

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 March 2006 (23.03.2006)

PCT

(10) International Publication Number
WO 2006/029676 A1

(51) International Patent Classification⁷: **C11D 3/08**,
3/02, 11/02, 1/02

(21) International Application Number:
PCT/EP2005/008628

(22) International Filing Date: 8 August 2005 (08.08.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0420356.8 13 September 2004 (13.09.2004) GB

(71) Applicant (for AE, AG, AU, BB, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NA, NG, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; Unilever House, Blackfriars, London Greater London EC4P 4BQ (GB).

(71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KM, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NI, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SM, SN, SY, TD, TG, TJ, TM, TN, TR, UA, UZ, VN, YU only): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): **HINDUSTAN LEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **MESKER, Linda**

[NL/NL]; Unilever R & D Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). **PACHA, Fakhruddin, Esmail** [IN/NL]; Unilever R & D Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). **RUIJTER, Michel, Jan, de** [NL/BE]; Stuivenbergbaan 198, B-2800 Mechelen (BE).

(74) Agents: **BRISTOW, Stephen, Robert** et al.; Unilever Patent Group, Colworth House, Sharnbrook, Bedfordshire MK44 1LQ (GB).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DETERGENT COMPOSITIONS AND THEIR MANUFACTURE

(57) Abstract: A process for the manufacture of a detergent base powder composition comprising the steps of mixing together an inorganic spray drying filler material, anionic surfactant, sodium silicate and a soluble alkaline earth salt, optionally with other ingredients of a detergent formulation, to form a sprayable slurry, then spray drying the slurry to form a base powder including amorphous silicate seeds formed in the base powder by the precipitation of the silicate seeds from the reaction of the sodium silicate with the soluble alkaline earth salt in the slurry. Also, a process for the manufacture of a detergent composition comprising optional post dosed additives or granules and a base powder formed by drying a base powder slurry comprising an anionic surfactant, characterised in that the base powder includes amorphous silicate seeds formed in situ in the base powder by the precipitation of the silicate seeds from the reaction of a soluble silicate in the base powder slurry with a soluble alkaline earth salt also in the base powder slurry. Also a laundry detergent base powder composition, especially one comprising anionic surfactant, and having amorphous silicate seeds intimately mixed with and dispersed throughout the composition.

WO 2006/029676 A1

DETERGENT COMPOSITIONS AND THEIR MANUFACTURE

This invention relates detergent compositions and their manufacture and in particular to laundry detergent compositions including a builder and base compositions for their preparation.

Builders are normally included in detergent compositions so that calcium and magnesium ions present in some water supplies do not complex with the surfactant in the detergent formulation and thereby lead to an undesirable loss in detergency. Traditionally sodium tripolyphosphate was employed as a builder, but environmental concerns have in recent years resulted in the replacement of phosphate by crystalline aluminium silicate (zeolite) as a builder. Zeolite, however, has slower kinetics of building and can result in the formation of undesired precipitates.

Carbonate is a known alternative to these builders. However carbonate built products have never been very satisfactory due to significant ash build-up on fabrics and machine parts under medium and hard water conditions. Also carbonate precipitation is quickly poisoned, resulting in a higher level of free calcium. Although polymers have been developed to prevent ash build-up, they are expensive and suffer from environmental concerns due to the non-biodegradable nature of these polymers.

GB 1 460 646 proposes that the problem of an initial slow building function associated with carbonate builders can be solved by the use of crystallisation seeds. The crystallisation seeds are preferably selected from the group

- 2 -

consisting of: calcium carbonate; calcium and magnesium oxalates; barium sulphate; calcium, magnesium and aluminium silicates; calcium and magnesium oxides; calcium and magnesium salts of fatty acids having 12 to 22 carbon atoms; 5 calcium and magnesium hydroxides; calcium fluoride; and barium carbonate.

WO 02/086042 describes a seed system comprising amorphous calcium silicate and/or amorphous magnesium silicate. It is 10 preferred to precipitate calcium silicate in an aqueous solution of a soluble silicate, such as sodium silicate, by adding an aqueous solution of a soluble calcium salt, for example calcium chloride, to the sodium silicate liquor. The calcium silicate so formed may be dried to form granules 15 that can be used for the preparation of a detergent composition. The addition of amorphous calcium and/or magnesium silicates to the wash is said to assist in the prevention of deposition onto fibres or machine parts. The presence of amorphous calcium and/or magnesium silicate also 20 improves the calcium and magnesium building of the wash liquor, necessary to prevent calcium and magnesium ions reacting with anionic surfactants. Hence, it improves the effectiveness of the surfactants and consequently the cleaning performance. As such, it can function as a 25 builder, anti-ashing and anti-scaling ingredient. As an alternative to granulation, the seeds can be added to the detergent composition in the form of a powder or a sol. However, these forms are not ideal because the process described in WO 02/086042 requires an additional, costly 30 step of drying silicate particles, or preparation of a silicate sol. Use of such a sol with high moisture content

- 3 -

(40% solids) limits the level at which it may be used and puts a big doubt over the storage stability of any composition or base to which it is added. Furthermore, the use of a post dosed granule, may lead to a loss of seed activity with time and requires care to ensure that the seeds are available at the start of a wash and yet are not damaged by moisture or other problems during storage of the detergent composition. If the granules are post dosed at high levels of from about 5 to about 20% by weight, it is necessary for the base powder processing to be modified to enable such high levels to be achieved. This is because to provide a space for inclusion of this level of the post dosed ingredient, the base powder has to be dried to a higher active level, which can affect base powder properties, or even be impossible, if the level of active is already at a maximum level.

According to the present invention there is provided a laundry detergent composition comprising a soluble alkali metal silicate and between 0.01 - 25% of alkaline earth silicate seeds, the alkaline earth silicate seeds being formed *in-situ* by reaction of sodium silicate and a soluble alkaline earth metal salt in the presence of an anionic surfactant during laundry detergent base powder processing. Preferably, the alkaline earth metal is selected from the group comprising calcium and magnesium and mixtures thereof, more preferably it is substantially one alkaline earth metal and most preferably it is calcium. In addition to providing an alternative to the use of post dosed silicate granules this process has been found to give surprising and distinct advantages.

- 4 -

The invention allows the formulation of storage stable laundry and/or machine dish wash formulations or bases substantially free from phosphate and/or crystalline aluminium silicate (zeolite) with efficient building
5 properties i.e. quick and efficient de-activation of hardness ions.

It is preferable that at least 50%, preferably at least 80%, most preferably at least 90% of the of alkaline earth
10 silicate seeds are amorphous, the balance being crystalline material. It has been observed that in the presence of carbonate the amorphous material rapidly builds up large particles with a d_{50} of about 80 microns in the wash when it reacts with hardness ions and the large particles so formed,
15 in combination with a very low level of small particles under 10 microns, seems to reduce the amount of build-up or ashing on the fabric or the machine parts. The particle size of the precipitates is such that they do not form a scale or ash on articles being washed or on machine parts or
20 other contact surfaces.

Also according to the present invention there is provided a method to produce alkaline earth silicate seeds in-situ during the manufacture of a laundry detergent base powder,
25 the method comprising adding a soluble alkaline earth salt to a slurry containing sodium silicate, anionic surfactant and optionally other components of a laundry detergent base powder and spray drying the slurry. Laundry detergent compositions produced by this method have better handling
30 properties than those produced using the granules taught in WO 02/086042.

- 5 -

Another advantage over the use of post dosed granules of the seed additive, which is thought to arise from the fact that the calcium silicate is dispersed/dissolved into the wash liquor while intimately mixed with the other actives, is that better cleaning performance is achieved on certain stains.

Preferably the process comprises the addition of calcium chloride and/or magnesium sulphate to a slurry that contains surfactant and sodium silicate in a molar ratio of silicate: calcium and/or magnesium salt in the range 20:1 to 2:1 with about 10:1 being most preferred. The mixture is then dried to further precipitate the amorphous silicate. It is advantageous to spray dry the reaction mixture in the presence of a surfactant. It is thought that calcium silicate is thereby formed as very small, amorphous "seeds". Most preferably, calcium chloride is used.

Soluble silicates are common ingredients in laundry detergent compositions. Some commercial grades of silicates may contain a trace level of calcium and/or magnesium silicate, as contamination. The composition of trace materials in the water used for making a detergent slurry may also contribute calcium/magnesium. However, the amount of amorphous material introduced via this impurity route will be low. The compositions of the invention therefore advantageously comprise more than 2 wt% amorphous calcium silicate.

The presence of alkaline earth silicate seeds results in rapid deactivation of hardness ions by rapid growth of

- 6 -

larger carbonate particles in a carbonate built, surfactant containing, wash solution. The growth was found to be insensitive to typical poisons of calcium precipitates.

5 The detergent compositions of the invention will contain surfactants; builders and other detergent ingredients as required or desired. These may be included in the base formulation, and/or post dosed, as separate granules or spray on components, or both.

10

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, non-ionic, amphoteric and
15 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.

20

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

25 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 alkylsulphates, particularly C8-C22 primary alkyl sulphates;
30 alkyl ether sulphates; olefin sulphonates; alkyl xylene

- 7 -

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

Non-ionic surfactants that may be used include the primary
5 and secondary alcohol ethoxylates, especially the C8-20
aliphatic alcohols ethoxylated with an average of from 1 to
20 moles of ethylene oxide per mole of alcohol, and more
especially the C10-C15 primary and secondary aliphatic
alcohols ethoxylated with an average of from 1 to 10 moles
10 of ethylene oxide per mole of alcohol. Non-ethoxylated non-
ionic surfactants include alkylpolyglycosides,
alkanolamides, glycerol monoethers, and polyhydroxyamides
(glucamides).

15 Cationic surfactants that may be used include quaternary
ammonium salts of the general formula $R_1R_2R_3R_4N^+ X^-$ wherein
the R groups are long or short hydrocarbyl chains, typically
alkyl, hydroxyalkyl or ethoxylated alkyl groups, and X is a
solubilising anion (for example, compounds in which R1 is a
20 C8-C22 alkyl group, preferably a C8-C10 or C12-C14 alkyl
group, R2 is a methyl group, and R3 and R4, which may be the
same or different, are methyl or hydroxyethyl groups); and
cationic esters (for example, choline esters).

25 Amphoteric and zwitterionic surfactants that may be used
include alkyl amine oxides, betaines and sulphobetaines.

The detergent surfactant most preferably comprises an
anionic sulphonate or sulphonate surfactant optionally in
30 admixture with one or more cosurfactants selected from
ethoxylated non-ionic surfactants, non-ethoxylated non-ionic

- 8 -

surfactants, ethoxylated sulphate anionic surfactants, cationic surfactants, amine oxides, alkanolamides and combinations thereof.

- 5 Surfactants are preferably present in a total amount of from 5 to 60 wt%, more preferably from 10 to 40 wt%.

10 In addition to the amorphous silicate seeds, the detergent compositions of the invention will also contain one or more detergency builders. The total amount of detergency builder in the compositions will suitably range from 5 to 80 wt%, preferably from 10 to 60 wt%.

15 Inorganic builders that may be present include sodium carbonate; crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 (Henkel) and mixed crystalline/amorphous aluminosilicates as disclosed in GB 1 470 250 (Procter & Gamble); sodium
20 alkaline silicates and layered silicates as disclosed in EP 164 514B (Hoechst). Inorganic phosphate builders, for example, sodium orthophosphate, pyrophosphate and tripolyphosphate, may also be present, but on environmental grounds those should be used at relatively low levels, for
25 example less than 5%.

Sodium silicate may be postdosed, for example as granular sodium disilicate or as a sodium carbonate and sodium silicate cogranule, for example Nabion (trademark) ex Rhodia
30 Chemie.

- 9 -

Zeolite builders may suitably be present in amounts of from 5 to 80 wt%, preferably from 10 to 60 wt%. The zeolite used in most commercial particulate detergent compositions is zeolite A. Advantageously, however, maximum aluminium
5 zeolite P (zeolite MAP) described and claimed in EP 384 070A (Unilever) may be used. Zeolite MAP is an alkali metal aluminosilicate 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.

10 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-
15 and trisuccinates, carboxymethyloxysuccinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts.

20 Organic builders may be used in minor amounts as supplements to inorganic builders such as phosphates and zeolites. Preferred supplementary 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
25 acrylic/maleic copolymers, suitably used in amounts of from 0.5 to 15 wt %, preferably from 1 to 10 wt%.

Detergent compositions according to the invention may also suitably contain a bleach system. This may desirably
30 include a peroxy bleach compound, for example, an inorganic persalt or an organic peroxyacid, capable of yielding

- 10 -

hydrogen peroxide in aqueous solution. Suitable peroxy bleach compounds include organic peracids, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, persilicates and persulphates. Preferred
5 inorganic persalts are sodium perborate monohydrate or tetrahydrate, and sodium percarbonate. Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a protective coating comprising sodium metaborate and sodium
10 silicate is disclosed in GB 2 123 044B (Kao).

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

15 The peroxy bleach compound may be used in conjunction with a bleach activator to improve bleaching action at low wash temperatures. The bleach activator is suitably present in an amount of from 1 to 8 wt%, preferably from 2 to 5 wt%. Preferred bleach activators are peroxycarboxylic acid
20 precursors, more especially peracetic acid precursors and peroxybenzoic acid precursors and peroxycarbonic acid precursors. An especially preferred bleach activator suitable for use in the present invention is N,N,N',N'-tetracetyl ethylenediamine (TAED).

25

A bleach stabiliser (heavy metal sequestrant) may also be present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA) and the polyphosphonates such as Dequest (trademark), EDTMP. EHDP may also be used.

30

- 11 -

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).

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

Further optional ingredients may include, but are not limited to, any one or more of the following: soap, sequestrants, sodium sulphate, sodium chloride, calcium chloride, sodium bicarbonate, other inorganic salts, fluorescers, photobleaches, polyvinyl pyrrolidone, other dye transfer inhibiting polymers, foam controllers, foam boosters, fabric conditioning compounds, dyes, coloured speckles and perfume. Detergent enzymes may be present. Suitable enzymes include the proteases, amylases, cellulases, oxidases, peroxidases and lipases usable for incorporation in detergent compositions.

In particulate detergent compositions, detergency enzymes are commonly employed in granular form in amounts of from about 0.1 to about 3.0 wt%. However, any suitable physical form of enzyme may be used in any effective amount.

- 12 -

Antiredeposition agents, for example cellulose esters and ethers, for example sodium carboxymethyl cellulose, may also be present.

- 5 The compositions may also contain soil release polymers, for example sulphonated and unsulphonated PET/POET polymers, both end-capped and non-end-capped, and polyethylene glycol/polyvinyl alcohol graft copolymers such as Sokolan (trademark) HP22. Especially preferred soil release
10 polymers are the sulphonated non-end-capped polyesters described and claimed in WO 95 32997A (Rhodia Chimie).

- Detergent compositions of low to moderate bulk density may be prepared by spray-drying a slurry, to form a base powder
15 and optionally postdosing (dry-mixing) further ingredients. "Concentrated" or "compact" powders may be prepared by further mixing this spray dried powder, for example, using a high-speed mixer/granulator, or other non-tower processes. Tablets may be prepared by compacting powders, especially
20 "concentrated" powders.

The invention will now be further described with reference to the following non-limiting examples.

- 25 The examples refer to standard tests, which are carried out as follows:

Volume Compression Test (%C)

- 30 In this test a known volume of powder is filled into a cylinder and then compressed by application of a standard

- 13 -

weight and the % volume reduction of the powder over a set period of 1 minute is noted. The pressure applied is 1050 g/cm².

5 % Decrease in volume = ((Initial volume - Final volume) / (Initial volume)) x 100

Unconfined Compression Test (UCT)

- 10 In this test freshly produced powder is compressed into a compact and the force required to break the compact is measured. The powder is loaded into a cylinder and the surface levelled. A 50 g plastic disc is placed on top of the powder and a 10 kg weighted plunger is placed slowly on
15 top of the disc and allowed to remain in position for 2 minutes. The weight and plunger are then removed and the cylinder removed carefully from the powder to leave a free-standing cylinder of powder with the 50g plastic disc on top of it. If the compact is unbroken, a second 50 g plastic
20 disc is placed on top of the first and left for approximately ten seconds. Then if the compact is still unbroken a 100 g disc is added to the plastic discs and left for ten seconds. Then the weight is increased in 250g increments at 10 second intervals until the compact
25 collapses. The total weight needed to effect collapse is noted.

For freshly made powder tested under ambient temperature conditions, the cohesiveness of the powder is classified by
30 the weight (w) as follows, (assuming the standard 10.0 kg compaction load is used).

- 14 -

w < 1 kg good flowing
1 kg < w < 2 kg Moderate flowing.
2 kg < w < 5 kg Cohesive.
5 kg < w Very cohesive.

5

As a general rule, w > 2 kg indicate difficult to handle powder in silos. However, some designs of silo show less difficulty, and in those cases the limit may be extended to w < 3 kg.

10

Caking test

Test powders are placed in laminated cartons. The cartons are stored at 37°C and 70%RH in a climate room and the
15 cartons are carefully removed after 7 and 14 days and examined as follows. First the closed cartons are allowed to cool down to room temperature. Then the package is opened at the top and inverted. The quantity of powder remaining in the carton is weighed.

20

Caking = remaining powder in the package x 100% / original total quantity of powder in the package

Laundr-o-meter test.

25

Predissolve 4g/l powder for 3 minutes in 40°FH water to make a suds liquor.

30

Fill pots with 800ml suds liquor, add monitors, and immerse cloth, close pots and soak for 15 minutes. Then place the pots into the Laundr-o-meter and run for 10 minutes at 25°C

- 15 -

(programme 30). Next the test cloth/stains are removed from the pots and placed in a bucket of water (same hardness as during the wash). After the rinsing the monitors are spin-dried and placed on a clean towel to dry completely.

5

All monitors are measured (Datacolor reflectance to measure absorption spectra) before and after the wash. The greater the difference at a given wavelength (e.g. DR 460) the better the cleaning/stain removal is.

10

Stain monitors used are supplied from standard test fabrics manufacturers or made up in laboratory using standardised test protocols, they include: Ballpoint ink, Tomato ketchup/olive oil, Cooking oil, Grass, Lipstick, and Spinach.

15

Example 1 - Powder properties

20

Two base powders were produced by spray-drying. The corresponding slurries were made in a 2-tonne vessel, according to Table 1. Formulation B contains sodium silicate, and calcium chloride is added. In formulation A, the calcium chloride is left out, for comparison. The slurries were made by adding premix ingredients including the surfactant precursor and water then mixing in the sodium silicate and the calcium chloride before adding the final components, including the sodium carbonate. The slurry was then spray dried and the coarse particles (> 2mm) were sieved off and the fines were separated and recycled back to the tower. Free flowing powders were obtained.

30

- 16 -

Table 1 - Slurry composition (parts)

Ingredients	A	B
Sodium carbonate	31.66	31.32
Water	27.00	27.00
Dobanic acid	17.97	17.78
Alkaline sodium silicate	14.60	14.60
Caustic solution (50%)	4.75	4.70
STP	1.89	1.87
Sodium sulphate	1.68	1.67
Sodium carboxymethyl cellulose	0.99	0.98
Calcium chloride solution (77%)	-	1.95

An important characteristic is the compressibility of the powder. When powders are stored in silos, or big-bags, they
 5 undergo undesired densification due to compression under their own weight. The densification is measured by the above defined volume compression test. Acceptable base powders have a volume compression of 20% or less. In addition, base powder may consolidate, making the emptying
 10 of silos more difficult. This consolidation may be predicted by using the above defined unconfined compression test. Base powders suited for silo storage have an unconfined compression of 2000g or lower. These properties normally change with moisture content of the powder: the
 15 higher the moisture content, the higher the unconfined compression. In Table 2 the properties of the two base powders are given. Powder B has improved properties compared to powder A. The presence of amorphous calcium

- 17 -

silicate in powder B may be confirmed by X Ray diffraction. The amount of amorphous material produced by this process is nearly 100% of the total amount of the calcium silicate. Use of the excess of the sodium silicate prevents the
5 formation of the less soluble crystalline form of calcium silicate.

Table 2 - Powder properties

Property	A	B
Volume compression (%)	32	11
Unconfined compression test (g)	2700	200
Moisture content (%)	6.4	6.9

10 Example 2 - Stain removal

Three fully formulated detergent compositions were made according to Table 3 by dry-mixing base powders with additional solid ingredients. C1 is silicated powder, made
15 from base powder A in Table 1. It does not contain calcium silicate. C2 is base powder without silicate, but with dry-mixing of silicate granules containing calcium silicate made according to WO 02/086042. Formulation D is made with base powder B from Table 1, which includes in-situ made calcium
20 silicates. Formulation D is the topic of this invention.

- 18 -

Table 3 - Detergent Compositions

Ingredients	C1	C2	D
Sodium LAS	19.00	19.00	19.00
STP	1.84	-	2.30
Sodium carbonate	31.30	30.54	38.90
Sodium sulphate	32.65	23.53	20.10
Sodium disilicate	7.50	-	-
Sodium carboxymethyl cellulose	1.00	0.75	1.20
Fluorescer adjunct	0.33	0.33	0.33
Enzymes	0.30	0.30	0.30
Sodium succinate	-	3.67	-
Silicate granules	-	20.00	-
Sodium disilicate + calcium disilicate	-	-	9.33
Water and minors	6.00	7.80	8.60

These three compositions were tested in bench-scale Laundr-O-meters with a set of stain monitors. The stain removal was measured by the difference in light reflectance of the stains before and after the test. In Table 4, the results are given for the stain removal of several stain monitors. On ballpoint ink for example, the change in stain removal is small and comparable for the three compositions. For ketchup-with-oil stain monitor, compositions C2 and D perform better than C1, as an effect of the presence of calcium silicate. For cooking oil, grass, lipstick and spinach monitors, composition D performs better than composition C1 and C2. These results show that the

- 19 -

inclusion of calcium silicate improves the stain removal, and that the in-situ formed calcium silicate (D) is more effective.

5 Table 4 - Cleaning results, difference in reflectance (DR 460)

Stain monitor	C1	C2	D
Ballpoint Ink	2.7	2.9	3.1
Ketchup/Oil	13.7	15.8	15.6
Cooking Oil	24.6	24.4	27.3
Grass	16.4	15.2	17.2
Lipstick	4.1	4.0	5.6
Spinach	11.2	9.3	18.5

Example 3 - Caking

10

Detergent base powder compositions were tested for caking in accordance with the method outlined above. The formulations of the slurries that were spray dried are given in table 5 and the results of caking tests on the spray dried base

15

powders are given in table 6.

- 20 -

Table 5 - Base powder formulations tested for caking

Base composition type	Na-silicate	Ca-silicate	Mg-silicate
Sodium alkylbenzene sulphonate (AD)	28.62	23.66	24.30
Sodium alkaline silicate	10.77	11.30	9.91
Sodium tripolyphosphate -phase 1	2.90	3.02	3.11
Sodium sulphate	2.58	2.69	2.79
Sodium carboxymethyl cellulose	1.13	1.17	1.21
Carbonate light	48.64	50.52	51.80
Calcium chloride	0.00	2.42	0.00
Magnesium sulphate	0.00	0.00	1.62
Sodium sulphate (ex-paste+STPP)	0.48	0.40	0.41
Impurities (from paste + SCMC)	0.89	0.82	0.85
Water	4.00	4.00	4.00

- 21 -

Table 6 - Caking test results

Base composition type	Storage time (days)	Caking (%)
Na silicate	0	0
	7	26
	14	83
Ca silicate	0	0
	7	0
	14	15.7
Mg silicate	0	0
	7	31
	14	31

The prior art sodium silicate type of base can be seen to produce a much worse caking score than either the inventive
5 calcium or magnesium silicate containing bases.

- 22 -

CLAIMS

1. A process for the manufacture of a detergent base powder composition comprising the steps of mixing
5 together an inorganic spray drying filler material, anionic surfactant, sodium silicate and a soluble alkaline earth salt, optionally with other ingredients of a detergent formulation, to form a sprayable slurry, then spray drying the slurry to form a base powder
10 including amorphous silicate seeds formed in the base powder by the precipitation of the silicate seeds from the reaction of the sodium silicate with the soluble alkaline earth salt in the slurry.
- 15 2. A process according to claim 1 in which the alkaline earth salt is selected from calcium and magnesium salts, preferably calcium salts.
- 20 3. A process according to claim 2 in which the alkaline earth salt is selected from the group comprising calcium chloride and magnesium sulphate, preferably calcium chloride.
- 25 4. A process for the manufacture of a detergent composition comprising optional post dosed additives or granules and a base powder formed by drying a base powder slurry comprising an anionic surfactant, characterised in that the base powder includes
30 amorphous silicate seeds formed *in situ* in the base powder by the precipitation of the silicate seeds from the reaction of a soluble silicate in the base powder

- 23 -

slurry with a soluble alkaline earth salt also in the base powder slurry.

5. A process according to claim 4 in which the silicate
5 seeds are precipitated in the presence of an anionic surfactant.

6. A laundry detergent base powder composition comprising
anionic surfactant and having amorphous silicate seeds
10 intimately mixed with and dispersed throughout the composition.

7. A base powder composition according to claim 6 further
comprising sodium carbonate.
15

8. A base powder composition according to claim 7 further
comprising sodium tripolyphosphate.

9. A base powder composition according to claim 7 further
20 comprising zeolite.

10. A laundry detergent composition including a builder and
amorphous silicate seeds obtainable by the process of
any one of claims 1 to 5, the seeds being uniformly
25 dispersed throughout the composition.

11. A laundry detergent composition according to claim 10
comprising a carbonate builder.

30 12. A laundry detergent composition according to claim 10
or claim 11 comprising:

- 24 -

a) 10 to 60% by weight surfactant, including 5 to 40%
anionic

b) 2 to 40 % sodium sulphate.

- 5 13. A laundry detergent composition according to any one of
claims 10 to 12 and further comprising one or more
ingredients selected from: Sodium tripolyphosphate
(STP), sodium disilicate, sodium carboxymethyl
cellulose, fluorescer, enzyme, sodium succinate and
10 mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/008628

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D3/08 C11D3/02 C11D11/02 C11D1/02

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 7 C11D

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)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 849 346 A (KUWAMURA H, JA ET AL) 19 November 1974 (1974-11-19) column 2, line 10 - column 3, line 5; claims 1,2 column 3, lines 6-14	1-6,8, 10-13
X	EP 0 657 527 A (THE PROCTER & GAMBLE COMPANY) 14 June 1995 (1995-06-14) example I	1-6,9-13
X	US 4 502 986 A (ROBSON ET AL) 5 March 1985 (1985-03-05) column 10, line 7; examples I-II,V,Vi	1-6,8, 10-13
X	US 4 102 823 A (MATHESON ET AL) 25 July 1978 (1978-07-25) column 5, lines 65,66 claims 1,8	1-7,10, 11

-/--



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

8 November 2005

Date of mailing of the international search report

18/11/2005

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Klier, E

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2005/008628

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 232 009 A (UNILEVER LIMITED) 19 May 1971 (1971-05-19) examples 2,15-18 -----	1-6,8, 10-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2005/008628

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3849346	A	19-11-1974	JP 53035081 B	25-09-1978
EP 0657527	A	14-06-1995	AT 183543 T	15-09-1999
			CA 2177677 A1	15-06-1995
			CN 1142850 A	12-02-1997
			DE 69326073 D1	23-09-1999
			DE 69326073 T2	09-03-2000
			ES 2134830 T3	16-10-1999
			JP 9506388 T	24-06-1997
			WO 9516019 A1	15-06-1995
US 4502986	A	05-03-1985	CA 1185869 A1	23-04-1985
			DE 3169000 D1	28-03-1985
			EP 0040038 A2	18-11-1981
			ES 8301499 A1	01-03-1983
			GR 75249 A1	13-07-1984
			IE 51245 B1	12-11-1986
			JP 57036196 A	26-02-1982
US 4102823	A	25-07-1978	NONE	
GB 1232009	A	19-05-1971	AT 329721 B	25-05-1976
			AT 853868 A	15-08-1975
			BE 720396 A	04-03-1969
			CH 517173 A	31-12-1971
			DE 1792434 A1	18-11-1971
			ES 357806 A1	16-03-1970
			FR 1579246 A	22-08-1969
			IE 32519 B1	05-09-1973
			NL 6812605 A	06-03-1969
			NO 129636 B	06-05-1974
			SE 364982 B	11-03-1974