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㉙ **Detergent compositions.**

㉚ Detergent compositions which comprise base powder granules containing detergent active materials and amorphous aluminosilicate together with a post-dosed per-oxygen bleach compound exhibit improved ion-exchange properties and bleach stability if the level of moisture in the granules lies between given limits which depend on the levels of aluminosilicate, detergent active and alkaline salt if any present in the granules.

Exemplified moisture contents lie between 10.7% and 21.0% of the base powder granules.

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DETERGENT COMPOSITIONS

It is known to formulate spray-dried detergent
5 compositions containing detergent active materials,
detergency builders and optionally other components
including bleaches. In GB 1 473 202 (HENKEL & CIE GmbH)
it is proposed to use X-ray amorphous aluminosilicate
materials as detergency builders, in place of the more
10 usual alkali metal phosphates used hitherto. However,
detergent compositions containing amorphous
aluminosilicate often suffer from the disadvantage of poor
ion exchange properties when first formed, which ion
exchange properties deteriorate still further on storage
15 and, where the composition additionally contains bleach
materials, the stability of such bleach materials on
storage is often poor.

We have discovered that granular detergent
20 compositions based on amorphous aluminosilicate and having
improved initial and long term ion exchange properties can
be achieved by controlling the level of moisture in such
compositions. We have also discovered that when such
compositions additionally contain bleach materials,

the storage stability of such bleach materials is also improved.

Granular detergent compositions invariably contain
5 water. Most or all of this water is relatively loosely
bound and is lost when the composition is heated to say
135°C. This loosely bound water is constituted by water
of crystallisation of the components in the composition,
and further water which is more loosely bound to
10 ingredients such as detergent active materials.

As used herein, the term "moisture" is the water
which is lost from the composition when it is heated to
135°C.

15

However, in compositions containing amorphous
aluminosilicate and also in compositions containing NTA
(sodium nitrilotriacetate), some water is not lost at
135°C. This more tightly bound water however adds to the
20 total water content of the composition.

We have discovered that the properties of
compositions containing amorphous aluminosilicate are
dependent upon the moisture content of the composition
25 rather than the total water content.

Where the composition comprises a spray-dried base
powder containing at least a detergent active and an
amorphous aluminosilicate builder material, to which have
30 been post-dosed various further components such as
bleaches, the critical factor in the ion-exchange
properties of the composition is the moisture content of
the base powder.

35 Thus, according to the invention there is provided a
detergent composition comprising spray-dried base powder

granules, together with one or more post-dosed ingredients which include a peroxygen bleach compound, the base powder granules containing at least a synthetic detergent active material, an amorphous aluminosilicate builder material, moisture, optionally soap, optionally crystalline aluminosilicate builder material, and optionally an alkaline salt selected from alkali metal silicates, alkali metal carbonates, alkali metal phosphates and mixtures thereof, characterised in that the moisture content of said granules is determined by the formula

$$M = 0.075A + 0.25 S + (y - 0.125)X$$

where M is the moisture content of said granules in parts by weight, as measured by the water loss from said granules at 135°C, A is the amount of the detergent active material including soap, if any, in said granules in parts by weight, S is the amount of the alkaline salt in said granules in parts by weight, X is the amount of the aluminosilicate builder material including crystalline aluminosilicate builder material, if any, in said granules in parts by weight and y is a number from 0.25 to 0.7, preferably from 0.5 to 0.6.

Where the base powder contains no sodium silicate and/or where it contains crystalline aluminosilicate (zeolite) in addition to the amorphous material, y preferably lies between 0.25 and 0.5. Otherwise, the preferred level for y is from 0.5 to 0.6.

When the value of y is too low (which corresponds to a relatively dry powder) it is found that the ion exchange properties of the powder may be unsatisfactory. When the value of y is too high (which corresponds to a relatively high moisture content), the powder properties and the

bleach stability may become unacceptable and in extreme cases discolouration of the powder may occur.

THE SYNTHETIC DETERGENT ACTIVE MATERIAL

5

The compositions of the invention necessarily contain a synthetic detergent active material otherwise known as a detergent surfactant, preferably present at an overall level of between 2% and 60% by weight, especially about
10 between 5% and 40% of the composition.

Suitable detergent surfactants are well known and readily available, as described for example in "Surface Active Agents and Detergents", Volumes I and II by
15 Schwartz, Perry and Berch.

Synthetic anionic detergent compounds which can be used are usually water soluble alkali metal salts of organic sulphates and sulphonates having alkyl radicals
20 containing from about 8 to 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating the
25 higher (C₈-C₁₈) alcohols produced by reducing the glycerides of tallow or coconut oil; sodium and potassium alkyl (C₉-C₂₀) benzene sulphonates, particularly sodium linear secondary alkyl (C₁₀-C₁₅) benzene sulphonates, sodium alkyl glyceryl ether sulphates, especially those
30 ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum; sodium coconut oil fatty acid monoglyceride sulphates and sulphonates; sodium and potassium salts of sulphuric acid esters of higher (C₈-C₁₈) fatty alcohol-alkylene oxide,
35 particularly ethylene oxide, reaction products; the reaction of fatty acids such as coconut fatty acids

esterified with isethionic acid and neutralised with sodium hydroxide; sodium and potassium salts of fatty acid amides of methyl taurine; alkane monosulphonates such as those derived by reacting alpha-olefins (C_8-C_{20}) with sodium bisulphite and those derived by reacting paraffins with SO_2 and Cl_2 and then hydrolysing with a base to produce a random sulphonate; and olefin sulphonates, which term is used to describe the material made by reacting olefins, particularly $C_{10}-C_{20}$ alphaolefins, with SO_3 and then neutralising and hydrolysing the reaction product.

Nonionic detergent active compounds may alternatively or additionally be used. Examples of nonionic detergent active compounds include the reaction products of alkylene oxides, usually ethylene oxide, with alkyl (C_6-C_{22}) phenols, generally 5 to 25 EO; ie 5 to 25 units of ethylene oxide per molecule; the condensation products of aliphatic (C_8-C_{18}) primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO, and products made by condensation of ethylene oxide with the reaction products of propylene oxide and ethylene-diamine. Other so-called nonionic detergent active compounds include long chain tertiary amine oxides, long chain tertiary phosphine oxides and dialkyl sulphoxides.

Mixtures of detergent active compounds, for example mixed anionic or mixed anionic and nonionic compounds, may be used in the detergent compositions, particularly to impart thereto controlled low sudsing properties. This is beneficial for compositions intended for use in suds-intolerant automatic washing machines.

Amounts of amphoteric or zwitterionic detergent active compounds can also be used in the compositions of the invention but this is not normally desired due to their relatively high cost. If any amphoteric or

zwitterionic detergent active compounds are used, especially sulphobetaines such as hexadecyl dimethyl ammoniopropene sulphonate, it is generally in small amounts in compositions based on the much more commonly
5 used anionic and/or nonionic detergent active compositions.

Some soap can also be present in the compositions, especially in low sudsing compositions together with mixed
10 synthetic and nonionic detergent compounds. Such soaps are the sodium, or less desirably potassium, salts of C_{12} - C_{22} fatty acids, especially natural fatty acids derived from nut oils, such as coconut oil or palm kernel oil, or preferably tallow class fats, such as beef and
15 mutton tallows, palm oil, lard, some vegetable butters and castor oil, or mixtures thereof. Mixtures are preferred of tallow class soaps, which are soaps of predominantly C_{14} - C_{20} (mainly C_{18}) fatty acids of which normally at least about 40% are saturated fatty acids, with soaps from
20 nut oils, which are soaps of predominantly C_{10} - C_{14} (mainly C_{12}) fatty acids, of which normally at least about 75% are saturated fatty acids. The amount of soap can be varied widely from about 0.5% to about 20% by weight of the composition, but is normally from about 1% to about 5% if
25 present for lather control purposes. Higher amounts of soap can be used as a supplementary detergent active compound.

THE AMORPHOUS ALUMINOSILICATE BUILDER MATERIAL

30

The compositions of the invention necessarily contain an amorphous aluminosilicate builder material, preferably present at a level of from 10% to 60% by weight, especially 12.5% to 50% by weight of the composition.

35

Amorphous aluminosilicate builder materials are described in detail in GB 1 473 202 (HENKEL).

5 However, the amorphous aluminosilicates described therein have one significant defect, namely that they react with sodium silicate, which is an important constituent of most detergent compositions. The mechanism of the reaction between amorphous aluminosilicate and sodium silicate is not fully understood, but
10 its effect is to lessen the effectiveness of the aluminosilicate as a detergent builder in that it slows down the removal of hardness ions and may also reduce the capacity of the aluminosilicate for such ions.

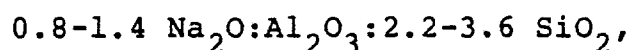
15 Efforts have been made to overcome this deficiency in amorphous aluminosilicates by modifying the production process of detergent compositions containing these two materials. For example, British Patent Specification No 2 013 707 suggests an alternative route for manufacturing
20 detergent compositions in which the sodium silicate is added to the detergent composition in such a way as to minimise the reaction between the sodium silicate and the sodium aluminosilicate.

25 In the context of the present invention we prefer to use an amorphous aluminosilicate which can be used in the preparation of detergent compositions, using orthodox spray-drying equipment and not requiring special techniques to prevent the interaction between the sodium
30 silicate and amorphous sodium aluminosilicate. This amorphous aluminosilicate can be produced in a particle size which is such that it can be used in detergent compositions without further size reduction and, also, in a sufficiently high solids content that excessive
35 quantities of water do not have to be removed from the aluminosilicate and, hence, from a detergent slurry

composition containing the aluminosilicate, making it commercially less attractive.

5 A stable slurry of the aluminosilicate can be prepared in the presence of suitable dispersing agents and size reduced aluminosilicate by grinding or milling a slurry of aluminosilicate and dispersing agent.

10 The preferred amorphous hydrated sodium aluminosilicate is characterised by a chemical composition calculated on an anhydrous basis:

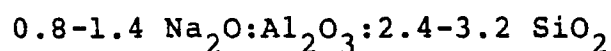


15 and has, calculated on a dry basis, a calcium ion-exchange capacity greater than 100 mg CaO/g, a magnesium capacity greater than 50 mg MgO/g, an average particle size in the range 2 to 20 μm , and the ability to form a filter cake having a solids content in the range 35-50%, in a filter
20 press with a closing pressure of 5.62 kg/cm², which filter cake can be converted into a pumpable slurry in said solids range, and has a silicate resistance (as hereinafter defined) such that the second order rate constant k_s for the calcium exchange process is greater
25 than 0.2 °H⁻¹ min⁻¹ and a residual water hardness after 10 minutes of less than 1.5 °H and which after drying at 50°C to 80% solids has a rate constant k_d (as hereinafter defined) greater than 0.42 °H⁻¹ min⁻¹ and a residual water hardness after 10 minutes of less than 1 °H.

30

References to °H in this specification and claims are to French degrees hardness defined as
1°H Ca = 10⁻⁴ molar Ca⁺⁺.

35 Preferably the amorphous hydrated sodium aluminosilicate has a chemical composition of:



and may optionally contain an inert soluble salt such as sodium sulphate.

5

The calcium and magnesium ion-exchange capacities are determined as follows.

10 Sodium aluminosilicate (equivalent to 1.00 g anhydrous solids determined as the residue after heating to constant weight at 700°C) is added to 1 litre of 5.0×10^{-3} M CaCl_2 solution and stirred for 15 minutes at 20°C. The aluminosilicate is then removed by Millipore membrane filtration and the residual calcium concentration
15 ($Z \times 10^{-3}$ M) of the filtrate is determined by complexometric titration or atomic absorption spectrophotometry.

The calcium exchange capacity is calculated as
20 $56(5.0-Z)$ mg CaO/g aluminosilicate.

Magnesium ion-exchange capacity is measured in a similar fashion using a 5×10^{-3} M MgCl_2 stock solution and a pH in the range 9.5-10.5.

25

To quantify the water softening performance of these sodium aluminosilicates and to compare them with known amorphous aluminosilicates and the known zeolites, the following test is used.

30

The test is designed to simulate some of the conditions which prevail when sodium aluminosilicate is used in a detergent system.

35

The response of a Radiometer calcium ion specific electrode is determined by the addition of aliquots (0-20

mls) of calcium chloride (3×10^{-2} M) to a solution of 5 mls M NaCl in 175 mls of water at 50°C. The resulting solution is 0.025 M in Na^+ and 3×10^{-3} M in Ca^{++} . To this is added sufficient aluminosilicate to give
5 2.5 g/litre (anhydrous basis) and stirring is maintained throughout the water softening measurement. The electrode response is measured over the next 10 minutes and, using the calibration data, is calculated as Ca^{++} concentration ($^{\circ}\text{H}$) versus time. Water softening may be
10 conveniently summarised by the hardness remaining after 1 and 10 minutes.

The electrode test is applied to filter cake, dried powders and to the slurries produced by the silicate
15 resistance test.

To test the resistance of the various aluminosilicates to sodium silicate a sample of the aluminosilicate under test is mixed with sodium silicate,
20 sodium sulphate and water to form a homogeneous slurry having the composition:

Sodium aluminosilicate	22.5 parts (anhydrous basis)
Sodium sulphate	11.0 parts (anhydrous basis)
25 Sodium silicate $\text{Na}_2\text{O}:3.4\text{SiO}_2$	6.0 parts (38% liquor)
Water*	51.0 parts

* Including the water contained in the aluminosilicate filter cake or powder sample.

30 A sample of this slurry is tested for water softening activity by the calcium ion specific electrode method, allowance being made for the fact that 4.0 grams of slurry contains 1.0 g of aluminosilicate (anhydrous basis). The slurry is heated at 80°C for 1 hour in a water bath and
35 the electrode measurement repeated on the further sample. Differences in the two water softening measurements

indicate the adverse interaction between the components. For convenience this can be summarised in terms of the calcium hardness values attained in 1 and 10 minutes.

5 If the aluminosilicate sample is of very low solids, eg less than 30%, or if extra water must be added to the mix to enable a fluid slurry to be produced, the test may still be performed provided allowance is made when weighing samples for the ion-exchange measurement.

10

The water softening kinetics involved in the determination of the rate constant k involve the use of data obtained using the calcium ion specific electrode as described above.

15

The water softening curve, °H Ca versus time (minutes), is summarised by a second order rate equation of the form:

20

$$\frac{-dCa}{dt} = k (Ca - Ca_{eq})^2$$

which on integration becomes:

25

$$Ca = \frac{1}{kt + \frac{1}{Ca_0 - Ca_{eq}}} + Ca_{eq}$$

30

where Ca_0 is the initial hardness, (30°H);

Ca_{eq} is the equilibrium hardness at $t = \infty$;

k is the rate constant having dimensions of $\text{minute}^{-1} \text{ } ^\circ\text{H Ca}^{-1}$;

35

k_s is the rate constant for exchange after the silicate treatment;

k_d is the rate constant for the filter cake or stabilised slurry dried in the absence of silicate;

t is the time in minutes.

5

A convenient method of evaluating these constants in the case where exchange is virtually complete in 10 minutes is to select the hardness remaining after 1 minute and 10 minutes and solve the equation.

$$Ca_{1 \text{ min}} - Ca_{10 \text{ min}} = \frac{1}{k + 0.03} - \frac{1}{10k + 0.03}$$

This contains the approximation that $Ca_o - Ca_{eq} = 30$ (ie $Ca_{eq} = 0$), but in practice this does not significantly affect the result.

The equilibrium hardness is determined from:

$$Ca_{eq} = Ca_{1 \text{ min}} - \frac{1/k}{1 + 1/30k} \text{ or } Ca_{10 \text{ min}} - \frac{1/k}{10 + 1/30k}$$

In situations where it is evident that significant exchange is still occurring after 10 minutes, albeit slowly, the test period should be extended until virtually no further exchange is occurring and a measured value of Ca equilibrium can be obtained. The k value can then be determined from the above equilibrium hardness equation.

30

The most effective sodium aluminosilicates for use according to this invention have a rate constant k_s greater than 2 and an equilibrium calcium concentration (Ca_{eq}) less than 1 °H after silicate treatment.

35

Amorphous aluminosilicates, which will yield, economically, a filter cake of relatively high solids

content containing an aluminosilicate at a particle size suitable for inclusion in detergent compositions according to the invention and having the benefits of silicate resistance previously spelt out, may be prepared by a process in which aqueous sodium silicate, having a composition Na_2O 2-4 SiO_2 and a concentration in the range 1-4 moles/litre SiO_2 ; an aqueous aluminate having a composition 1-2 Na_2O Al_2O_3 and a concentration in the range 0.5 to 2.0 moles/litre Al_2O_3 , are intimately mixed together at a temperature of up to 45°C in a mixing device to produce a sodium aluminosilicate composition which is immediately subjected to high shear in a disintegrator to produce a particle size of aluminosilicate less than $20\text{ }\mu\text{m}$ and subsequently aged.

The intimate mixing of the aluminate and silicate solutions can conveniently be achieved using a mixer such as that described in Handbook of Chemical Engineering by Perry & Chilton, 5th Edition, Chapter 21, ref 21-4, under the heading "Jet Mixers".

The objective of such mixers is to ensure a rapid and intimate mixing of the two solutions.

This is achieved by applying a positive pressure, for example, by pumping each of the solutions and forcing one through a small nozzle or orifice into a flowing stream of the other solution.

Suitable disintegrators for use in reducing the particle size of the sodium aluminosilicate include devices designed to impart high shear, such as the Waring (Trade Mark) blender supplied by Waring Products Division, Dynamics Corporation of America, New Hartford, Connecticut, USA, and Greaves SM (Trade Mark) mixer, as supplied by Joshua Greaves & Sons Limited, Ramsbottom,

Lancashire, England. Various other devices can be used but it is believed that where the shear is provided by rotation of a stirrer blade in the reaction mixture, no such device will be satisfactory unless the tip speed of
5 the rotor exceeds 300 m/min. Preferably the tip speed is in the range 1000-3000 m/min.

The processing subsequent to the high shear treatment can comprise an ageing step for the free-flowing slurry
10 which typically extends for a period of 1-2 hours, but can be longer. The precipitate formation and ageing can take place in the presence of an inert salt such as sodium sulphate. The aged slurry can also be treated with a dilute mineral acid such as sulphuric acid to reduce its
15 pH to about 10.0 or 11.0 prior to washing and filtering.

THE PEROXYGEN BLEACH COMPOUND

The compositions of the invention necessarily contain
20 a peroxxygen bleach compound, preferably at a level of between 5% and 50% by weight of the composition, especially between 8% and 32% by weight. Suitable peroxxygen bleaches include sodium perborate (for example as the tetrahydrate) and sodium percarbonate.

25

THE ALKALINE SALT

The compositions of the invention may include an alkaline salt selected from alkalimetal silicates,
30 carbonates and phosphates.

The amount of sodium silicate used can vary widely according to the type of composition involved, that is from a minimum of about 0.1% to about 50% by weight of the
35 resultant detergent composition. Normally, however, amounts in the range of from about 0.5% to about 20%, especially about 1% to about 15%, are used for

conventional purposes, that is for corrosion inhibition, pH buffer control and powder structuring properties. Amounts of sodium silicate in excess of this up to about 40% are sometimes used for supplementary detergency building properties in fabric washing compositions. Still higher levels of sodium silicate can be present in other types of powdered detergent compositions, for example for dishwashing or industrial purposes in which high alkalinity is usual.

10

Any normal type of sodium silicate can be used, preferably with a sodium oxide to silica ratio of from about 2:1 to about 1:4, for example sodium alkaline silicate ($\text{Na}_2\text{O} \cdot 2\text{SiO}_2$) sodium neutral silicate ($\text{Na}_2\text{O} \cdot 3\text{SiO}_2$), sodium metasilicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2$) or sodium orthosilicate ($2\text{Na}_2\text{O} \cdot \text{SiO}_2$), or mixtures thereof, the less alkaline silicates ($\text{Na}_2\text{O} \cdot 1-4\text{SiO}_2$) being preferred.

Examples of other suitable alkaline materials include sodium carbonate, sodium tripolyphosphate, sodium orthophosphate and sodium pyrophosphate. These alkaline materials will also add to the building capacity of the compositions. The use of sodium pyrophosphate may lead to unacceptably high levels of inorganic deposition on the fabrics and it is therefore preferred to include less than 5% pyrophosphate in the compositions, most preferably substantially no pyrophosphates.

30

OTHER INGREDIENTS

The detergent compositions made according to the invention can contain any of the conventional additives in the amounts in which such additives are normally employed in fabric washing detergent compositions. Examples of these additives include lather boosters such as alkanolamides, particularly the monoethanolamides derived

35

from palm kernel fatty acids and coconut fatty acids, powder flow aids such as finely divided silicas and other aluminosilicates, lather depressants, antiredeposition agents such as sodium carboxymethyl-cellulose, per-acid
5 bleach precursors, chlorine-releasing bleaching agents such as trichloroisocyanuric acid and alkali metal salts of dichloroisocyanuric acid, fabric softening agents such as clays of the smectite and illite types, anti-ashing aids, starches, soap scum dispersants, inorganic salts
10 such as sodium sulphate, and usually present in very minor amounts, fluorescent agents, perfumes, enzymes such as proteases and amylases, germicides and colourants. In addition, especially in the case of nonionic-based detergent compositions, it may be desirable to add slurry
15 stabilisers such as copoly-ethylene-maleic anhydride and copolyvinylmethylether-maleic anhydride, usually in salt form.

Besides the essential aluminosilicate detergency
20 builders which have been mentioned above, other conventional detergency builders may be present such as sodium carboxymethyloxysuccinate, sodium nitrilotriacetate and crystalline aluminosilicates (zeolites).

25 PROCESSING THE COMPOSITIONS

The invention necessarily requires that the base powder granules be made by spray-drying.

30 The slurry making and spray drying steps in the process of the present invention may be accomplished using conventional equipment for this purpose, for example in crutcher, paddle or turbo mixers and spray drying towers. Normal temperatures may be used for these operations, for
35 example from about 30°C to about 100°C, preferably about 70°C to 90°C for the slurry making and about 200°C to

450°C for the drying gas inlet in the spray drying process, with higher temperatures within this range being generally preferred for economic reasons.

5 The base powder necessarily contains the detergent surfactant and the amorphous aluminosilicate. The peroxybleach, together with any other heat sensitive ingredients may be subsequently mixed with the base powder granules. The alkaline salt, if present, may be included
10 in the granules, mixed therewith subsequently or both. Where sodium silicate is the alkaline salt, it may be advantageous to add it subsequently to further reduce the risk of interaction with the sodium aluminosilicate in the slurry. It is preferred that any subsequently added
15 materials be in their fully hydrated forms.

The invention is further illustrated by the following Examples.

20 PREPARATION OF AMORPHOUS ALUMINOSILICATE MATERIAL (NAS)

Using the mixer described below the following method of preparation was followed. Batches of aluminate and silicate were prepared by adjusting commercial liquors to
25 suitable concentration and temperature. These were each pumped at 7 litres/min to the mixing device (jet) and the resultant stream passed through a vessel of 30 litre capacity where it was subjected to intense agitation. The volume of product in the stirred reactor was
30 maintained around 17 litres by adjusting overflow rate. The reaction product was collected and allowed to age, with mild agitation, for 2 hours before the aluminosilicate was recovered on a filter and washed free of the alkaline reaction liquor.

The filter cake was processed so as to produce a stable, pumpable aqueous suspension by incorporating a suitable dispersing agent and reducing the particle size of the aluminosilicate to between 4.0 and 6.0 microns by
5 milling or grinding the aluminosilicate in an aqueous medium containing the said dispersing agent, all in accordance with the teaching of British Patent Specification No 1 051 336 (MOBIL OIL CORPORATION).

10 Note that alternatively the filter cake, or the suspension as prepared above, can be converted into dry powder form by a variety of drying techniques. In order to preserve the ion exchange properties it is important that the residual moisture content (loss on ignition) of
15 the aluminosilicate is not less than about 20% by weight. Filter cakes can be conveniently dried in an oven at a temperature of 50°C for the purpose of testing the preservation of the ion exchange properties and the determination of the k_d value.

20 For the following Examples, the mixer used was a Greaves SM mixer, having a high speed impeller rotating at about 3000 rpm with a tip speed of 1975 m/min.

25 Intense stirring is required to (a) prevent gelation which would lead to low solids content filter cakes and (b) control the particle size of the aluminosilicate.

For small scale laboratory preparations, a Waring blender
30 (Model CB 6 "1 gallon capacity") having a high speed impeller, about 13000 rpm, producing a tip speed of about 2800 m/min may be used.

	Aluminate composition	1.4 Na ₂ O:Al ₂ O ₃
	Silicate composition	Na ₂ O:3.32 SiO ₂
	Reaction Na ₂ O	2.1
	Mixture Al ₂ O ₃	1.0
5	(moles) SiO ₂	2.3
	H ₂ O	54
	Reaction temperature (°C)	30
	Agitation	Greaves
	Filter cake solids	48.4
10	Average particle size (μm)	11.8
	Composition of NAS	1.0 Na ₂ O:Al ₂ O ₃ : 2.6 SiO ₂

Ion exchange performance - Ca electrode method (°HCa)

15	Filter cake activity (1/10 min)	0.5/0.3
	Silicate test (1 min/10 min)	4.0/0.5
	(k _s value)	0.22
	Drying test (1 min/10 min)	0.8/0.2
20	(k _d value)	1.54
	Ca capacity (mgm CaO/gm)	158

EXAMPLES 1 TO 4

25 Using the amorphous aluminosilicate material prepared
as above, particulate detergent compositions were prepared
by spray-drying a base powder and adding thereto a number
of post-dosed ingredients. The base powders had the
following formulations, in parts by weight expressed as
30 anhydrous material.

<u>EXAMPLE NO:</u>		<u>1</u>	<u>2</u>	<u>2A</u>	<u>3</u>	<u>3A</u>	<u>4</u>	<u>4A</u>	<u>4B</u>
<u>Ingredient</u>									
5	Synthetic anionic detergent active	6.0	6.5	6.5	6.5	6.5	7.0	7.0	7.0
	Nonionic detergent active	1.5	3.0	3.0	3.0	3.0	4.0	4.0	4.0
	Soap	-	5.0	5.0	5.0	5.0	2.0	2.0	2.0
	Sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O}=1.6$)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Amorphous aluminosilicate	21.0	30.0	30.0	40.0	40.0	21.0	21.0	21.0
10	NTA	-	10.0	10.0	-	-	-	-	-
	Sodium sulphate	9.9	5.4	5.4	2.4	2.4	7.3	7.3	7.3
	Minor ingredients	1.0	1.0	1.0	1.0	1.0	1.4	1.4	1.4
15	Water (total - including water of hydration)	12.9	11.9	8.6	23.0	17.9	13.6	9.5	16.0
	Total base powder weight	57.3	77.8	74.5	85.9	80.8	61.3	57.2	63.7
	Moisture content (M) - parts	10.3	8.3	4.1	18.0	12.9	11.0	6.9	13.4
	Moisture content - %	18.0	10.7	5.5	21.0	16.0	18.0	12.1	21.0

From the above moisture contents of the base powder, measured by weight loss at 135°C, the values of "y" were calculated, using the formula

$$y = \frac{M - 0.075A - 0.25S}{X} + 0.125$$

where A is the total amount of anionic and nonionic detergent active materials in parts by weight, including soap where present, S is the amount of alkaline salt (sodium silicate) in parts by weight and X is the amount of amorphous aluminosilicate in parts by weight. The calculated values for "y" were:

<u>EXAMPLE NO</u>	<u>1</u>	<u>2</u>	<u>2A</u>	<u>3</u>	<u>3A</u>	<u>4</u>	<u>4A</u>	<u>4B</u>
Y	0.53	0.32	0.18	0.52	0.39	0.54	0.35	0.66

5 To these spray dried base powders were added various post-dosed ingredients as follows:

<u>EXAMPLE NO:</u>		<u>1</u>	<u>2</u>	<u>2A</u>	<u>3</u>	<u>3A</u>	<u>4</u>	<u>4A</u>	<u>4B</u>
<u>Ingredients (parts by weight)</u>									
5	Base powder	57.3	77.8	74.5	85.9	80.8	61.3	57.2	63.7
	Sodium perborate (expressed as $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$)	15.0	15.0	15.0	15.0	15.0	20.0	20.0	20.0
	TAED granules (expressed as neat TAED)	2.0	2.0	2.0	2.0	2.0	-	-	-
	Calcium dequest (expressed as dequest acid)	0.3	0.3	0.3	0.3	0.3	-	-	-
	Sodium tripolyphosphate (expressed as anhydrous)	18.0	-	-	-	-	18.0	18.0	18.0
15	Water and miscellaneous	6.6	2.6	2.6	2.6	2.6	4.0	4.0	4.0
	Totals (parts by weight)	99.2	97.7	94.4	105.8	100.7	103.3	99.2	105.4

The ion exchange properties of these powders after storage was determined by washing the powders with de-ionised water on a filter cake to extract the insoluble aluminosilicate material and drying. 0.5g of the dried material was then added to 200 ml of water having a hardness of 30°FH (equivalent to a calcium ion concentration of 3×10^{-3} molar). The free calcium ion concentration was measured after 1 minute. The powders were stored for 6 weeks at 37°C and 70% relative humidity (Examples 4, 4A and 4B) or for 12 weeks at 28°C and 70% relative humidity (Examples 1, 2, 2A, 3 and 3A). In the same manner, the ion exchange properties of the base powders were measured immediately after spray drying. The results were as follows:

15

	<u>Example No</u>	°FH Ca after 1 minute	full formulation
		<u>base powder</u>	<u>after storage</u>
	1	0.7	2.4
20	2	1.2	2.7
	2A	3.6	*
	3	0.8	0.8
	3A	0.7	*
	4	0.3	0.9
25	4A	0.6	3.0
	4B	0.3	0.8

* - not measured

30 A water hardness of 3°FH or less is considered to be a reasonable target. It follows therefore that all the powders tested were satisfactory except Example 2A.

Note that for Example 2A, $y = 0.18$ ie well below the limit of 0.25 set by the present invention.

35

The powders of Examples 1 to 4 were stored under various conditions after which the percentage of perborate which had decomposed was measured. Similar powders were produced in which the amorphous aluminosilicate was replaced by Zeolite-4A, of similar particle size, to provide control Examples. With the zeolite containing powders the moisture content was lower, namely between about 4.5% and 8% of the base powders. Moisture contents identical to Examples 1 to 4 lead to poor powder properties and even more perborate decomposition on storage. The results were as follows:

	<u>Example No</u>	<u>Storage conditions</u>			<u>% Perborate decomposed</u>
		<u>Weeks</u>	<u>Temperature</u>	<u>RH</u>	
15	1	4	37°C	70%	39%
	1 (Control)	4	37°C	70%	>80%
	2	4	37°C	70%	27%
	2 (Control)	4	37°C	70%	87%
20	3	4	37°C	70%	62%
	3 (Control)	4	37°C	70%	89%
	4	6	37°C	70%	20%
	4 (Control)	6	37°C	70%	73%

25 These Examples demonstrate the benefit of using amorphous aluminosilicate rather than zeolite.

EXAMPLES 5 AND 6

30 Two spray dried base powders were prepared having the following formulations:

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<u>Example No</u>			
<u>Ingredients</u> (parts by weight)		<u>5</u>	<u>6</u>
5	Anionic detergent active	6.0	6.0
	Nonionic detergent active	1.5	1.5
	Soap	0.5	0.5
	Sodium tripolyphosphate	6.0	6.0
	Amorphous aluminosilicate	16.0	16.0
10	Sodium sulphate	15.8	19.9
	Sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O}=2$)	4.0	-
	Minor ingredients	1.1	1.1
	Total water	12.0	7.9
15	Total base powder weight	62.9	58.9
	Moisture content (parts)	10.0 (15.9%)	5.9 (10.0%)
	y	0.65	0.46

The following ingredients were then post-dosed to
 20 this spray-dried base powder as follows:

<u>Example No</u>		<u>5</u>	<u>6</u>
<u>Ingredient</u>			
25	Base Powder	62.9	52.9
	Sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O}=2$)	-	4.0
	TAED granules (measured as neat TAED)	3.0	3.0
30	Sodium perborate	12.0	12.0
	Sodium tripolyphosphate	14.5	14.5
	Dequest	0.3	0.3
	Water and minor ingredients	5.7	5.7
35	Total	98.4	92.4

After storage at 37°C and 70% relative humidity for 4 weeks, 39% and 28% of the sodium perborate in Example 5 and 6 respectively had decomposed. By way of comparison where the amorphous aluminosilicate was replaced in
5 Example 5 with zeolite 4A of similar particle size, more than 80% of the sodium perborate decomposed under the same conditions.

EXAMPLE 7

10

A base powder was spray dried having a composition identical to Example 4, but in which no sodium silicate was included. The water level was 9.7 parts and the total base powder weight was 53.4 parts. The moisture
15 content was 7.1 parts (13.3%), giving a value of y equal to 0.42.

The base powder was granulated with 5 parts of sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 2.0$), 18 parts of sodium tripolyphosphate (measured as anhydrous), 4 parts of water and
20 19.6 parts of sodium perborate (measured as $\text{NaBo}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$), giving a total powder weight of 100 parts.

25 After storage at 37°C and 70% relative humidity for 6 weeks, 23% of the sodium perborate had decomposed.

By way of comparison, where the amorphous aluminosilicate was replaced with zeolite 4A, 82% of the sodium
30 perborate decomposed under the same conditions.

This powder was then assessed for its ion-exchange properties in the same manner as described in connection with Examples 1 to 4, except that the time was measured
35 for the water hardness the fall to 3.3°FH. Immediately after preparation this time was 0.4 minutes. After

storage of the powder for 6 weeks at 28°C and 70% relative humidity this time was 0.7 minutes. These results indicated a satisfactory powder.

5 EXAMPLES 8 TO 10

A number of detergent compositions was prepared by spray-drying an aqueous slurry containing the following ingredients:

10

<u>Ingredient</u>	<u>parts by weight</u>
Anionic detergent active	7.0
Nonionic detergent active	4.0
15 Soap	2.0
Amorphous aluminosilicate	21.0 (measured as anhydrous)
Sodium silicate ($\text{Na}_2\text{O}:\text{SiO}_2=1.6$)	5.0
Sodium sulphate	7.3
20 Miscellaneous minor ingredients	1.4

This slurry was spray-dried to give detergent base powders of the following moisture contents:

25

<u>Example No</u>	<u>A</u>	<u>B</u>	<u>8</u>	<u>9</u>	<u>10</u>
Moisture (loss at 135°C(%))	1.5	3.8	14.8	18.2	21.0
(parts by weight)	0.65	1.9	9.9	11.2	13.3

30 The values of y can be calculated from these moisture contents, using A=13.0, X=21.0 and S=5.0 as follows:

<u>Example No</u>	<u>A</u>	<u>B</u>	<u>8</u>	<u>9</u>	<u>10</u>
35 y	0.05	0.11	0.49	0.55	0.65

It will be seen that Examples 8, 9 and 10 have γ values within the present invention, while Examples A and B are included for comparison purposes.

5 To these spray-dried base powders were added 22 parts by weight of partially hydrated sodium tripolyphosphate (18 parts calculated on an anhydrous basis) and 25 parts by weight of sodium perborate, tetrahydrate.

10 The initial ion-exchange rate of these compositions was measured in the same manner as described in Example 7. The time taken for the water hardness to fall to 3.3° FH was as follows:

15	<u>Example No</u>	<u>A</u>	<u>B</u>	<u>8</u>	<u>9</u>	<u>10</u>
	Time (min) to 3.3° FH	>10	>10	0.3	0.3	0.3

20 The powders of Examples B and 10 were stored for 12 weeks at 28°C and 70% relative humidity. After this storage the ion-exchange rate was again measured. In the case of Example B the time taken to reach 3.3° FH was greater than 10 minutes and in the case of Example 10, 0.9 minutes.

25

These results demonstrate the benefit to the ion-exchange properties of spray-drying the base powder to a moisture content giving a value of γ according to the invention.

30

The powders of Examples B and 10 were stored for 12 weeks under various conditions, whereafter the bleach stability was determined by measuring the percentage of perborate which had decomposed after that time. The results were:

35

<u>Example No</u>	<u>B</u>	<u>10</u>
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% decomposition after:

	12 weeks at 20°C and 90% relative humidity	8	6
5	12 weeks at 28°C and 70% relative humidity	15	11
	12 weeks at 37°C and 70% relative humidity	38	30

These results show that the composition according to the invention, Example 10, shows improved bleach stability over the comparison composition, Example B.

The composition of Example B approximates to that disclosed in Example 1 of British Patent Specification GB 2 013 707.

The detergent actives used in the foregoing examples were approximately:

anionic detergent active - sodium linear alkyl
(C_{10/13}) benzene sulphonate;

nonionic detergent active - C_{14/15} alcohol exothylated
with 11 moles of ethylene
oxide

soap - hardened tallow (C_{16/18})
sodium soap

C L A I M S

1. A detergent composition comprising spray-dried base powder granules, together with one or more post-dosed
5 ingredients which include a peroxygen bleach compound, the base powder granules containing at least a synthetic detergent active material, an amorphous aluminosilicate builder material, moisture, optionally soap, optionally crystalline aluminosilicate builder material, and
10 optionally an alkaline salt selected from alkali metal silicates, alkali metal carbonates, alkali metal phosphates and mixtures thereof, characterised in that the moisture content of said granules is determined by the formula

15

$$M = 0.075A + 0.25 S + (y - 0.125)X$$

where M is the moisture content of said granules in parts by weight, as measured by the water loss from said
20 granules at 135°C, A is the amount of the detergent active material including soap, if any, in said granules in parts by weight, S is the amount of the alkaline salt in said granules in parts by weight, X is the amount of the aluminosilicate builder material including crystalline
25 aluminosilicate builder material, if any, in said granules in parts by weight and y is a number from 0.25 to 0.7.

2. A composition according to Claim 1, characterised in that the moisture content of the base powder granules
30 corresponds to a value of y between 0.5 and 0.6.

3. A composition according to Claim 1, characterised in that the base powder granules contain no sodium silicate and the moisture content thereof corresponds to a value
35 of y between 0.25 and 0.5.

4. A composition according to Claim 1, characterised in that the base powder granules contain crystalline aluminosilicate builder material and the moisture content of the base powder granules corresponds to a value of y
5 between 0.25 and 0.5.

5. A composition according to Claim 1, characterised in that it comprises, based on the overall formulation:

10 from 5% to 40% by weight synthetic detergent active material;

from 1% to 5% by weight soap;

15 from 12.5% to 50% by weight amorphous aluminosilicate;

from 1% to 15% by weight sodium silicate;

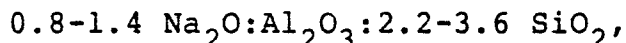
20 from 8% to 32% by weight sodium perborate; and

water.

6. A composition according to Claim 5, wherein at least
25 the synthetic detergent active, the soap, the amorphous aluminosilicate and the sodium silicate are contained in the spray-dried base granules, the sodium perborate is a post-dosed ingredient and the moisture content of the base granules is from 10.7% to 21% by weight, based on
30 the weight of the base granules.

7. A composition according to any one of Claims 1 to 6, characterised in that the amorphous aluminosilicate builder is an amorphous hydrated sodium aluminosilicate of chemical composition calculated on an anhydrous basis:

5



having, calculated on a dry basis, a calcium ion-exchange capacity greater than 100 mg CaO/g, a magnesium capacity greater than 50 mg MgO/g, an average particle size in the range 2 to 20 μm , and the ability to form a filter cake having a solids content in the range 35-50%, in a filter press with a closing pressure of 5.62 kg/cm², which filter cake can be converted into a pumpable slurry in said solids range, and having a silicate resistance (as hereinbefore defined) such that the second order rate constant k_s for the calcium exchange process is greater than $0.2^\circ\text{H}^{-1} \text{ min}^{-1}$ and a residual water hardness after 10 minutes of less than 1.5°H and which after drying at 50°C to 80% solids has a rate constant k_d (as hereinbefore defined) greater than $0.42^\circ\text{H}^{-1} \text{ min}^{-1}$ and a residual water hardness after 10 minutes of less than 1°H .

8. A method of preparing a detergent composition which comprises spray-drying an aqueous slurry containing at least a synthetic detergent active material, an amorphous aluminosilicate material, optionally soap, optionally
5 crystalline aluminosilicate builder material and optionally an alkaline salt selected from alkalimetal silicates, alkalimetal carbonates, alkalimetal phosphates and mixtures thereof to form spray-dried base powder granules, and post-dosing to said granules one or more
10 ingredients which include a peroxygen bleach compound, characterised in that the base powder granules have a moisture content which is determined by the formula

$$M = 0.075A + 0.25 S + (y - 0.125)X$$

15

where M is the moisture content of said granules in parts by weight, as measured by the water loss from said granules at 135°C, A is the amount of the detergent active material including soap, if any, in said granules in parts
20 by weight, S is the amount of the alkaline salt in said granules in parts by weight, X is the amount of the aluminosilicate builder material including crystalline aluminosilicate builder material, if any, in said granules in parts by weight and y is a number from 0.25 to 0.7.

25