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(54) **DETERGENT COMPOSITIONS**

WASCHMITTELZUSAMMENSETZUNGEN

COMPOSITIONS DETERGENTES

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• **HOUGHTON, Mark, Phillip**
NL-2651 VG Berkel en Rodenrijs (NL)

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(74) Representative: **Elliott, Peter William et al**
Unilever Patent Group
Colworth House
Sharnbrook
Bedford, MK44 1LQ (GB)

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(73) Proprietors:
• **UNILEVER PLC**
London EC4P 4BQ (GB)
Designated Contracting States:
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• **UNILEVER N.V.**
3013 AL Rotterdam (NL)
Designated Contracting States:
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(72) Inventors:
• **BOSKAMP, Jelles, Vincent**
NL-3137 PG Vlaardingen (NL)

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DescriptionTECHNICAL FIELD

5 **[0001]** The present invention is concerned with high-performance particulate laundry detergent compositions of high bulk density.

BACKGROUND AND PRIOR ART

10 **[0002]** EP 544 492A (Unilever), published on 2 June 1993, discloses and claims particulate detergent compositions having a bulk density of at least 650 g/l, preferably at least 700 g/l and advantageously at least 800 g/l. The compositions contain 20-60 wt% of zeolite builder and 15-50 wt% of a high-performance surfactant system rich in nonionic surfactant: 60-100 wt% of ethoxylated nonionic surfactant having a relatively low average degree of ethoxylation ($\leq 6.5\text{EO}$), and optionally 0-40 wt% of primary alcohol sulphate. It will be seen that the ratio of primary alcohol, sulphate to nonionic surfactant cannot exceed 0.67:1.

15 **[0003]** The zeolite builder is preferably zeolite P having a silicon to aluminium ratio not exceeding 1.33 (zeolite MAP) as described and claimed in EP 384 070A (Unilever). This material has exceptionally good carrying capacity for liquid detergent ingredients, as described and claimed in EP 521 635A (Unilever). When used at relatively high levels the zeolite MAP enables high concentrations of the mobile surfactant system to be carried without loss of powder flow properties, and the zeolite also acts as a highly efficient builder, with a greater calcium binding capacity than that of conventional zeolite 4A.

[0004] However, the relatively high levels of the insoluble zeolite A24 may, under certain wash conditions, lead to deposition of insoluble residues on the wash load; but reduction of the zeolite level would reduce both liquid carrying capacity and building capacity, causing a deterioration in detergency as well as in powder properties.

25 **[0005]** It has now been found that the residue problem can be reduced or eliminated surprisingly without resulting in a significant loss of detergency performance or deterioration in powder properties, by using a surfactant system containing less nonionic surfactant and more primary alcohol sulphate.

[0006] It has been found that the level of zeolite can then be lowered, thus further reducing the incidence of residues. Any loss of building capacity resulting in the use of a lower level of zeolite may be made good by the inclusion of a soluble organic builder such as sodium citrate.

30 **[0007]** It has also been found that, in these formulations, the average degree of ethoxylation of the nonionic surfactant need not be 6.5 or less, as specified in EP 544 492A (Unilever) referred to above, but may be as high as 8 without significant loss of detergency.

[0008] The compositions of EP 544 492A (Unilever) are intended primarily for use in automatic washing machines, especially the front-loading drum-type washing machines used in Europe.

[0009] Compositions of the present invention having a higher ratio of anionic surfactant to nonionic surfactant, and thus a higher potential for foaming in the absence of a foam controller, are also useful for washing fabrics by hand. These compositions have been found to have advantageous foam profiles when compared with conventional handwash formulations.

40 **[0010]** JP 02 049 099A (Asahi Denko) discloses particulate fabric washing detergent compositions of high bulk density containing alkyl sulphate (25-45 wt%), ethoxylated alcohol nonionic surfactant (1-10 wt%), soap and zeolite. In the compositions disclosed, the amount of nonionic surfactant is low, and the ratio of alkyl sulphate to nonionic surfactant high (typically from 5:1 to 12:1), but a comparative Example, said to be disadvantageous because of poor anticaking and rinsing properties, contains alkyl sulphate and nonionic surfactant in a ratio of 2.08:1.

45 **[0011]** WO-A-94 13771, published on 23 June 1994, discloses a granulated washing and cleaning agent with high surfactant content in which the ratio of anionic alkyl sulphate surfactant to nonionic surfactant is in the range 10:1 to 1:2.5. The builder may comprise zeolite but zeolite MAP is not mentioned.

DEFINITION OF THE INVENTION

50 **[0012]** The present invention accordingly provides a particulate detergent composition having a bulk density of at least 700 g/l, comprising:

(a) from 15 to 35 wt% of a surfactant system consisting essentially of:

- 55 (i) primary $\text{C}_8\text{-C}_{18}$ alkyl sulphate, and
- (ii) ethoxylated nonionic surfactant which is a primary $\text{C}_8\text{-C}_{18}$ alcohol having an average degree of ethoxylation

within the range of from 3 to 8,
the ratio of (i) to (ii) being within the range of from 0.68:1 to 2:1;

(b) from 10 to 35 wt% (anhydrous basis) of zeolite P having a silicon to aluminium ratio not exceeding 1.33 (zeolite MAP);

(c) optionally from 0 to 30 wt% of a water-soluble organic builder,

(d) optionally other detergent ingredients to 100 wt%.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The particulate detergent composition of the invention has a bulk density of at least 700 g/l.

[0014] It contains a relatively high level of surfactant: from 15 to 35 wt%, and advantageously at least 20 wt%. In formulations intended for use in machine washing, the surfactant level is preferably from 15 to 30 wt%, while for hand-washing formulations the surfactant level is preferably from 25 to 35 wt%.

[0015] The surfactant system consists essentially of primary alcohol sulphate (PAS) and ethoxylated alcohol nonionic surfactant, in a ratio of from 0.68:1 to 2:1. Preferably the ratio ranges from 1:1 to 2:1.

[0016] The surfactant system thus consists essentially of more than 40 wt% of PAS and less than 60 wt% of nonionic surfactant, preferably from 40.5 to 66.7 wt% of PAS and from 33.3 to 59.5 wt% of ethoxylated nonionic surfactant.

The ethoxylated alcohol nonionic surfactant

[0017] The nonionic surfactant has an average degree of ethoxylation within the range of from 3 to 8. A mixture of two or more nonionic surfactants may be used, provided that the aggregate average degree of ethoxylation is within the stated range.

[0018] In order to achieve the best possible detergency, the nonionic surfactant may, as in EP 544 492A (Unilever) mentioned above, have an average degree of ethoxylation not exceeding 6.5, especially from 4 to 6, and more especially from 4 to 5.5.

[0019] However, it has been found that in the compositions of the present invention, where the ratio of PAS to nonionic surfactant is higher, the average degree of ethoxylation of the nonionic surfactant may be higher without significant loss of detergency. Thus the present invention allows greater formulation flexibility using a wider range of nonionic surfactants.

[0020] Thus, the nonionic surfactant may if desired have an average degree of ethoxylation anywhere within the range of from 3 to 8, advantageously from 5 to 8. Nonionic surfactant systems having overall average degrees of ethoxylation within the range of from 6 to 8, preferably from 6.5 to 8, have been found to give good results in compositions of the invention.

[0021] For optimum detergency, the nonionic surfactant may advantageously have a hydrophilic/lipophilic balance (HLB) of 10.0 or more.

[0022] The ethoxylated alcohol is preferably primary, but in principle secondary alcohol ethoxylates could be used.

[0023] The alcohol may be straight-chain or branched-chain. Suitable alcohols are vegetable-derived, for example, coconut. Both Ziegler and oxo synthetic alcohols may be used, Ziegler alcohols being preferred.

[0024] The amount of nonionic surfactant present in the compositions of the invention is preferably within the range of from 6 to 12 wt%.

The primary alcohol sulphate (PAS)

[0025] The primary alcohol sulphate (PAS) that is present in the compositions of the invention may have a chain length in the range of C₈ to C₁₈, preferably C₁₂ to C₁₆, with a mean value preferably in the C₁₂₋₁₅ range. Especially preferred is PAS consisting wholly or predominantly of C₁₂ and C₁₄ material.

[0026] However, if desired mixtures of different chain lengths may be used as described and claimed in EP 342 917A (Unilever).

[0027] As for the ethoxylated alcohol, the PAS may be straight-chain or branched-chain. Vegetable-derived PAS, especially PAS from coconut oil (cocoPAS), is especially preferred. Use of branched-chain PAS as described and claimed in EP 439 316A (Unilever) is also within the scope of the invention.

[0028] The PAS is normally present in the form of the sodium or potassium salt, the sodium salt being generally preferred.

[0029] The amount of PAS present in the compositions of the present invention is preferably within the range of from 10 to 30 wt%.

The zeolite detergency builder

[0030] The amount of zeolite builder in the compositions of the invention is from 10 to 35 wt%. These percentages are based on the (notional) anhydrous material, rather than the hydrated material actually used.

[0031] As mentioned above, the use of higher ratios of PAS to nonionic surfactant than in EP 544 492A (Unilever) enables lower levels of zeolite to be employed without loss of performance. Thus formulations intended for machine washing will contain from 10 to 35 wt%, the range of 15 to 30 wt% being especially preferred. However, compositions having higher levels of zeolite (up to and including 35 wt%) are also within the scope of the invention, and are of especial interest for handwashing formulations.

[0032] The total surfactant loading and/or the proportion of nonionic surfactant is or are increased, the more difficult it is to obtain acceptable powder flow properties. According to the invention, the zeolite builder incorporated in the compositions of the invention is zeolite MAP as described and claimed in EP 384 070A (Unilever).

[0033] 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 not exceeding 1.15, and more preferably not exceeding 1.07. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO/g (anhydrous).

[0034] In the present invention, the use of zeolite MAP has two advantages quite independent of its greater building efficacy: it enables higher total surfactant levels, and more mobile surfactant systems, to be used without loss of powder flow properties; and it gives improved bleach stability.

[0035] Preferred zeolite MAP for use in the present invention is especially finely divided and has a d_{50} (as defined below) within the range of from 0.1 to 5.0 μm , more preferably from 0.4 to 2.0 μm and most preferably from 0.4 to 1.0 μm . The quantity " d_{50} " indicates that 50 wt% of the particles have a diameter smaller than that figure, and there are corresponding quantities " d_{60} ", " d_{90} " etc. Especially preferred materials have a d_{90} below 3 μm as well as a d_{50} below 1 μm .

The optional soluble organic builder

[0036] The compositions of the invention may advantageously comprise up to 30 wt%, suitably from 5 to 30 wt% and preferably from 10 to 25 wt%, of a soluble organic builder.

[0037] Organic builders that may be present include polycarboxylate polymers such as polyacrylates, acrylic/maleic copolymers, and acrylic phosphinates; monomeric polycarboxylates such as citrates, gluconates, oxydisuccinates, glycerol mono-, di- and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

[0038] Especially preferred supplementary builders for use in conjunction with zeolite include citric acid salts, more especially sodium citrate, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%. The combination of zeolite MAP with citrate as a detergency builder system is described and claimed in EP 448 297A (Unilever).

[0039] Also preferred are polycarboxylate polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, especially from 1 to 10 wt%, of the detergent composition; the combination of zeolite MAP with polymeric builders is described and claimed in EP 502 675A (Unilever).

[0040] The use of supplementary organic builders allows formulation with a lower level of zeolite, thus reducing the level of insoluble material present, without loss of calcium binding capacity.

[0041] Builders are preferably present in alkali metal salt, especially sodium salt, form.

Bleach system

[0042] Compositions of the invention that are intended for heavy duty use will generally contain a bleach system.

[0043] The bleach system preferably comprises an inorganic or organic peroxy bleach compound capable of yielding hydrogen peroxide in aqueous solution. Peroxy bleach compounds suitable for use in the compositions of the invention include organic peroxides such as urea peroxide, and inorganic persalts, such as the alkali metal perborates, percarbonates, perphosphates, persulfates and persulphates. Mixtures of two or more such compounds may also be suitable. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and, most preferably, sodium percarbonate.

[0044] Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium silicate is disclosed in GB 2 123 044B (Kao).

[0045] The peroxy bleach compound is suitably present in an amount of from 5 to 35 wt%, preferably from 10 to 25 wt%.

[0046] 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%.

[0047] Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and peroxybenzoic acid precursors; and peroxyacetic acid precursors. An especially preferred bleach precursor suitable for use in the present invention is N,N',N',N'-tetracetyl ethylenediamine (TAED).

[0048] 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.

[0049] An especially preferred bleach system comprises a peroxy bleach compound (preferably sodium percarbonate optionally together with a bleach activator), and a transition metal bleach catalyst as described and claimed in EP 458 397A, EP 458 398A and EP 509 787A (Unilever).

[0050] Compositions containing relatively large amounts of bleach ingredients will generally contain correspondingly smaller amounts of surfactant, builder and other ingredients than will similar light-duty bleach-free formulations. The preferred amounts of surfactant and zeolite for such formulations will therefore generally be towards the lower ends of the ranges claimed in the present invention, while the preferred amounts for handwash or light-duty (non-bleaching) machine wash formulations will be higher.

Other ingredients

[0051] The compositions of the invention may contain alkali metal, preferably sodium, carbonate, in order to increase detergency and ease processing. Sodium carbonate may suitably be present in amounts ranging from 1 to 60 wt%, preferably from 2 to 40 wt%. However, compositions containing little or no sodium carbonate are also within the scope of the invention.

[0052] Powder flow may be improved by the incorporation of a small amount of a powder structurant, for example, a fatty acid (or fatty acid soap), a sugar, an acrylate or acrylate/maleale polymer, or sodium silicate.

[0053] One preferred powder structurant is fatty acid soap, suitably present in an amount of from 1 to 5 wt%.

[0054] Other materials that may be present in detergent compositions of the invention include sodium silicate; antire-deposition agents such as cellulosic polymers; fluoresters; inorganic salts such as sodium sulphate; lather control agents or lather boosters as appropriate; proteolytic and lipolytic enzymes; dyes; coloured speckles; perfumes; foam controllers; and fabric softening compounds. This list is not intended to be exhaustive.

Preparation of the detergent compositions

[0055] The particulate detergent compositions of the invention may be prepared by any method suitable for the production of powders of high bulk density, ie at least 700 g/litre, preferably at least 800 g/litre.

[0056] Such powders may be prepared either by post-tower densification of spray-dried powder, or by wholly non-tower methods such as dry mixing and granulation; in both cases a high-speed mixer/granulator may advantageously be used.

[0057] Processes using high-speed mixer/granulators are disclosed, for example, in EP 340 013A, EP 367 339A, EP 390 251 A and EP 420 317A (Unilever).

EXAMPLES

[0058] The invention is further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated. Examples 6, 12 and 13 are not in accordance with the invention.

[0059] The following abbreviations are used in the Examples:

CocoPAS: linear C₁₂₋₁₄, primary alcohol sulphate prepared from coconut-derived linear alcohol: Laurex (Trade Mark) L1 ex Kolb.

Nonionic 7EO: coconut (linear C₁₂₋₁₄) alcohol having an average degree of ethoxylation of 7.0: Lorodac (Trade Mark) 7EO ex Enichem/DAC.

Nonionic 6.5 EO, nonionic 3EO: corresponding Lorodac materials having lower degrees of ethoxylation.

Zeolite MAP: zeolite P having a silicon to aluminium ratio of 1.00, as described in EP 384 070A (Unilever).

Percarbonate: sodium percarbonate having a protective coating as disclosed in GB 2 123 044B (Kao), ex Interlox.

TAED: totetraacetylenediamine, as 83 wt% granules, ex BASF.

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Mn catalyst: transition metal bleach catalyst (manganese complex) as described and claimed in EP 458 397A, EP 458 398A and EP 509 787A (Unilever)

EHTMP: ethylenediaminetetramethylene phosphonic acid, calcium salt (34 wt% active): Dequest (Trade Mark) 2047 ex Monsanto.

SCMC: sodium carboxymethylcellulose ex Lamberti.

Antifoam: antifoam granules as described and claimed in EP 266 863B (Unilever).

Powder properties

[0060] Powder flow values are expressed in terms of the dynamic flow rate in ml/s, measured by means of the following procedure. The apparatus used consists of a cylindrical glass tube having an internal diameter of 35 mm and a length of 600 mm. The tube is securely clamped in a position such that its longitudinal axis is vertical. Its lower end is terminated by means of a smooth cone of polyvinyl chloride having an internal angle of 15° and a lower outlet orifice. A first beam sensor is positioned 150 mm above the outlet, and a second beam sensor is positioned 250 mm above the first sensor.

[0061] To determine the dynamic flow rate of a powder sample, the outlet orifice is temporarily closed, for example, by covering with a piece of card, and powder is poured through a funnel into the top of the cylinder until the powder level is about 10 cm higher than the upper sensor; a spacer between the funnel and the tube ensures that filling is uniform. The outlet is then opened and the time t (seconds) taken for the powder level to fall from the upper sensor to the lower sensor is measured electronically.

[0062] The measurement is normally repeated two or three times and an average value taken. If V is the volume (ml) of the tube between the upper and lower sensors, the dynamic flow rate DFR (ml/s) is given by the following equation:

$$DFR = \frac{V}{t} \text{ ml/s}$$

[0063] The averaging and calculation are carried out electronically and a direct read-out of the DFR value obtained.

[0064] Values of 90 ml/s and above indicate good flow properties, and values of 120 ml/s and above indicate outstanding flow properties. The compositions of the invention generally exhibit dynamic flow rates in excess of 130 ml/s.

Examples 1 and 2, Comparative Example A

[0065] Detergent powders having bulk densities above 700 g/l were prepared by a non-tower process to the following formulations:

	A	1	2
CocoPAS	6.79	14.63	14.64
Nonionic 7EO	6.69	4.10	7.33
Nonionic 3EO	8.49	3.23	-
Soap	2.25		
Zeolite MAP	36.47	23.48	24.46
Sodium carbonate	1.19	2.57	2.57
SCMC	0.68	0.53	0.54
Moisture and salts	6.13	5.02	5.13
	68.70	53.57	54.66
Sodium citrate	-	15.13	14.04
Antifoam, fluorescer	3.00	3.00	3.00
Silicate	3.67	3.67	3.67

Table continued

	A	1	2
Percarbonate	16.85	16.85	16.85
TAED	3.75	3.75	3.75
Mn catalyst	1.27	1.27	1.27
EDTMP	0.37	0.37	0.37
Enzymes	1.75	1.75	1.75
Perfume	0.65	0.65	0.65
	100.00	100.00	100.00
Bulk density. (g/l)	781	727	775
Dynamic flow rate (ml/s)	142	134	148

[0066] Compositions 1 and 2 according to the invention had a 2:1 ratio of PAS to nonionic surfactant, while Comparative Example A had a ratio of PAS to nonionic surfactant of 0.44:1.

[0067] Comparative Example B was a commercially available high bulk density powder having a surfactant system consisting of alkylbenzene sulphonate and nonionic surfactant.

[0068] Delivery characteristics and residues were compared using a washing machine test. Two front-loading automatic machines were used: the Siemens Siwamat (Trade Mark) Plus 3700, which has a conventional water fill system, and the Zanussi (Trade Mark) Jet System, which incorporates a spray system to reduce water usage.

[0069] The test methodology was as follows. A 100 g dose of powder was placed in 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.

[0070] The delivery device was placed inside a black cotton pillowcase having dimensions of 30 cm by 60 cm, taking care to keep it upright, and the pillowcase was then closed by means of a zip fastener. The pillowcase containing the (upright) delivery device was then placed on top of a 3.5 kg dry cotton washload in the drum of the washing machine.

[0071] The machine was operated on the "heavy duty cycle" at a wash temperature of 40°C, using water of 15° French hardness and an inlet temperature of 20°C. At the end of the wash cycle the pillowcase was removed, opened and turned inside out, and the level of powder residues on its inside surfaces determined by visual assessment using a scoring system of 1 to 5: a score of 3 corresponds to a residue of approximately 75 wt% of the powder, while 0 indicates no residue.

[0072] A panel of five assessors was used to judge each pillowcase and allot a score. With each powder the wash process was carried out ten times and the scores were averaged over the ten repeats.

[0073] The results were as shown below.

Powder	Zanussi	Siemens
A	0.5	0.6
1	0	0
2	0	0
B	2.5	1.8

[0074] In a further test, delivery of a 100 g powder dose from the dispenser drawer of a Phillips (Trade Mark) AWB 126/7 washing machine using a 10°C water fill (5 litre/min) was compared. The results below show the dry weight percentage of powder left behind as a residue in the dispenser drawer.

Powder	Residues (%)
A	11
1	0
2	0
B	58

[0075] It will be noted that the commercially available product (Comparative Example B) gave residues in excess of 50%, and indeed current products of this type are sold with delivery devices and are not intended for dosing via the dispenser drawer. The results above show that the compositions of the invention may be used in the traditional manner without the need for a delivery device.

Examples 3 and 4

[0076] Compositions containing a 1:1 ratio of PAS to nonionic surfactant were prepared, to the following formulations:

	3	4
CocoPAS	10.99	10.97
Nonionic 7EO	6.14	11.00
Nonionic 3EO	4.84	
Zeolite MAP	28.99	28.26
Sodium carbonate	1.93	1.92
SCMC	0.58	0.57
Moisture and salts	5.03	4.95
	58.49	57.67
Sodium citrate	10.21	11.03
Antifoam, fluorescer	3.00	3.00
Silicate	3.67	3.67
Prcarbonate	16.85	16.85
TAED	3.75	3.75
Mn catalyst	1.27	1.27
EDTMP	0.37	0.37
Enzymes	1.75	1.75
Perfume	0.65	0.65
	100.00	100.00
Bulk density (g/litre)	840	817
Dynamic flow rate (ml/s)	152	146

Delivery into the washing machine

[0077] Delivery from the dispenser drawer of a Phillips washing machine was measured as in Examples 1 and 2. The results were as follows, Comparative Example A again being shown as a control:

Powder	Residues (wt%)
A	11
3	0
4	0

Examples 1 to 4: Detergency results

[0078] A tergotomeler test was also carried out to compare the detergencies of the compositions of the invention (Examples 1 to 4) with those of Comparative Example A having a lower PAS to nonionic surfactant ratio.

[0079] The tergotometer tests were carried out in 15° (French) hard water at a product concentration of 4.8 g/litre. The temperature and time conditions were as follows: initially 20°C, warming up to 60°C at 2°/minute, then remaining at 60°C for a 20-minute wash. The agitation rate throughout was 120 oscillations/minute.

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[0080] Detergencies were compared on four different commercially available test cloth monitors:

WFK-10C: mixed fatty and particulate soil (88% wool fat, 12% kaolin) on cotton;

WFK-30C: mixed fatty and particulate soil (88% wool fat, 12% kaolin) on polyester;

EMPA-101: Indian ink (67%) and olive oil (33%) on cotton;

EMPA-104: Indian ink (67%) and olive oil (33%) on polyester/cotton.

[0081] Detergency results, expressed as the differences between the reflectance increases at 460 nm of the test cloth monitors for the Example under test and those for Comparative Example A), were as follows:

Example Reflectance difference compared with Comparative Example A

[0082]

	WFK-10C	WFK-30C	EMPA-101	EMPA-104
1	- 0.9	- 0.4	+ 1.8	+0.8
2	- 1.1	- 0.8	+ 1.0	- 0.5
3	- 0.6	- 0.8	+1.0	+0.2
4	-0.5	- 0.9	+0.8	- 0.1
Standard deviation	4.1	3.8	2.8	2.3

[0083] These results demonstrate that there were no significant detergency differences between the various formulations.

[0084] Subsequent washing machine tests using a range of different test cloths and wash conditions confirmed that there were no statistically significant differences in detergency.

Example 5

[0085] A composition similar to those of Examples 3 and 4, containing a 1:1 ratio of PAS to nonionic but having a high zeolite content and a higher proportion of low-EO nonionic surfactant, was prepared to the following formulation:

	5
CocoPAS	10.28
Nonionic 7EO	5.14
Nonionic 3EO	6.55
Zeolite MAP	38.50
Sodium carbonate	-
SCMC	0,84
Moisture and salts	2.93
	64.24
Sodium citrate	4.46
Antifoam, fluorescer	3.00
Silicate	3.67
Prcarbonate	16.85
TAED	3.75
Mn catalyst	1.27
EDTMP	0.37
Enzymes	1.75

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Table continued

	5
Perfume	0.64
	100.00
Bulk density (g/l)	920
Dynamic flow rate (ml/s)	123

[0086] In the black pillow case test described earlier, this formulation gave zero residues.

Examples 6 to 9

[0087] Four further machine wash formulations having different PAS:nonionic ratios are shown below.

	6	7	8	9
CocoPAS	8.47	10.60	12.71	13.77
Nonionic 6.5EO	12.71	10.58	8.47	7.41
Soap	1.95	1.63	1.30	1.14
Zeolite MAP	34.34	26.29	18.33	14.35
Sodium carbonate	1.44	1.80	2.16	2.34
SCMC	0.89	0.74	0.59	0.52
Moisture, salts	1.80	2.26	2.71	2.93
Sodium citrate	7.08	14.80	22.42	26.23
Antifoam/fluorescer	3.00	3.00	3.00	3.00
Silicate	3.67	3.67	3.67	3.67
Percarbonate	16.85	16.85	16.85	16.85
TAED	3.75	3.75	3.75	3.75
Mn catalyst	1.27	1.27	1.27	1.27
EDTMP	0.37	0.37	0.37	0.37
Enzymes	1.75	1.75	1.75	1.75
Perfume	0.65	0.65	0.65	0.65
	100.00	100.00	100.00	100.00
PAS:nonionic ratio	0.67	1.00	1.50	1.86

Examples 10 to 14

[0088] Detergent compositions intended for washing fabrics by hand were prepared to the following formulations:

	10	11	12	13	14
CocoPAS	13.15	19.12	24.04	21.85	20.49
Nonionic 7EO	7.35	5.36	6.74	6.13	5.75
Nonionic 3EO	5.79	4.22	5.31	4.83	4.53
Zeolite MAP	34.69	30.69	38.58	35.07	32.88
Sodium carbonate	2.31	3.35	4.22	3.83	3.59
SCMC	0.69	0.69	0.87	0.79	0.74
Moisture, salts	6.02	6.56	8.25	7.50	7.03

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Table continued

	10	11	12	13	14
Sodium citrate	4.38	4.38		--	-
Fluorescer	-	-	0.15	0.15	-
Silicate	5.00	5.00	10.00	6.00	7.60
Percarbonate	14.00	14.00		--	-
TAED	4.00	4.00		--	-
Mn catalyst	-	-		--	-
EDTMP	0.37	0.37		--	-
Enzymes	1.75	1.75	1.20	1.20	1.75
Perfume	0.50	0.50	0.65	0.65	0.65
Sodium sulphate	-	-	-	12.00	15.00
	100.00	100.00	100.00	100.00	100.00
Ratio PAS:NI	1.00	2.00	2.00	1.99	1.99
Bulk density (g/l)	865	880	915	925	915
Dynamic flow rate (ml/s)	115	120	135	130	140

[0089] In a handwashing test, the foam profiles of these compositions were compared with that of a commercially available composition (Comparative Example B) having the following formulation:

	B
LAS	20.00
Nonionic 7EO	2.00
Zeolite 4A	25.00
Sodium silicate	2.00
Sodium carbonate	10.00
SCMC	1.00
Acrylic/maleic copolymer	4.00
Fluorescer	0.20
Sodium sulphate	26.00
Enzymes	2.00
Water	7.80
	100.00
Ratio LAS : nonionic	10.0
Bulk density	450 g/litre
Dynamic flow rate	84 ml/s

Foam height

[0090] As a measure of foam generation in the hand wash, foam heights at a product dosage of 3 g/l in 250 ml of 10° (French) hard water in a 1-litre measuring cylinder (diameter 6 cm) at 20°C was determined. The cylinder was inverted twice before reading the foam height. The results were as follows:

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Composition	Foam height (cm)	
	initial	after 10 minutes
B	12	8
10	14	9
11	17	11
12	18	12
13	17.5	12
14	18	13

[0091] Thus all the compositions of the invention generated more foam than the control. Compositions 11 to 14 having a PAS to nonionic surfactant ratio of 2:1 were especially good, but Composition 10 having the lower ratio of 1:1 was also better than the control.

Foam behaviour in the rinse

[0092] With each composition, a handwash was performed in 10 litres of 18° (French) hard water in a bowl at 40°C. The product dosage was 3 g/l, and the washload consisted of 1.5 kg of light cotton shirts. Five agitations of the load were carried out in 20 seconds. The wash liquor was then drained away, a further 5 litres of water (10°C) added, the load was agitated for 20 seconds, the foam was assessed, and then the rinse water was drained away. The rinse operation was repeated until only a few bubbles were left behind on the rim of the bowl. The following table gives the number of rinse operations required to reach this endpoint: in this test, Composition 10 (PAS:nonionic ratio 1:1) gave especially good results, and Compositions 11, 13 and 14 were also better than the control.

Example	Number of rinses required to "zero foam" endpoint
B	4
10	2
11	3
12	4
13	3
14	3

Dissolution

[0093] In this test, the times required for 90% dissolution to take place in 500 ml of deionised water at 20°C in a 750 ml glass beaker fitted with a magnetic stirrer (length 3 cm) rotating at 100 rpm were determined. The ionic strength was used as a measure of dissolution, the ionic strength after 60 minutes being taken as 100% dissolution (including a visual check). The results were as follows:

	Time for 90% dissolution (sec)
B	245
10	190
11	174
12	230
13	210
14	205

[0094] All the compositions of the invention were better than the control, Compositions 10 and 11 giving especially good results.

Claims

1. A particulate detergent composition having a bulk density of at least 700 g/l, comprising:

(a) from 15 to 35 wt% of a surfactant system consisting essentially of:

(i) primary C₈-C₁₈ alkyl sulphate, and

(ii) ethoxylated nonionic surfactant which is a primary C₈-C₁₈ alcohol having an average degree of ethoxylation within the range of from 3 to 8,

the ratio of (i) to (ii) being within the range of from 0.68:1 to 2:1;

(b) from 10 to 35 wt% (anhydrous basis) of zeolite P having a silicon to aluminium ratio not exceeding 1.33 (zeolite MAP);

(c) optionally from 0 to 30 wt% of a water-soluble organic builder;

(d) optionally other detergent ingredients to 100 wt%.

2. A detergent composition as claimed in claim 1, wherein the ratio of (a)(i) to (a)(ii) is within the range of from 1:1 to 2:1.

3. A detergent composition as claimed in claim 1, which contains from 10 to 30 wt% of primary alcohol sulphate (a)(i).

4. A detergent composition as claimed in claim 1, which contains from 6 to 12 wt% of nonionic surfactant (a)(ii).

5. A detergent composition as claimed in claim 1, wherein the nonionic surfactant (a)(ii) has an average degree of ethoxylation within the range of from 6 to 8.

6. A detergent composition as claimed in claim 1, which comprises from 5 to 30 wt% of soluble organic builder (d).

7. A detergent composition as claimed in claim 6, wherein the soluble organic builder (d) comprises a water-soluble salt of citric acid.

Patentansprüche

1. Teilchenförmiges Waschmittel mit einer Schüttdichte von mindestens 700 g/l, umfassend:

(a) 15 bis 35 Gewichtsprozent eines Tensidsystems, bestehend im wesentlichen aus:

(i) primärem C₈-C₁₈-Alkylsulfat und

(ii) ethoxyliertem nichtionischem Tensid, nämlich ein primärer C₈-C₁₈-Alkohol mit einem mittleren Ethoxylierungsgrad im Bereich von 3 bis 8,

wobei das Verhältnis von (i) zu (ii) im Bereich von 0,68:1 bis 2:1 liegt,

(b) 10 bis 35 Gewichtsprozent (wasserfreie Basis) Zeolith P mit einem Silizium-zu-Aluminium-Verhältnis, das 1,33 nicht übersteigt (Zeolith MAP);

(c) gegebenenfalls 0 bis 30 Gewichtsprozent eines wasserlöslichen organischen Builders;

(d) gegebenenfalls weitere Waschmittelbestandteile auf 100 Gewichtsprozent.

2. Waschmittel nach Anspruch 1, wobei das Verhältnis von (a)(i) zu (a)(ii) im Bereich von 1:1 bis 2:1 liegt.

3. Waschmittel nach Anspruch 1, das 10 bis 30 Gewichtsprozent primäres Alkoholsulfat (a)(i) enthält.

4. Waschmittel nach Anspruch 1, das 6 bis 12 Gewichtsprozent nichtionisches Tensid (a)(ii) enthält.

5. Waschmittel nach Anspruch 1, wobei das nichtionische Tensid (a)(ii) einen mittleren Ethoxylierungsgrad im Bereich von 6 bis 8 aufweist.

6. Waschmittel nach Anspruch 1, das 5 bis 30 Gewichtsprozent löslichen organischen Builder (d) enthält.

7. Waschmittel nach Anspruch 6, wobei der lösliche organische Builder (d) ein wasserlösliches Salz von Zitronensäure umfaßt.

Revendications

1. Composition détergente particulière ayant une densité apparente d'au moins 700 g/l, comprenant :

(a) de 15 à 35 % en poids d'un système tensioactif consistant essentiellement en :

- (i) un alkylsulfate primaire en $C_8 - C_{18}$, et
 - (ii) un tensioactif non ionique éthoxylé qui est un alcool primaire en $C_8 - C_{18}$ ayant un degré moyen d'éthoxylation dans la gamme de 3 à 8,
- le rapport de (i) à (ii) étant dans la gamme de 0,68 :1 à 2 :1 ;

(b) de 10 à 35 % en poids (base anhydre) de zéolite P ayant un rapport silicium : magnésium n'excédant pas 1,33 (zéolite PAM) ;

(c) facultativement, de 0 à 30 % en poids d'adjuvant organique hydrosoluble ;

(d) facultativement, d'autres ingrédients détergents jusqu'à 100 % en poids.

2. Composition détergente selon la revendication 1, dans laquelle le rapport de (a) (i) à (a) (ii) est dans la gamme de 1 :1 à 2 :1.

3. Composition détergente selon la revendication 1, contenant de 10 à 30 % en poids de l'alcool sulfate primaire (a) (i).

4. Composition détergente selon la revendication 1, contenant de 6 à 12 % en poids du tensioactif non ionique (a) (ii).

5. Composition détergente selon la revendication 1, dans laquelle le tensioactif non ionique (a) (ii) a un degré moyen d'éthoxylation dans la gamme de 6 à 8.

6. Composition détergente selon la revendication 1, comprenant de 5 à 30 % en poids d'adjuvant organique soluble (d).

7. Composition détergente selon la revendication 6, dans laquelle l'adjuvant organique soluble (d) comprend un sel hydrosoluble de l'acide citrique.