



Publication number : **0 518 576 A2**

EUROPEAN PATENT APPLICATION

Application number : **92305203.9**

Date of filing : **05.06.92**

Int. Cl.⁵ : **C11D 3/10, C11D 3/12,
C11D 3/39, C11D 1/83,
C11D 17/06**

Priority : **10.06.91 GB 9112384**

Date of publication of application :
16.12.92 Bulletin 92/51

Designated Contracting States :
CH DE ES FR GB IT LI NL SE

Applicant : **UNILEVER PLC**
Unilever House Blackfriars
London EC4P 4BQ (GB)
GB

Applicant : **UNILEVER N.V.**
Weena 455
NL-3013 AL Rotterdam (NL)
CH DE ES FR IT LI NL SE

Inventor : **Allan, Alexander, c/o Unilever**
Research
Port Sunlight Lab., Quarry Road East,
Bebington
Wirral, Merseyside L63 3JW (GB)
Inventor : **Chapple, Andrew Paul, c/o Unilever**
Research
Port Sunlight Lab., Quarry Road East,
Bebington
Wirral, Merseyside L63 3JW (GB)
Inventor : **Emery, William Derek, c/o Unilever**
Research
Port Sunlight Lab., Quarry Road East,
Bebington
Wirral, Merseyside L63 3JW (GB)
Inventor : **Farnsworth, Pauline, c/o Unilever**
Research
Port Sunlight Lab., Quarry Road East,
Bebington
Wirral, Merseyside L63 3JW (GB)

Representative : **Fransella, Mary Evelyn et al**
Unilever PLC Patent Division Colworth House
Sharnbrook
GB-Bedford MK44 1LQ (GB)

EP 0 518 576 A2

High bulk density granular detergent compositions.

A granular detergent composition comprises at least one detergent-active compound, an alkali metal carbonate detergency builder, finely divided calcium carbonate having a surface area of at least 10 m²/g, a peroxy bleach system, and optionally other detergent ingredients ; has a bulk density of at least 750 g/litre ; and contains not more than 4 wt%, and preferably not more than 2 wt%, of water removable at 75°C.

TECHNICAL FIELD

The present invention relates to granular detergent compositions built with alkali metal carbonate and finely divided calcium carbonate, and containing a peroxy bleach system.

BACKGROUND AND PRIOR ART

Granular detergent compositions built with alkali metal carbonate and finely divided calcium carbonate are disclosed in a series of Unilever patents, the earliest of which is GB 1 437 950. Compositions containing peroxy bleaching compounds such as sodium perborate are disclosed, for example, GB 1 437 950 discloses in Example 18 a fully formulated detergent composition comprising a spray-dried base powder containing detergent-active compounds, sodium carbonate, calcite and sodium silicate, and postdosed sodium perborate. The moisture content of the powder is about 10 wt%, a value typical of a spray-dried powder.

GB 1 583 081 (Unilever) discloses granular detergent compositions built with sodium carbonate and finely divided calcite and containing sodium percarbonate. The compositions are prepared by contacting the sodium carbonate with liquid or pasty detergent active compound to form granules, and then adhering the finely divided calcite to the granules. In these compositions, the sodium carbonate is generally wholly or predominantly in monohydrate form to ensure that all moisture present (generally about 4-5 wt% of the formulation) is bound as water of hydration of sodium carbonate monohydrate; preferably sodium carbonate monohydrate prepared by spray-drying an aqueous solution is used. The compositions are not densified; bulk densities ranging from 520 to 740 g/litre are disclosed, but the higher figures are apparently achieved only by the incorporation of very high levels of sodium carbonate (eg 60 wt%).

The present invention is based on the discovery that stable detergent powders of high bulk density (750 g/litre and above, especially 800 g/litre and above), built with alkali metal carbonate and finely divided calcium carbonate, may be prepared to very low moisture contents indeed (2 wt% or less, or even zero), without the need to use large amounts of sodium carbonate in monohydrate form, and these powders exhibit enhanced peroxy bleach, especially sodium percarbonate, stability.

DEFINITION OF THE INVENTION

The present invention provides a granular detergent composition comprising

- (a) at least one detergent-active compound,
- (b) an alkali metal carbonate detergency builder,
- (c) finely divided calcium carbonate having a surface area of at least 10 m²/g,
- (d) a peroxy bleach system,
- (e) optionally other detergent ingredients,

the composition having a bulk density of at least 750 g/litre and containing not more than 4 wt%, preferably not more than 2 wt%, of water removable at 75°C.

DETAILED DESCRIPTION OF THE INVENTION

The subject of the present invention is a bleaching granular detergent composition containing detergent-active compounds, a builder system based on alkali metal carbonate and finely divided calcium carbonate, and a peroxy bleach system. Other optional ingredients may also be present as desired or required, provided that the content of water removable at 75°C does not exceed 4 wt%, and preferably does not exceed 2 wt%.

The detergent-active compound

The detergent compositions of the invention will contain, as essential ingredients, 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. Many suitable detergent-active compounds are available and are fully described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

The preferred detergent-active compounds that can be used are soaps and synthetic non-soap anionic and nonionic compounds.

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 alkyl sulphates, particularly C₁₂-C₁₅ primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene

sulphonates; dialkyl sulposuccinates; and fatty acid ester sulphonates. Sodium salts are generally preferred.

Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C₁₀-C₂₀ aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the C₁₂-C₁₅ primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol; and alkylpolyglycosides.

The choice of detergent-active compound (surfactant), and the amount present, will depend on the intended use of the detergent composition: different surfactant systems may be chosen, as is well known to the skilled formulator, for handwashing products and for products intended for use in different types of washing machine.

The total amount of surfactant present will also depend on the intended end use, but will generally range from 5 to 60 wt%, preferably from 5 to 40 wt%.

Detergent compositions suitable for use in most automatic fabric washing machines generally contain anionic non-soap surfactant, or nonionic surfactant, or combination of the two in any ratio, optionally together with soap.

According to one preferred embodiment of the invention, compositions contain the anionic surfactant, linear alkylbenzene sulphonate, optionally in combination with one or more nonionic surfactants. In this embodiment of the invention the content of water removable at 75°C does not exceed 4 wt%.

According to another preferred embodiment of the invention, compositions contain the anionic surfactant, primary alcohol sulphate, optionally in combination with one or more nonionic surfactants. In this embodiment of the invention the content of water removable at 75°C preferably does not exceed 2 wt%.

The detergency builder system

The compositions of the invention comprise, as detergency builder, alkali metal (preferably sodium) carbonate. In principle this may be present in any amount of from 10 to 60 wt%, but preferably the amount present does not exceed 30 wt%, and more preferably does not exceed 20 wt%, in order to avoid excessive alkalinity. The compositions of the present invention do not need high sodium carbonate contents in order to achieve high bulk densities.

Unlike the sodium carbonate used in GB 1 583 081 (Unilever), discussed above, the sodium carbonate used in the composition need not be in sodium carbonate monohydrate form; there is no need for special processing steps to effect partial hydration of the carbonate, which can simply be used in normal anhydrous form (soda ash). A small amount of partial hydration may fortuitously occur during processing, but that is not essential to the present invention.

The compositions of the invention also comprise finely divided, high-surface-area calcium carbonate, suitably in an amount of from 5 to 40 wt%, preferably from 10 to 30 wt%. The calcium carbonate has a surface area of at least 10 m²/g, preferably at least 20 m²/g. Particularly preferred forms of calcium carbonate have surface areas in the range of from 30 to 100 m²/g. Surface areas are determined by the standard Brunauer, Emmett and Teller (BET) method. The preferred form of calcium carbonate is calcite, but vaterite and aragonite are possible alternatives. Suitable forms of calcium carbonate are commercially available. For more detailed disclosure on possible forms of calcium carbonate the reader is referred to the aforementioned GB 1 437 950 and GB 1 583 081 (Unilever).

The bleach system

The detergent compositions of the invention also contain a peroxy bleach system, which may comprise a peracid; an inorganic or organic persalt which acts as a source of hydrogen peroxide; or an inorganic or organic persalt together with a peracid precursor (also known as a bleach precursor or bleach activator).

The invention is especially concerned with compositions containing bleach systems based on the inorganic persalts, sodium perborate (more especially the monohydrate) and sodium percarbonate. These salts are suitably present in amounts of from 5 to 30 wt%, preferably from 10 to 20 wt%.

Compositions containing sodium percarbonate are of especial interest because of that salt's high sensitivity to moisture. The replacement of phosphates by zeolites in detergent powders in recent years has virtually outlawed the use of sodium percarbonate because of the high levels of mobile water inevitably present in zeolite-built powders. The alkali metal carbonate/calcium carbonate builder system represents an alternative route to zero-phosphate powders that circumvents this difficulty.

As indicated above, the compositions may advantageously contain a bleach activator (bleach precursor), to improve bleaching performance at lower wash temperatures. Preferred examples include peracetic acid precursors, for example, tetraacetylene diamine (TAED), now in widespread commercial use in conjunction

with sodium perborate; and perbenzoic acid precursors.

The molar ratio of percarbonate to precursor may suitably range from 0.5:1 to 20:1, preferably from 1:1 to 10:1.

If desired, a bleach stabiliser (heavy metal sequestrant), for example, a salt of ethylenediaminetetracetic acid (EDTA) or ethylenediamine tetramethylenephosphonic acid (EDTMP or Dequest (Trade Mark)) may be present.

Other ingredients

Other materials that may be present in detergent compositions of the invention include sodium silicate; antiredeposition agents such as cellulosic polymers; fluorescers; inorganic salts such as sodium sulphate; enzymes, such as proteases, amylases, cellulases and lipases; lather control agents or lather boosters as appropriate; pigments; and perfumes. This list is not intended to be exhaustive.

Water content

The compositions of the invention have low free or mobile water contents, not greater than 4 wt%, preferably not greater than 2 wt%, and advantageously not greater than 1 wt%. These figures refer to water removable at 75°C, which represents relatively mobile water that could adversely effect the stability of water-sensitive ingredients such as sodium percarbonate.

Bulk density, processing

The compositions of the invention have bulk densities of at least 750 g/litre, preferably at least 800 g/litre. Stability of compositions containing moisture-sensitive ingredients is especially problematic at higher bulk densities where ingredients are forced into closer proximity with each other.

Preferred compositions of the invention are produced by processes which include use of a high-speed mixer/granulator. This apparatus, described in more detail below, can be used both to densify a preformed powder prepared by spray-drying or other conventional technique, and to produce a powder directly from its raw materials by mixing and granulation; intermediate "part-part" processes are of course also possible.

Preferred high-speed batch mixer/granulators have both a stirring action and a cutting action, as described in EP 340 013A (Unilever). Preferably the stirrer and the cutter may be operated independently of one another, and at separately variable speeds. Such a mixer is capable of combining a high energy stirring input with a cutting action, but can also be used to provide other, gentler stirring regimes with or without the cutter in operation. It is thus a highly versatile and flexible piece of apparatus.

A preferred type of batch high-speed mixer/granulator is bowl-shaped and preferably has a substantially vertical stirrer axis. Especially preferred are mixers of the Fukae (Trade Mark) FS-G series manufactured by Fukae Powtech Kogyo Co., Japan; this apparatus is essentially in the form of a bowl-shaped vessel accessible via a top port, provided near its base with a stirrer having a substantially vertical axis, and a cutter positioned on a side wall. The stirrer and cutter may be operated independently of one another, and at separately variable speeds.

As indicated previously, the Fukae mixer requires batch operation. Alternatively, continuous processes may be employed, for example, using a continuous high-speed mixer/granulator such as the Lödige (Trade Mark) Recycler, optionally followed by a moderate-speed continuous mixer/granulator such as the Lödige Ploughshare. Suitable processes are disclosed in EP 367 339A, EP 390 251A and EP 420 317A (Unilever), and in our copending European Patent Application No. 91 200 740.8.

A first preferred process for the production of compositions in accordance with the invention includes the steps of:

- (i) spray-drying an aqueous slurry of ingredients other than the finely divided calcium carbonate and the peroxy bleach system, to form a particulate detergent base composition; and
- (ii) granulating and densifying the spray-dried detergent base composition in a high-speed mixer/granulator to give a particulate product having a bulk density of at least 750 g/litre, preferably at least 800 g/litre, and containing not more than 4 wt%, preferably not more than 2 wt%, of water removable at 75°C; the finely divided calcium carbonate being admixed either before or after step (ii) and the peroxy bleach system being admixed after step (ii).

A second preferred process for the preparation of compositions in accordance with the invention includes the steps of:

- (i) mixing and granulating detergent-active compound, alkali metal carbonate detergency builder, finely div-

ided calcium carbonate and optionally other detergent ingredients in a high-speed mixer/granulator to give a particulate detergent base composition having a bulk density of at least 750 g/litre, preferably at least 800 g/litre, and containing not more than 4 wt%, preferably not more than 2 wt%, of water removable at 75°C; and

5 (ii) admixing the peroxy bleach system.

EXAMPLES

10 The invention is further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated. Examples identified by numbers are in accordance with the invention, while those identified by letter are comparative.

The calcite used was Socal (Trade Mark) U3 ex Solvay, having a surface area of 70 m²/g.

The sodium carbonate used was anhydrous (light soda ash).

The zeolite A used in the Comparative Examples was Wessalith (Trade Mark) P powder ex Degussa.

15 The following inorganic persalts were used:

(a) commercial sodium percarbonate, having a surface area of 0.5 m²/g: Oxyper (Trade Mark) ex Interlox.

(b) fractionated sodium percarbonate: the 500-710 micrometre sieve fraction of Oxyper.

(c) sodium percarbonate/sodium carbonate compound (about 65 wt% sodium percarbonate) ex FMC;

(d) sodium perborate monohydrate, ex EKA, having a surface area of 7.56 m²/g.

20 The nonionic surfactants used were Synperonic (Trade Mark) A7 and A3 ex ICI, which are C₁₂-C₁₅ alcohols ethoxylated respectively with an average of 7 and 3 moles of ethylene oxide.

Examples 1 and 2, Comparative Examples A and B

25 Detergent powders of high bulk density were prepared to the following formulations (in wt %):

	<u>1, 2</u>	<u>A, B</u>
30 Linear alkylbenzene sulphonate	8.4	10.4
Nonionic surfactant 7EO	2.9	6.9
Soap	—	2.3
35 Sodium carbonate	30.0	10.2
Zeolite 4A	—	33.9
Acrylic/maleic copolymer	—	5.7
40 Sodium neutral silicate	6.3	—
SCMC	0.5	0.6
Nonionic surfactant 3EO	4.3	2.6
Calcite	20.0	—
45 Moisture (nominal)	10.6	14.6
Sodium percarbonate	11.3	12.5
50 Tetraacetylenediamine	2.5	—
Silicone antifoam granules	3.2	—
	-----	-----
55	100.00	100.00
Bulk density (g/l)	803	850

Powders 1 and 2 were prepared by granulation in a Magimix (Trade Mark) Cuisine System 5000 food mixer. The dry ingredients (linear alkylbenzene sulphonate, sodium carbonate, calcite, SCMC) were mixed, then aqueous sodium silicate solution was added, followed by a mixture of the two nonionic surfactants. The powders were then dried at 80°C for 1-10 minutes using a fluid bed dryer (Johnson Mathey), to the desired final moisture content (see below). Sodium percarbonate, TAED, and antifoam granules were then admixed.

Powders A and B were prepared as follows. A base powder containing the linear alkylbenzene sulphonate, the nonionic surfactant 7EO, the soap, the sodium carbonate, the zeolite, the polymer and the SCMC was prepared by spray-drying an aqueous slurry; the nonionic surfactant 3EO was sprayed on using a rotating pan. The powder was then granulated and densified using the Fukae (Trade Mark) FS-30 high-speed mixer/granulator, some water being added to effect granulation. The mixer was operated at a stirrer speed of 200 rpm and a cutter speed of 3000 rpm, the temperature being controlled at 60°C by means of a water jacket; the granulation time was 2 minutes. The densified powders were then dried at 80°C in a fluid bed as described above for powders 1 and A; and the sodium percarbonate (commercial) then admixed (1.25 g per 8.75 g of base).

Immediately after the fluid bed drying stage, the powders had the following content of free water, ie water removable at 75°C:

Example	<u>1</u>	<u>2</u>	<u>A</u>	<u>B</u>
Free water content	1.0	3.7	0.73	4.1

Thus Example 1 was a calcite/carbonate powder of very low free water content; Example 2 was an otherwise identical calcite/carbonate powder of slightly higher, but still low, free water content; Comparative Example A was a zeolite powder of comparable (very low) free water content to that of Example 1; and Comparative Example B was a zeolite powder of comparable free water content to that of Example 2.

The powders were then stored in sealed bottles at at 37°C. Storage stabilities were assessed by removing samples at different time intervals and measuring their available oxygen content by titration with potassium permanganate. The results, expressed as percentages of the initial value, were as follows:

<u>Storage time</u> (days)	<u>1</u>	<u>2</u>	<u>A</u>	<u>B</u>
0	100	100	100	100
7	98.3	97.6	98.4	76.6
14	96.6	95.3	83.6	76.6
28	93.2	90.8	72.8	65.6

Thus both calcite/carbonate powders showed significantly better storage stability than those of the zeolite powders; and that of the very low water content powder 1 was significantly better than that of the powder 2 of higher water content. Both calcite/carbonate powders were substantially more stable than the zeolite powders, which both showed unacceptable storage characteristics, the very low water content powder A not being significantly better than the higher water content powder B.

Examples 3 to 6, Comparative Example C

In a separate series of experiments, the storage stabilities of the powders used for Examples 1 and 2 above, and three more of the same composition and bulk density but different free water contents, were measured both at 37°C and at 28°C. The free water contents of the powders were as follows:

EP 0 518 576 A2

<u>Example</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>C</u>
	1.0	1.5	1.8	3.7	6.1

Example C was outside the invention because its free water content was greater than 4 wt%.

Storage results in sealed bottles at 37°C

<u>Time</u> (days)	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>C</u>
14	91	90	88	84	65
28	90	90	83	-	38
42	90	87	-	81	26
63	83	83	79	78	-

Storage results in sealed bottles at 28°C

<u>Time</u> (days)	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>C</u>
14	100	98	97	91	86
28	96	97	93	93	54
42	95	95	91	86	54
63	95	94	86	87	34

Comparative Examples D and E

A powder (Comparative Example D) was prepared in accordance with Example 11 of GB 1 583 081, to the following formulation:

Sodium lauryl sulphate	2.0
Nonionic surfactant 7EO	15.0
Sodium carbonate (anhydrous basis)	35.0
SCMC	1.0
Calcite	19.0
Moisture* (nominal) and perfume	5.2
Sodium percarbonate	22.0
Fluorescer	0.8

	100.0

*as water of hydration of sodium carbonate.

The powder was prepared as follows. Sodium carbonate monohydrate was first prepared by spray-drying an aqueous suspension of sodium carbonate containing the sodium lauryl sulphate to lower the density of the product. The powder was then prepared by a continuous granulation process in which all the dry particulate ingredients, except the sodium percarbonate, were premixed and fed at constant rate to an inclined pan granulator, and the nonionic surfactant and perfume (premixed) were sprayed on at a constant rate according to the relative amounts required in the product. The sodium percarbonate was then postdosed.

The product had a bulk density of 508 g/l. The total water content was found to be 5.5 wt%, and the free water content (content of water removable at 75°C) was 1.8 wt%.

A sample of the powder was densified, using the Fukae mixer, to a bulk density of 780 g/litre (Comparative Example E). Its total water content was 6.0 wt% and its free water content was 1.6 wt%.

Bleach stability on storage was monitored as described in Example 1. The results (% available oxygen remaining) were as follows:

<u>Storage time</u> (days)	<u>D</u>	<u>E</u>
0	100	100
14	73.0	63.6
21	69.7	55.8
28	60.3	41.7

It will therefore be seen that, although most of the water in Comparative Example D was tied up as water of hydration of sodium carbonate monohydrate, the bleach stability of this prior art composition was markedly inferior to that of Example 1.

As previously observed, the powder (Comparative Example D) obtained by following the directions of Example 11 of GB 1 583 081 had a bulk density of 508 g/litre. On densification to a bulk density comparable with that of Example 1, the bleach stability deteriorated still further.

Thus GB 1 583 081 does not teach a composition of high bulk density having good bleach stability on storage.

Examples 7 to 10, Comparative Example F

Powders of the composition and bulk density given for Examples 1 and 2, but containing fractionated sodium percarbonate instead of standard sodium percarbonate, were prepared by the process described for Examples 1 and 2.

Free water contents

<u>Example</u>	7	8	9	10	F
	1.0	1.5	1.8	3.7	6.1

Storage results in sealed bottles at 37°C

5	<u>Time</u> (days)	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>F</u>
10	7	—	100	98	91	67
	14	98	97	93	—	55
15	28	96	92	87	77	44
	42	90	87	84	73	—
20	63	87	86	82	64	17

Examples 11 to 14, Comparative Example G

25

Powders of the composition and bulk density given for Examples 1 and 2, but containing FMC sodium percarbonate compound instead of standard sodium percarbonate, were prepared by the process described for Examples 1 and 2.

30 Free water contents

	<u>Example</u>	11	12	13	14	G
35		1.0	1.5	1.8	3.7	6.1

40

45

50

55

Storage results in sealed bottles at 37°C

	<u>Time</u> (days)	<u>11</u>	<u>12</u>	<u>13</u>	<u>14</u>	<u>G</u>
5						
10	7	99	—	—	95	—
	14	98	98	96	93	70
15	28	—	97	96	—	51
	42	96	93	93	91	53
20	63	95	93	94	85	22

Examples 15 to 18, Comparative Example H

25

Powders of the composition given for Examples 1 and 2, but containing sodium perborate monohydrate instead of standard sodium percarbonate, were prepared by the process described for Examples 1 and 2.

Free water contents

30

	<u>Example</u>	15	16	17	18	H
35		1.0	1.5	1.8	3.7	6.1

40

45

50

55

Storage results in sealed bottles at 37°C

5	<u>Time</u> (days)	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	<u>H</u>
10	7	-	-	99	99	-
	14	96	-	97	91	88
15	28	98	-	96	-	88
	42	-	95	95	92	80
20	63	95	93	94	88	-

25 Examples 19 to 22

High bulk density powders having a formulation similar to that of Examples 1 and 2 but containing a different anionic detergent active compound - primary alcohol sulphate instead of linear alkylbenzene sulphonate - were prepared by the food mixer method described for Examples 1 and 2. Bulk density was 878 g/litre. The bleach compound was commercial sodium percarbonate.

Free water contents

35	<u>Example</u>	19	20	21	22
		0.4	0.7	1.2	1.7

40

45

50

55

Storage results in sealed bottles at 37°C

	<u>Time</u> (days)	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>
5	7	96	97	93	87
10	14	95	92	84	77
	28	89	90	78	75
15	42	84	87	66	52
20	63	77	81	58	39

Storage results in sealed bottles at 28°C

	<u>Time</u> (days)	<u>19</u>	<u>20</u>	<u>21</u>	<u>22</u>
25	7	100	99	96	96
30	14	97	97	94	92
35	28	98	96	88	88
	42	97	96	85	84
40	63	94	94	77	80

These results show a preference for a free water content below 1 wt% for this formulation.

45 Examples 23 to 26

High bulk density powders having the formulation of Examples 19 to 22 but containing a different bleach compound, FMC sodium percarbonate compound, were prepared by the food mixer method described for Examples 1 and 2.

50

Free water contents

	<u>Example</u>	23	24	25	26
55		0.4	0.7	1.2	1.7

Storage results in sealed bottles at 37°C

	<u>Time</u> (days)	<u>23</u>	<u>24</u>	<u>25</u>	<u>26</u>
5					
	7	99	96	100	97
10					
	14	97	97	96	94
	28	94	93	91	89
15					
	42	95	96	90	87
20					
	63	93	93	85	87

With FMC percarbonate, this formulation gave good storage stability at moisture contents below 2 wt%.

Examples 27 to 30

25

High bulk density powders having the formulation of Examples 19 to 22 but containing a different bleach compound, sodium perborate monohydrate, were prepared by the food mixer method described in Examples 1 and 2.

30 Free water contents

	<u>Example</u>	<u>27</u>	<u>28</u>	<u>29</u>	<u>30</u>
35					
		0.4	0.7	1.2	1.7

Storage results in sealed bottles at 37°C

	<u>Time</u> (days)	<u>27</u>	<u>28</u>	<u>29</u>	<u>30</u>
40					
	7	98	99	95	97
45					
	14	99	–	94	91
50					
	28	97	98	92	93
	42	95	94	–	89
55					
	63	95	95	89	88

With sodium perborate monohydrate, this formulation gave good storage stability at moisture contents below 2 wt%.

Examples 31 to 33

High bulk density powders were prepared to the formulation given below.

	<u>parts</u>	<u>%</u>
Primary alcohol sulphate	5.2	5.6
Nonionic surfactant (3EO)	6.6	7.1
Nonionic surfactant (7EO)	5.2	5.6
Soap	2.5	2.7
Sodium carbonate	19.0	20.5
Calcite	20.0	21.5
Sodium neutral silicate	6.0	6.5
Sodium percarbonate*	16.3	17.6
TAED	6.6	7.1
Sodium carboxymethylcellulose	0.6	0.6
Antifoam granule	3.0	3.2
Enzyme granule	0.66	0.7
Perfume	0.2	0.2
Total water	1.0	1.1
	----	-----
	92.86	100.0

*commercial sodium percarbonate

The powders were prepared by spray-drying an aqueous slurry of the non-heat sensitive ingredients (primary alcohol sulphate, part of the nonionic surfactant, soap, sodium carbonate, sodium silicate, sodium carboxymethylcellulose); densifying the resulting base powder in the Fukae mixer, then postdosing the remaining nonionic surfactant, calcite, sodium percarbonate, TAED, antifoam granules, enzyme granules and perfume. The bulk density was 756 g/litre.

Free water contents

<u>Example</u>	31	32	33
	0.3	0.9	1.8

EP 0 518 576 A2

Storage results in sealed bottles at 28°C

	<u>Time</u> (days)	<u>31</u>	<u>32</u>	<u>33</u>
5	7	99.4	93.6	95.0
10	14	95.0	-	-
	28	93.8	-	90.0
15	42	92.4	91.7	87.2
20	56	87.5	91.3	90.0

Storage results in sealed bottles at 37°C

	<u>Time</u> (days)	<u>31</u>	<u>32</u>	<u>33</u>
25	7	-	89.6	88.5
30	14	95.0	84.4	-
35	28	93.6	-	82.2
	56	84.6	80.4	73.5

Examples 34 to 36

High bulk density powders of the formulation of Examples 31 to 33 were prepared by a different process: mixing and granulation of the surfactants, soap, sodium carbonate, sodium silicate, calcite and SCMC in the Fukae mixer, then postdosing the bleach ingredients, enzyme granules, antifoam granules and perfume. The bulk density was 840 g/litre.

Free water contents

<u>Example</u>	34	35	36
	0.5	1.4	1.7

Storage results in sealed bottles at 28°C

	<u>Time</u> (days)	<u>34</u>	<u>35</u>	<u>36</u>
5	7	98.0	93.5	92.2
10	14	97.2	88.9	91.3
	28	—	87.4	85.5
15	42	90.3	—	87.1
20	56	88.3	82.2	83.6

Storage results in sealed bottles at 37°C

	<u>Time</u> (days)	<u>34</u>	<u>35</u>	<u>36</u>
25	7	94.9	89.6	86.4
30	14	88.9	83.5	75.5
35	28	87.9	72.3	63.9
	56	83.3	62.3	55.3

40 These results demonstrate a preference for a free water content below 1 wt% for this formulation.

Claims

- 45 **1** A granular detergent composition comprising
- (a) at least one detergent-active compound,
 - (b) an alkali metal carbonate detergency builder,
 - (c) finely divided calcium carbonate having a surface area of at least 10 m²/g,
 - (d) a peroxy bleach system,
 - 50 (e) optionally other detergent ingredients,
- characterised in that the composition has a bulk density of at least 750 g/litre and contains not more than 4 wt% of water removable at 75°C.
- 2** A detergent composition as claimed in claim 1, characterised in that it contains not more than 2 wt% of water removable at 75°C.
- 55 **3** A detergent composition as claimed in claim 2, characterised in that it contains not more than 1 wt% of water removable at 75°C.
- 4** A detergent composition as claimed in claim 1, which comprises
- (a) at least one detergent-active compound,

- (b) an alkali metal carbonate detergency builder,
- (c) finely divided calcium carbonate having a surface area of at least 10 m²/g,
- (d) a peroxy bleach system,
- (e) optionally other detergent ingredients,

characterised in that the composition comprises as detergent-active compounds (a) linear alkylbenzene sulphonate optionally in admixture with one or more nonionic surfactants, and in that the composition has a bulk density of at least 750 g/litre and contains not more than 4 wt% of water removable at 75°C.

5 A detergent composition as claimed in claim 1, which comprises

- (a) at least one detergent-active compound,
- (b) an alkali metal carbonate detergency builder,
- (c) finely divided calcium carbonate having a surface area of at least 10 m²/g,
- (d) a peroxy bleach system,
- (e) optionally other detergent ingredients,

characterised in that the composition comprises as detergent-active compounds (a) primary alcohol sulphate optionally in admixture with one or more nonionic surfactants, and in that the composition has a bulk density of at least 750 g/litre and contains not more than 2 wt% of water removable at 75°C.

6 A detergent composition as claimed in any preceding claim, characterised in that the peroxy bleach system comprises an inorganic persalt.

7 A detergent composition as claimed in claim 6, characterised in that the inorganic persalt comprises sodium percarbonate.

8 A detergent composition as claimed in claim 6, characterised in that the inorganic persalt comprises sodium perborate monohydrate.

9 A detergent composition as claimed in any preceding claim, characterised in that it comprises not more than 30 wt% alkali metal carbonate (b).

10 A detergent composition as claimed in claim 9, characterised in that it comprises not more than 20 wt% alkali metal carbonate (b).

11 A detergent composition as claimed in any preceding claim, characterised by a bulk density of at least 800 g/litre.

12 A detergent composition as claimed in any preceding claim, characterised in that the sodium carbonate is not wholly or predominantly in monohydrate form.

13 A process for the preparation of a detergent composition as claimed in claim 1, characterised in that it includes the step of granulation and/or densification in a high-speed mixer/granulator.

14 A process as claimed in claim 13, characterised in that it includes the steps of:

- (i) spray-drying an aqueous slurry of ingredients other than the finely divided calcium carbonate and the bleach system, to form a particulate detergent base composition;
- (ii) granulating and densifying the spray-dried particulate detergent base composition in a high-speed mixer/granulator to give a particulate product having a bulk density of at least 750 g/litre and containing not more than 4 wt% of water removable at 75°C;

the finely divided calcium carbonate being admixed either before or after step (ii) and the peroxy bleach system being admixed after step (ii).

15 A process as claimed in claim 13, characterised in that it includes the steps of:

- (i) mixing and granulating detergent-active compound, alkali metal carbonate detergency builder, finely divided calcium carbonate and optionally other detergent ingredients in a high-speed mixer/granulator to give a particulate detergent base composition having a bulk density of at least 750 g/litre and containing not more than 4 wt% of water removable at 75°C;
- (ii) admixing the peroxy bleach system.