. Mittel nach einem der vorangehenden Ansprüche, wobei die mittlere Zahl an Kohlenstoffatomen pro Fettsäurerest in dem Triglycerid mindestens 16, vorzugsweise mindestens 18, ist.

6. Mittel nach einem der vorangehenden Ansprüche, wobei das Additiv Talgfett ist.

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7. Mittel nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß ein Vergleichsmittel ohne das Additiv einen Ausgabereist von mindestens 10 %, vorzugsweise mindestens 20 Gew.-% in dem definierten Test ergibt.

8. Mittel nach einem der vorangehenden Ansprüche, dadurch gekennzeichnet, daß ein Vergleichsmittel ohne das Additiv einen Ausgabereist von mindestens 30 Gew.-% in dem definierten Test ergibt.

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9. Mittel nach einem der vorangehenden Ansprüche, enthaltend mindestens 5 Gew.-% ein oder mehrere Tenside.

10. Mittel nach einem der vorangehenden Ansprüche, umfassend 20 bis 80 Gew.-% kristallinen oder amorphen Aluminosilicat-Waschmittelbuilder.

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11. Mittel nach einem der vorangehenden Ansprüche, enthaltend nicht mehr als 10 Gew.-% Alkalimetallsilicat.

12. Mittel nach einem der vorangehenden Ansprüche mit einer Schüttdichte von mindestens 600 g/l, vorzugsweise mindestens 700 g/l.

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13. Verwendung eines Polyols, welches vollständig mit Fettsäuren verestert ist, wobei die mittlere Zahl an Kohlenstoffatomen pro Fettsäurerest mindestens 14 ist, zur Verbesserung der Ausgabeeigenschaften eines Waschmittels.

Revendications

- 5 1. Composition détergente granulaire comprenant un (ou plusieurs) tensioactif et un additif, ledit additif étant un polyol qui est complètement estérifié avec des acides gras, le nombre moyen d'atomes de carbone par reste d'acide gras étant d'au moins 14, ladite composition comprenant un adjuvant de détergence aluminosilicate cristallin ou amorphe et étant sensiblement exempte de phosphate minéral.
2. Composition selon la revendication 1, comprenant de 0,1 à 6,0 % en poids d'additif.
- 10 3. Composition selon l'une quelconque des revendications précédentes, comprenant de 0,2 à 4,0 % en poids d'additif.
4. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'additif est un triglycéride.
- 15 5. Composition selon l'une quelconque des revendications précédentes, dans laquelle le nombre moyen d'atomes de carbone par reste d'acide gras dans le triglycéride est d'au moins 16, de préférence d'au moins 18.
6. Composition selon l'une quelconque des revendications précédentes, dans laquelle l'additif est une graisse de suif.
- 20 7. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce qu'une composition comparative sans l'additif donne un résidu de distribution d'au moins 10 %, de préférence au moins 20 % en poids dans le test défini.
- 25 8. Composition selon l'une quelconque des revendications précédentes, caractérisée en ce qu'une composition comparative sans l'additif donne un résidu de distribution d'au moins 30 % en poids dans le test défini.
9. Composition selon l'une quelconque des revendications précédentes, contenant au moins 5 % en poids d'un (ou plusieurs) tensioactif anionique.
- 30 10. Composition selon l'une quelconque des revendications précédentes, comprenant de 20 à 80 % en poids d'adjuvant de détergence aluminosilicate amorphe ou cristallin.
11. Composition selon l'une quelconque des revendications précédentes, ne contenant pas plus de 10 % en poids de silicate de métal alcalin.
- 35 12. Composition selon l'une quelconque des revendications précédentes, ayant une densité apparente d'au moins 600 g/l, de préférence au moins 700 g/l.
- 40 13. Utilisation d'un polyol qui est complètement estérifié avec des acides gras, le nombre moyen d'atomes de carbone par reste d'acide gras étant d'au moins 14, pour améliorer les propriétés de distribution d'une composition détergente.

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