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<b>(54) Title:</b> GRANULAR DETERGENT COMPOSITIONS CONTAINING ZEOLITE AND PROCESS FOR THEIR PREPARATION		
<b>(57) Abstract</b>  A granular detergent composition of low moisture content, as indicated by a relative humidity (of air at 1 atmosphere and 20 °C in equilibrium with the composition) not exceeding 30 %, is prepared by a process which comprises the step of mixing and granulating zeolite having a less than equilibrium moisture content - a moisture content (removable at 800 °C) not exceeding 15 wt% - with organic detergent-active compounds and other detergent ingredient. The resulting granular composition needs no further drying and improved bleach stability is observed.		

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GRANULAR DETERGENT COMPOSITIONS CONTAINING ZEOLITE  
AND PROCESS FOR THEIR PREPARATION

5     TECHNICAL FIELD

          The present invention relates to granular detergent compositions containing zeolite and exhibiting improved storage stability of moisture sensitive ingredients such as  
10    persalt bleaches.

BACKGROUND AND PRIOR ART

15           The ability of crystalline aluminosilicates (zeolites) to sequester calcium ions from aqueous solution has led to their becoming a well-known replacement for phosphates as a detergency builder. Particulate detergent compositions containing zeolite are widely disclosed in the art, for  
20    example, in GB 1 473 201 (Henkel), and are sold commercially in many parts of Europe, Japan and the United States of America. The preferred zeolite for detergents use is generally zeolite A, which has the advantage of being a "maximum aluminium" structure containing the maximum possible  
25    proportion of aluminium to silicon - or the theoretical minimum Si:Al ratio of 1.0 - so that its capacity for taking up calcium ions from aqueous solution is intrinsically greater than those of zeolites X and P which generally contain a lower proportion of aluminium (or a higher Si:Al ratio).

30           Zeolites contain relatively high levels of relatively mobile water. For example, zeolite A in its equilibrium state contains 22 wt% of water of hydration, part of which is mobile at ambient temperatures. Incorporation of zeolites into  
35    particulate detergent compositions has therefore created a problem of lack of storage stability of ingredients sensitive to moisture, in particular, peroxy bleach compounds.

One of the most sensitive is sodium percarbonate, which until recently had been almost entirely superseded by the more stable sodium perborate tetrahydrate and monohydrate, but which is now coming back into favour following concern about the environmental impact of boron salts. Sodium percarbonate is an efficient, water-soluble weight-effective hydrogen-peroxide-generating bleaching agent, and leaves a useful product (sodium carbonate) on completion of the bleaching reaction.

Detergent compositions containing zeolite A and sodium percarbonate are disclosed in DE 2 656 009A (Colgate-Palmolive), but storage stability is not discussed. According to GB 2 013 259A (Kao), the problem of sodium percarbonate instability in the presence of zeolite is solved by the use of an amorphous or partially crystalline aluminosilicate (0-75% crystallinity), or by the use of a partially calcium- or magnesium-exchanged material.

Another approach which has received attention is the protection of sodium percarbonate by coating or encapsulation, for example, a coating comprising sodium metaborate and sodium silicate as disclosed in GB 2 123 044B (Kao). However, such techniques can be complex and add significantly to the cost of the material.

WO 92 06163A (Procter & Gamble) discloses granular detergent compositions of high bulk density prepared by dry-mixing sodium percarbonate bleach with a "multicomponent ingredient" (a granulate, spray-dried powder or mixture of these) containing surfactants, detergency builders and other components, having a low content of iron, manganese and copper and an equilibrium relative humidity at 32°C of less than 30%. The combination of low heavy metal content and low moisture content (low relative humidity) is said to give compositions in which unprotected sodium percarbonate shows acceptable stability, although coated percarbonate is preferred.

EP 384 070A (Unilever) discloses a novel zeolite P (maximum aluminium zeolite P, or zeolite MAP) having an especially low silicon to aluminium ratio (not exceeding 1.33, and preferably not exceeding 1.15), which is a more efficient  
5 detergent builder than zeolite A. EP 522 726A (Unilever) discloses that replacement of zeolite A by zeolite MAP in detergent compositions containing sodium percarbonate gives significantly improved percarbonate storage stability, even  
10 though the equilibrium moisture content of zeolite MAP (19 wt%) is little different from that of zeolite 4A.

Sodium percarbonate and other persalt bleaches are normally incorporated in a detergent composition at a late stage, by dry-mixing with a granular base powder prepared by  
15 spray-drying or non-tower granulation. The base powder will always contain water that is potentially available to destabilise the added bleach salt.

Spray-drying is a process that necessarily involves large  
20 volumes of water. Non-tower mixing and granulation processes are now becoming increasingly popular, especially for the preparation of granular detergent compositions of bulk densities of, for example, 600 g/l and above. Granulation processes using high-speed mixers are disclosed, for example,  
25 in EP 340 013A, EP 367 339A, EP 390 351A and EP 420 317A (Unilever). In non-tower processing, water content can be kept to a much lower level than in spray-drying processes, but some water is still inevitably introduced as part of surfactant raw materials: a non-tower powder may typically  
30 have a relative humidity of 45% or above.

Despite the various improvements mentioned above, therefore, it has been found desirable to dry zeolite-based powders, for example, on a fluidised bed, to a relative  
35 humidity of 30% or below, before admixture of water-sensitive bleach ingredients. However, fluidised bed drying is energy-

consuming and the necessary additional processing step adds expense and complexity to the manufacturing process.

The present invention is based on the observation this  
5 drying step may be omitted if zeolite pre-dried to a moisture content substantially less than its equilibrium value is used to prepare the base powder before addition of the bleach. Rehydration of the zeolite does not occur to any significant extent during the preparation of the base powder and bleach  
10 stability comparable to that of fluidised-bed-dried powders prepared from fully hydrated zeolite is observed.

Particular benefit is obtained from using low-moisture-content zeolite MAP, which has been found to be more readily  
15 dried than zeolite A, and which reabsorbs water from a humid atmosphere much more slowly than does zeolite A. Dried zeolite MAP can therefore be handled more easily in a humid ambience without deleterious amounts of water being taken up.

#### 20 DEFINITION OF THE INVENTION

The first subject of the present invention is a granular detergent composition wherein the relative humidity of air at  
25 1 atmosphere and 20°C in equilibrium with the composition does not exceed 30%, the composition being the product of a process which comprises the step of mixing and granulating zeolite having a moisture content (removable at 800°C) not exceeding 15 wt%, preferably from 5 to 15 wt%, with organic detergent-  
30 active compounds and other detergent ingredients.

The second subject of the present invention is a process for the preparation of a granular detergent composition, which includes the step of mixing and granulating zeolite having a  
35 moisture content (removable at 800°C) not exceeding 15 wt%, preferably from 5 to 15 wt%, with organic detergent-active compounds and other detergent ingredients.

The third subject of the present invention is zeolite P having a silicon to aluminium ratio not exceeding 1.33:1 (zeolite MAP), having a moisture content (removable at 800°C) not exceeding 15 wt%, preferably from 5 to 15 wt%, and more preferably from 5 to 13 wt%.

#### DETAILED DESCRIPTION OF THE INVENTION

The granular detergent composition of the invention is prepared by a non-tower process which includes the step of mixing and granulating zeolite of lower than equilibrium moisture content with organic detergent-active compounds and other ingredients. This process enables compositions of low relative humidity to be prepared by non-tower granulation without the need for a subsequent drying process, for example, on a fluidised bed, at an elevated temperature.

The compositions of the invention are characterised by a relative humidity value at 1 atm and 20°C not exceeding 30%. The term "relative humidity value" as used herein means the relative humidity of air in equilibrium with the composition: it is an indirect measurement of the water activity in a solid. It is the ratio of the current water concentration in the air (kg water/kg air) to the maximum at a given temperature and pressure, expressed as a percentage of the value for saturated air. For a solid an equilibrium is established between the water in the solid and the atmosphere, and the measured relative humidity is a characteristic for that solid at a given temperature and pressure. All relative humidity values quoted in the present specification are normalised to 1 atmosphere pressure and 20°C.

Preferred compositions of the invention have a relative humidity value not exceeding 25%, and especially preferred compositions have a relative humidity value not exceeding 20%.

Given that compositions of low relative humidity value are desirable in order that moisture-sensitive ingredients have acceptable storage stability, there are various advantages connected with using predried zeolite rather than post-drying a full base powder. The energy required to dry one single ingredient that will generally constitute at most 50 wt% of the base powder is lower than that required to dry the whole composition. Other ingredients do not have to be subjected to elevated temperatures; organic surfactants tend to be mobile liquids at the drying temperature and to migrate to the surface of the granules, causing stickiness, agglomeration, poor flow properties and even fluid bed fouling; and a fluidised bed imposes more stringent requirements on particle size distribution than would otherwise be necessary.

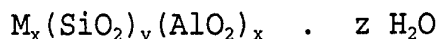
However, the surfactant raw materials generally have substantial amounts of water associated with them, and water may actually be generated during the preparation of the base powder if in-situ neutralisation of a surfactant acid is involved. Base powder preparation may take place in a humid atmosphere. It might therefore be expected that the predried zeolite would rehydrate during base powder preparation to an extent that the advantage of using it would be lost. Surprisingly, that has been found not to be the case; especially when the zeolite concerned is zeolite MAP.

Difficulties might also be expected in the drying of the zeolite itself to a constant and reproducible low moisture content, and with the stability of the dried zeolite itself before it comes into contact with other ingredients. Again, these expected problems have not been found in practice, zeolite MAP being especially advantageous in this respect.



The low-moisture-content zeolite

Ion-exchanging crystalline zeolites have the general formula



The ratio of silicon to aluminium (y:x) can vary, but for zeolites A and MAP approximates to the theoretical maximum of 1:1. The amount of water of hydration can also vary.

The zeolite used in the present invention initially has a moisture content lower than its equilibrium content, which for hydrated crystalline zeolites typically lies in the range of 18-22 wt%. This is the total water content, removable at 800°C.

In one embodiment of the invention, the zeolite is zeolite A, and has a moisture content (removable at 800°C) not exceeding 15 wt%, preferably from 10 to 15 wt%.

Zeolite A has an equilibrium water content of 22 wt%, based on the hydrated zeolite. This can be removed completely at the very high temperature of 800°C to leave the anhydrous material. About 75 wt% is removable at 135°C, ie at 135°C it can in principle be dried to a moisture content of about 7 wt%.

In another, especially preferred embodiment of the invention, the zeolite is zeolite MAP. The zeolite MAP preferably has a moisture content (removable at 800°C) not exceeding 13 wt%, more preferably from 5 to 13 wt%.

Zeolite MAP has an equilibrium water content of 19 wt%, based on the hydrated zeolite, of which 78 wt% is removable at 135°C, ie at 135°C it can in principle be dried to a moisture content of about 5 wt%.

Zeolite MAP was first disclosed in EP 384 070A (Unilever) and is defined as zeolite of the P type having a silicon to aluminium ratio not exceeding 1.33, preferably not exceeding 1.15, and more preferably not exceeding 1.07. It generally has a calcium binding capacity of at least 150 mg CaO/g anhydrous aluminosilicate, as measured by the standard method described in GB 1 473 201 (Henkel) and also described, as "Method I", in EP 384 070A (Unilever). The calcium binding capacity is normally at least 160 mg CaO/g and may be as high as 170 mg CaO/g. Zeolite MAP also generally has an "effective calcium binding capacity", measured as described under "Method II" in EP 384 070A (Unilever), of at least 145 mg CaO/g, preferably at least 150 mg CaO/g.

Surprisingly, it has been found that zeolite MAP is easier to dry than zeolite A; and the dried material also rehydrates less readily, so is much more stable and easy to handle.

The relative rates of drying of zeolites A and MAP at two temperatures are illustrated in the following experiment, in which the weight losses of samples under isothermal conditions in a thermogravimetric analyser (Perkin-Elmer (Trade Mark) TGA-7) under a flow of 100 ml/min dry nitrogen were measured.

The results are shown in Table 1 below. They show that it is significantly easier to dry zeolite MAP than to dry zeolite A. For example, to produce zeolites having a moisture content of approximately 10 wt%, at 80°C it would take 15 minutes for zeolite MAP, as compared with 50 minutes for zeolite A. Alternatively, to attain the same final moisture content of 10 wt% using the same drying time, a temperature of 80°C is needed for zeolite A while a temperature of 60°C suffices for zeolite MAP.

TABLE 1 - Drying times of zeolite A and zeolite MAP

Drying time (min)	<u>Moisture contents (wt%)</u>			
	<u>zeolite A</u>		<u>zeolite MAP</u>	
	60°C	80°C	60°C	80°C
5	4.5	18.9	16.9	16.8
10	8.9	18.0	15.5	15.8
	13.4	17.5	14.5	14.9
	17.9	17.1	13.8	14.1
	22.4	16.8	13.0	13.3
	26.8	16.6	12.4	12.5
15	35.8	16.0	11.5	11.0
	44.7	15.6	10.6	9.8
	53.5	14.3	9.9	8.7

TABLE 2: Rehydration behaviour of zeolite A and zeolite MAP

20

Time (hr)	<u>% of equilibrium water content</u>	
	<u>zeolite A</u>	<u>zeolite MAP</u>
25	0	25
	0.47	41.8
	1.25	60.1
	1.75	70.3
	3.0	86.2
30	3.5	90.1
	4.58	96.2
	5.42	98.4
	5.83	98.7
	7.33	99.0
35	9.0	99.1
	25.0	100.0

Table 2 shows the rehydration behaviour of zeolites A and MAP after drying at 135°C. A sample of each zeolite was dried at 135°C for 2 hours, allowed to cool to ambient temperature in a desiccator, then exposed to humid air (43% RH) at 25°C in a shallow (2-3 mm) bed. Hydration as a function of time was then measured by monitoring weight increase.

These results show the faster rehydration of zeolite A. The hydration of both zeolites obeys first order kinetics, and the rehydration rate constants are as follows, pointing the difference more strongly:

zeolite A	$0.708 \text{ hr}^{-1}$
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zeolite MAP	$0.247 \text{ hr}^{-1}$
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Such is the stability of zeolite MAP having intermediate, less than equilibrium levels of hydration, for example, 10 wt%, that it can actually be manufactured and supplied consistently to such levels.

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 micrometres, more preferably from 0.4 to 2.0 micrometres, and most preferably from 0.4 to 1.0 micrometres. The quantity  $d_{50}$  indicates that 50 wt% of the particles have a diameter smaller than that figure, and there are corresponding quantities  $d_{80}$ ,  $d_{90}$  etc. Especially preferred zeolite MAP has a  $d_{90}$  below 3.0 micrometres as well as a  $d_{50}$  below 1.0 micrometres. These quantities are as measured by means of a Malvern (Trade Mark) Mastersizer with a 45 mm lens, after dispersion in demineralised water and ultrasonification for 10 minutes.

Detergent compositions

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  $C_8$ - $C_{15}$ ; primary and secondary alkyl sulphates, particularly  $C_{12}$ - $C_{15}$  primary alkyl sulphates; alkyl ether sulphates; olefin sulphonates; alkyl xylene sulphonates; dialkyl sulphosuccinates; 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  $C_8$ - $C_{20}$  aliphatic alcohols ethoxylated with an average of from 1 to 20 moles of ethylene oxide per mole of alcohol, and more especially the  $C_{10}$ - $C_{15}$  primary and secondary aliphatic alcohols ethoxylated with an average of from 1 to 10 moles of ethylene oxide per mole of alcohol. Non-ethoxylated nonionic surfactants include alkylpolyglycosides, glycerol monoethers, and polyhydroxyamides (glucamide).

The total amount of detergent-active compound present may suitably range 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 combinations of the two in any ratio, optionally together with soap. Especially preferred surfactant systems for use in the present invention comprise linear alkylbenzene sulphonate in combination with ethoxylated alcohol nonionic surfactant, optionally together with soap; primary alcohol sulphate in combination with ethoxylated alcohol nonionic surfactant, optionally together with soap, more particularly as described in EP 544 492A (Unilever); and ethoxylated alcohol nonionic surfactant, optionally together with soap.

The detergent compositions of the invention also contain a detergency builder system consisting wholly or partially of zeolite. The total amount of detergency builder in the compositions will suitably range from 10 to 80 wt%, preferably from 15 to 60 wt%. The amount of zeolite present is suitably from 10 to 45 wt%, based on the anhydrous zeolite, and preferably from 15 to 45 wt%.

Supplementary organic or inorganic builders may be present if desired. 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.

Especially preferred organic builders are citrates, suitably used in amounts of from 5 to 30 wt%, preferably from 10 to 25 wt%; and acrylic polymers, more especially acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt%, preferably from 1 to 10 wt%. Supplementary inorganic builders include layered silicates (SKS-6).

Builders, both organic and inorganic, are preferably present in alkali metal, more preferably sodium, salt form.

5     Bleaching ingredients

10     The present invention is of especial advantage for compositions containing peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution. Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium  
15     perborate monohydrate and tetrahydrate, and sodium percarbonate.

20     As previously indicated, the invention is of especial applicability to compositions containing sodium percarbonate. The percarbonate may if desired have a protective coating against destabilisation by moisture, for example, a coating comprising sodium metaborate and sodium silicate as disclosed in GB 2 123 044B (Kao). However, coating or other protection of the percarbonate is not essential and the invention also  
25     encompasses the use of uncoated percarbonate.

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

35     The peroxy bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 1 to 8 wt%, preferably from 2 to 5 wt%. Preferred bleach precursors are peroxycarboxylic acid precursors, more especially peracetic acid precursors and peroxybenzoic acid precursors; and peroxycarbonic acid precursors. An especially preferred

bleach precursor suitable for use in the present invention is N,N,N',N'-tetracetyl ethylenediamine (TAED).

5 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.

10 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).

15 Other ingredients

The compositions of the invention may contain alkali metal, preferably sodium, carbonate, in order to increase  
20 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.

25 Powder flow may be improved by the incorporation of a small amount of a powder structurant, for example, a fatty acid soap, a sugar, an acrylate or acrylate/maleate polymer, or sodium silicate. A preferred powder structurant is fatty  
30 acid soap, suitably present in an amount of from 1 to 5 wt%.

Other materials that may be present in detergent compositions of the invention include sodium silicate; antiredeposition agents such as cellulosic polymers;  
35 fluorescers; 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

5 The granular detergent compositions of the invention are prepared by a granulation process which comprises the step of mixing and granulating zeolite having a moisture content (removable at 800°C) not exceeding 15 wt% with organic  
10 detergent-active compounds and other detergent ingredients.

The mixing and granulation process is advantageously carried out using a high-speed mixer/granulator, for example, as described in EP 340 013A, EP 367 339A, EP 390 351A and  
15 EP 420 317A (Unilever). Both batch and continuous processing are possible.

Batch processing may suitably be carried out in a high-speed mixer/granulator which is bowl-shaped and has a  
20 substantially vertical stirring axis. Preferred batch mixers are those 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  
25 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. The vessel can be fitted with a temperature control jacket.

30 Continuous operation may advantageously be carried out in a mixer comprising a hollow cylinder, mounted with its longitudinal axis in a substantially horizontal orientation, having therein an axial rotatable shaft with cutting and stirring blades mounted thereon. An examples of such a mixer  
35 is the Lödige (Trade Mark) CB30 Recycler.

This apparatus essentially consists of a large, static hollow cylinder having a diameter of about 30 cm which contains an axially mounted rotatable shaft carrying several different types of stirring and cutting blades. The shaft  
5 can be rotated at speeds of from 100 to 2500 rpm depending on the mixing intensity and particle size desired. Such a mixer provides a high energy stirring input and achieves very thorough mixing of both liquids and solids in a very short time. For larger scale operation, the CB50 Recycler with a  
10 50 cm diameter cylinder is suitable.

The granulation process in the high-speed mixer/granulator gives a base powder which may also contain robust ingredients such as fluorescers, supplementary organic  
15 or inorganic builders, sodium carbonate, and antiredeposition polymers. Nonionic surfactants may be incorporated during the granulation process, or subsequently admixed. Sensitive ingredients such as bleach compounds, enzyme granules, foam control granules and perfume are always admixed subsequently  
20 (postdosed).

Anionic surfactant, for example, linear alkylbenzene sulphonate or primary alcohol sulphate, to be incorporated in the base powder may take various forms, for example, a paste,  
25 or a mobile liquid blend with a nonionic surfactant as described in EP 265 203B and EP 544 365A (Unilever). Another possibility is an in-situ neutralisation process as described in EP 420 317A (Unilever) or EP 506 184A (Unilever), wherein surfactant acid, some water and at least a stoichiometric  
30 proportion of sodium carbonate are mixed and granulated together with the zeolite and other required ingredients. In all these cases, water is of necessity incorporated together with the surfactant; the in-situ neutralisation process requires water to initiate the reaction, and water is also  
35 generated by the reaction itself. Mobile anionic/nonionic blends must also contain water: generally 3-10 wt%.

Even if no non-soap anionic surfactant is present, blends of nonionic surfactants with soap may contain significant quantities of water derived from the soap. Surprisingly, however, the dry zeolite used according to the present  
5 invention appears to be able to adsorb the water from water-containing surfactants.

It has been found that, in order to obtain a base powder having a relative humidity of 30% or less, the starting  
10 zeolite must have a water content not exceeding 15 wt%, and in the case of zeolite MAP a water content not exceeding 13 wt% is strongly preferred.

15 Bulk density

Granular detergent compositions of the invention generally have bulk densities ranging upwards from about 600 g/l. The processes just described are especially  
20 suitable for the production of high bulk density compositions, - at least 650 g/l, especially at least 700 g/l and more especially at least 750 g/l. However, the invention is not limited to such compositions and is equally applicable to the production of compositions of lower bulk density.

EXAMPLES

The invention is further illustrated by the following non-limiting Examples, in which parts and percentages are by weight unless otherwise stated. Examples denoted by numbers are within the invention, while Examples denoted by letters are comparative.

The following abbreviations are used in the Examples:

CocoPAS: primary linear C<sub>12-14</sub> alcohol sulphate derived from coconut alcohol

Nonionic 1: primary linear C<sub>12-14</sub> alcohol (coconut) ethoxylated with an average of about 5 moles of ethylene oxide per mole of alcohol

Nonionic 2: synthetic C<sub>12-15</sub> alcohol ethoxylated with an average of about 5 moles of ethylene oxide per mole of alcohol

TAED: tetraacetythylenediamine (in granular form).

Examples 1 to 3

Detergent base powders were prepared by granulating zeolite MAP having a moisture content of 9.5 wt% with three different aqueous surfactant blends having the following compositions (wt%):

	<u>1</u>	<u>2</u>	<u>3</u>
10 CocoPAS	39.0	24.8	-
Nonionic 1	-	57.9	82.3
Nonionic 2	52.0	-	-
Sodium stearate	-	9.7	14.5
Water	9.0	7.6	4.2
15 -----	-----	-----	-----
	100.0	100.0	100.0

The zeolite MAP was mixed with the surfactant blends in the following proportions:

	<u>1</u>	<u>2</u>	<u>3</u>
20 Surfactant blend	37.9	41.4	37.9
Zeolite MAP (hydrated)	62.1	58.6	62.1
25 -----	-----	-----	-----
	100.0	100.0	100.0

Granulation was carried out in a Fukae (Trade Mark) FS-30 30-litre batch mixer, at a jacket temperature of 60°C. The solids (zeolite MAP) were introduced first into the mixer, then the liquid surfactant blend added in a single dose. The mixer was operated at a stirrer speed of 100 rpm and a cutter speed of 3000 rpm, for a residence time of 2-3 minutes; the product was then removed and allowed to cool to ambient temperature.

The resulting granular products (detergent base powders) had the following compositions:

	<u>1</u>	<u>2</u>	<u>3</u>
CocoPAS	14.8	10.3	-
Nonionic 1	19.8	-	31.2
Nonionic 2	-	24.0	-
Sodium stearate	-	4.0	5.5
Zeolite MAP (anhydr)	56.2	53.0	56.2
Total water	9.2	8.7	7.1
	-----	-----	-----
	100.0	100.0	100.0

In this composition table the amount of zeolite MAP is shown on a notional anhydrous basis, and the water content given is the total of the water of hydration of the zeolite and the water associated with the surfactant blend.

Bulk densities were as follows:

	<u>1</u>	<u>2</u>	<u>3</u>
Bulk density (g/l)	870	860	870

The granular products (detergent base powders) were placed in sealed containers and the relative humidity of the air in contact with each sample was measured at different times after preparation:

21

<u>Time (hours)</u>		<u>Relative humidity (%)</u>		
		<u>1</u>	<u>2</u>	<u>3</u>
5	1	35	35	24
	2	23	21	21
	24	22	20	20

10

It will be seen that although initial relative humidity values were above 30%, the powders rapidly settled to low equilibrium values.

15

#### Examples 4 to 7, Comparative Examples A to C

20

These Examples show how the relative humidity of a granulated base powder varies with the moisture content of the zeolite used.

25

The powders were prepared by granulation in the Fukae FS-30 mixer as described in Examples 1 to 3. The surfactant blend was that of Example 2, containing 7.6 wt% water. As in Example 2, each base powder was prepared by granulating 41.4 wt% of the surfactant blend and 58.6 wt% (hydrated basis) of zeolite MAP. The compositions were as shown in the following table.

30

Compositions of Examples 4 to 7 and Comparative Examples A to C

5

	A	B	C	4	5	6	7
CocOPAS	10.3	10.3	10.3	10.3	10.3	10.3	10.3
Nonionic 1	24.0	24.0	24.0	24.0	24.0	24.0	24.0
Sodium stearate	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Zeolite MAP (anhydr)	47.6	48.8	49.9	51.0	52.1	53.7	55.4
Total water	14.1	12.9	11.8	10.7	9.6	8.0	6.3
	-----	-----	-----	-----	-----	-----	-----
	100.0	100.0	100.0	100.0	100.0	100.0	100.0

22

15

20



Bulk densities, water contents of the zeolite MAP samples and the relative humidity values of the corresponding powders after 48 hours were as follows:

Example	<u>Zeolite MAP</u>	<u>Bulk density</u>	<u>Relative humidity</u>
	<u>water content</u>		<u>48 hours after</u> <u>preparation</u>
	(wt%)	(g/litre)	(%)
A	19.0	850	60
B	16.7	850	53
C	14.9	850	43
4	13.0	860	29
5	11.1	860	25
6	8.3	860	20
7	5.5	870	20

With these compositions, it was necessary to use zeolite MAP having a moisture content of 13.0 wt% or less in order to obtain a powder having a relative humidity value of less than 30%.

Examples 8 to 11. Comparative Examples D to F

5 A series of experiments similar to those of Examples 4 to 7 was carried out using zeolite A instead of zeolite MAP.

The surfactant blend was similar to that of Example 2 and had the following composition:

10		wt%
	CocoPAS	25.6
	Nonionic 1	57.9
	Sodium stearate	9.1
15	Water	7.4
		-----
		100.0

20 Each base powder was prepared by granulating 30.9 wt% of the surfactant blend with 61.5 wt% (hydrated basis) of zeolite A and 7.6 wt% of anhydrous sodium carbonate (light soda ash).

25 The compositions were as shown in the following table.

Compositions of Examples 8 to 11 and Comparative Examples D to F

	D	E	F	8	9	10	11
5							
	CocOPAS	7.9	7.9	7.9	7.9	7.9	7.9
	Nonionic 1	17.9	17.9	17.9	17.9	17.9	17.9
10	Sodium stearate	2.8	2.8	2.8	2.8	2.8	2.8
	Zeolite MAP (anhydr)	48.6	49.9	50.8	52.1	52.6	53.3
15	Light soda ash	7.6	7.6	7.6	7.6	7.6	7.6
	Total water	15.2	13.9	13.0	11.7	11.2	10.5
		-----	-----	-----	-----	-----	-----
20		100.0	100.0	100.0	100.0	100.0	100.0

Bulk densities, water contents of the zeolite MAP samples and the relative humidity values of the corresponding powders after 48 hours were as follows:

<u>Example</u>	<u>Zeolite A</u> <u>water content</u>	<u>Bulk density</u>	<u>Relative humidity</u> <u>48 hours after</u> <u>preparation</u>
	(wt%)	(g/litre)	(%)
D	21.0	850	65
E	18.9	850	61
F	17.4	850	55
8	16.1	850	42
9	15.3	850	29
10	14.4	855	20
11	13.4	860	9

With these compositions, it was necessary to use zeolite A having a moisture content of 15 wt% or less in order to obtain a powder having a relative humidity value of less than 30%. The use of zeolite A containing 13.4 wt% moisture allowed a powder having the very low relative humidity value of 9% to be produced.

Example 12, Comparative Examples G and H

These Examples show how the storage stability of sodium percarbonate, admixed to a granular detergent base powder, is improved by reduction of the relative humidity value of the base powder achieved by means of the present invention.

Detergent compositions were prepared by mixing detergent base powders from previous Examples with other ingredients as follows:

Example 12 (base powder of Example 2)

	% of base	% of product
CocoPAS	10.3	6.55
Nonionic 2	24.0	15.26
Sodium stearate	4.0	2.54
Zeolite MAP (anhydr)*	53.0	33.71
Total water	8.7	5.53
	-----	-----
	100.0	63.60
Sodium percarbonate		18.9
TAED (granules)		8.7
Sodium silicate		5.7
Enzyme granules		0.9
Minor solids		2.7
		-----
		100.0

\*Moisture content of zeolite MAP: 9.5 wt%.

Comparative Example G (base powder of Comparative Example A):

	% of base	% of product
5		
	CocoPAS	10.3
	Nonionic 2	24.0
	Sodium stearate	4.0
10	Zeolite MAP (anhydr)*	47.6
	Total water	14.1
	-----	-----
	100.0	63.60
	Sodium percarbonate	18.9
15	TAED (granules)	8.7
	Sodium silicate	5.7
	Enzyme granules	0.9
	Minor solids	2.7
		-----
20		100.0

\*Moisture content of zeolite MAP: 19.0 wt%.

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Comparative Example H used a base powder corresponding to that of Comparative Example G (Comparative Example A), but after fluidised bed drying.

30

Sodium percarbonate storage stability was measured in cardboard cartons under two sets of storage conditions: 28°C/70% relative humidity and 37°C/70% relative humidity.

The results were as follows:

5		<u>12</u>	<u>G</u>	<u>H</u>
	Relative humidity value	20	60	17
10	<u>Storage conditions</u>	<u>% available oxygen remaining</u>		
	4 weeks, 37°C/70% relative humidity	70	40	71
	6 weeks, 37°C/70% relative humidity	40	25	42
15	6 weeks, 28°C/70% relative humidity	72	62	70

20        These results show that the improvement in sodium  
percarbonate stability obtained by means of the present  
invention was the same (within experimental error) as that  
obtained with powder prepared using zeolite MAP of normal  
moisture content and then dried on a fluidised bed.

25

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CLAIMS

1 A granular detergent composition, wherein the relative  
5 humidity of air at 1 atmosphere and 20°C in equilibrium with  
the composition does not exceed 30%, prepared by a process  
which comprises the step of mixing and granulating zeolite  
having a moisture content (removable at 800°C) not exceeding  
15 wt% with organic detergent-active compounds and other  
10 detergent ingredients.

2 A granular detergent composition as claimed in claim 1,  
characterised in that the zeolite has a moisture content  
15 within the range of from 5 to 15 wt%.

3 A granular detergent composition as claimed in claim 1 or  
claim 2, characterised in that the zeolite is zeolite A and  
20 has a moisture content within the range of from 10 to 15 wt%.

4 A granular detergent composition as claimed in claim 1 or  
claim 2, characterised in that the zeolite is zeolite P having  
25 a silicon to aluminium ratio not exceeding 1.33:1 (zeolite  
MAP) and has a moisture content within the range of from 5 to  
13 wt%.

30 5 A granular detergent composition as claimed in claim 4,  
characterised in that the zeolite is zeolite MAP having a  
silicon to aluminium ratio not exceeding 1.15:1.

35



6 A granular detergent composition as claimed in any  
preceding claim, characterised in that the relative humidity  
of air at 1 atmosphere and 20°C in equilibrium with the  
composition does not exceed 25%.

5

7 A granular detergent composition as claimed in any  
preceding claim, which further comprises a peroxy bleach  
system.

10

8 A granular detergent composition as claimed in claim 7,  
characterised in that the peroxy bleach system comprises  
sodium percarbonate.

15

9 Zeolite P having a silicon to aluminium ratio not  
exceeding 1.33:1 (zeolite MAP), characterised by a moisture  
content (removable at 800°C) not exceeding 15 wt%.

20

10 Zeolite MAP as claimed in claim 9, characterised by a  
moisture content (removable at 800°C) within the range of from  
5 to 15 wt%.

25

11 Zeolite MAP as claimed in claim 10, characterised by a  
moisture content (removable at 800°C) within the range of from  
5 to 13 wt%.

30

12 Zeolite MAP as claimed in any one of claims 9 to 11,  
having a silicon to aluminium ratio not exceeding 1.15.

35

13 A process for the preparation of a granular detergent  
composition wherein the relative humidity of air at  
1 atmosphere and 20°C in equilibrium with the composition does  
not exceed 30%, which process comprises the step of mixing and  
5 granulating zeolite having a moisture content (removable at  
800°C) not exceeding 15 wt% with organic detergent-active  
compounds and other detergent ingredients.

10 14 A process as claimed in claim 13, characterised in that  
the zeolite has a moisture content within the range of from 5  
to 15 wt%.

15 15 A process as claimed in claim 14, characterised in that  
the zeolite is zeolite A and has a moisture content within the  
range of from 10 to 15 wt%.

20 16 A process as claimed in claim 14, characterised in that  
the zeolite is zeolite P having a silicon to aluminium ratio  
not exceeding 1.33 (zeolite MAP) and has a moisture content  
within the range of from 5 to 13 wt%.

25 17 A process as claimed in claim 16, characterised in that  
the zeolite MAP has a silicon to aluminium ratio not exceeding  
1.15.

30

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\*

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 94/02455

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/12 C11D3/39 C11D17/06 C01B39/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 552 054 (UNILEVER) 21 July 1993 see the whole document ---	1,4,5, 7-9
A	WO,A,92 06163 (PROCTER & GAMBLE) 16 April 1992 cited in the application see claims 1,2,11; examples ---	1,6,7
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 94/02455

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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