

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 December 2007 (27.12.2007)

PCT

(10) International Publication Number
WO 2007/147698 A1

(51) International Patent Classification:
C11D 3/382 (2006.01) *C11D 3/10* (2006.01)

(21) International Application Number:
PCT/EP2007/055064

(22) International Filing Date: 24 May 2007 (24.05.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
06253160.3 19 June 2006 (19.06.2006) EP

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

(71) Applicant (for all designated States except AE, AG, AU, BB, BH, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, IN, KE, KN, LC, LK, LS, MW, MY, NA, NG, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, US, VC, ZA, ZM, ZW): **UNILEVER N.V.** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): **HINDUSTAN UNILEVER LIMITED** [IN/IN]; Hindustan Lever House, Mumbai 400 020 (IN).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BATCHELOR, Stephen, Norman** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Quarry Road East, Bebington,

Wirral Merseyside CH63 3JW (GB). **DIXON, Sarah** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB). **WHITEOAK, Christopher, John** [GB/GB]; 18 Chesterton Court, Chester, CH2 2FA (GB).

(74) Agent: **ELLIOTT, Peter, William**; Unilever PLC, Unilever Patent Group, Colworth House, Sharnbrook, Bedford 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, BH, 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, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, 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, MT, 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: LAUNDRY COMPOSITION

(57) Abstract: The present provides a granular laundry detergent composition comprising from 2 to 70 wt. % of surfactant, from 2 to 40 wt. % of sodium carbonate, and from 5 to 80 wt. % of a base treated particulate insoluble agricultural plant by-product, and a method of treating a textile with said composition.



WO 2007/147698 A1

- 1 -

LAUNDRY COMPOSITIONFIELD OF INVENTION

5 This invention relates to the use of agricultural waste in laundry products.

BACKGROUND OF INVENTION

10 United States Patent 6677290, to Procter and Gamble, discloses a composition having a plasma-induced, graft polymerized, water-soluble coating for controlling solubility, chemical stability and physical properties is disclosed. A process for making such a composition is also disclosed which involves subjecting a particulate material
15 to plasma after which a water-soluble organic monomer is graft polymerized onto at least a portion of the particulate material. Examples of the particulate material used as cosmetic components include corn cob powder, peach pit powder, pecan shell powder, walnut shell powder, and wheat
20 bran.

WO9732966, to Colgate Palmolive Co, discloses liquid crystal detergent compositions that contain wood particles which are abrasive particles designed to improve the scouring power of
25 the instant liquid crystal detergent composition. The surfactant in the composition is also absorbed on the surface of the wood particles. The wood particles have a particle diameter of 200 millimicrons to 600 millimicrons. The concentration of the wood particles in the liquid
30 crystal detergent composition is from 0.1 to 10 wt%.

- 2 -

CN 1205358 discloses a natural plant washing powder prepared from edible plants containing rice husks, broken rice, corn, maize cob, egg shell, balsam pear, and Chinese prickly ash.

5 EP 0 004 111 discloses the use of base treated pre-gelatinized starch. Starch is a complex carbohydrate found chiefly in seeds, fruits, tubers, roots and stem pith of plants, notably in corn, potatoes, wheat, and rice; an important foodstuff and used otherwise especially in
10 adhesives and as fillers and stiffeners for paper and textiles. Starch is not an agricultural waste product but an agricultural end product. Starch is the most important carbohydrate source in human nutrition.

15 US 4,056,400 discloses the treatment of cellulose, hemicellulose and lignin with hypochlorite under base conditions. US 4,056,400 discloses a treatment that results in an aqueous solution that is filtered to remove insoluble material after which the aqueous solution is treated with a
20 water miscible organic solvent (methanol) to precipitate a material that may be used as a builder. There is no use ascribed to the insoluble material.

US 5,830,445 discloses the use of bleached plant by-products
25 in cosmetics as abrasive materials for scrubbing skin.

There is an ongoing search to find better performing ingredients that provide better cleaning, a cheaper product, and ingredients that come from sustainable resources.

- 3 -

SUMMARY OF INVENTION

Agricultural waste by-products (APB) suffer from low
detergency activity. The performance of the agricultural
waste product may be greatly increased by pre-treating the
5 material with a strongly basic solution.

The APBs are subjected to a minimum of processing before
being incorporated into a granular laundry detergent
composition but have been pre-treated with a strongly
10 alkaline solution, optionally rinsed and/or bleached, and
dried.

In one aspect the present invention provides a granular
laundry detergent composition comprising from 2 and 70 wt %
15 of a surfactant, 2 to 40 wt % of sodium carbonate, and from
5 to 80 wt % of an insoluble agricultural plant by-product,
the insoluble agricultural plant by-product is in the form
of a particulate having a particle size of 1 mm or below,
wherein the insoluble agricultural plant by-product has been
20 treated with an aqueous solution, the aqueous solution
having a pH of at least 12, and subjected to a drying step.

The aforementioned laundry detergent composition is also
applicable to other formats including a liquid detergent
25 composition.

In another aspect the present invention a method of treating
a textile comprising the following steps:

(i) treating a textile with the composition as defined in
30 any preceding claim in an aqueous medium, wherein the
aqueous medium comprises from 0.2 g/L to 5 g/L of a

- 4 -

surfactant, the aqueous medium having a pH in the range 4 to 11; and,

(ii) rinsing the textile with water; and,

(iii) drying the textile.

5

DETAILED DESCRIPTION OF THE INVENTION

Agricultural plant by-products (APB) in the context of the current invention are defined as waste parts of plants grown as animal food and waste products from natural materials
10 used to make consumer goods. The APB is the organic insoluble remnants of plant material and does not include vegetable oils that may be present on or in the material. The APB is insoluble in water in the pH range 3 to 11; in contrast, carboxymethylcellulose is soluble in some
15 solvents. The APB is also insoluble in organic solvents such as alcohols and hydrocarbons. The APB may have been subjected for example, to a drying step, solvent extraction to remove oils, a bleaching step or milling and sieving step. If the step of removing oils is omitted, the oils
20 present may form soaps in situ with the overall basically of the composition.

It will be evident to one skilled in the art that the agricultural plant by-products (APB) as described are the
25 fibrous remnants of the plant after removal of the higher value components. APB do not include starch per se. APB's are preferably the pith, chaff, stones, stems, husks, cobs and seed remnants of plants.

30 The APB is not solubilised and reclaimed by precipitation before use in a detergent product. The APB remains as a solid during base treatment and any optional oxidation step.

- 5 -

The APB is treated with a basic aqueous solution. The basic aqueous solution should have a pH of at least 12, preferably at least 13, most preferably at least 14. The alkaline pH may be provided by many common strong bases, but caustic
5 soda (NaOH) is preferred.

The APB is preferably left in contact with the alkaline solution for at least 20 minutes, preferably for at least 2 hours, most preferably for at least 6 hours. Preferably the
10 APB is treated for a maximum of 15 hours.

The treatment with the alkaline solution may take place at wide variety of temperatures, for example from 0 to 100 °C, but preferably in the range 15 to 40°C. The treatment is
15 preferably conducted with agitation.

The treatment may be carried out with bubbling of air through the alkaline solution.

20 For white products, the APB has preferably been subjected to a bleaching, hueing agent or a fluorescent agent. For coloured products, the APB is subject to colouring with a dye or pigment, preferably a pigment and most preferably a blue or violet pigment. The hueing agent or a fluorescent
25 agent is preferably applied to the ABP in the form of solution in the form of a spray. Hueing agents and fluorescent agent are discussed below with respect to the composition per se but these are equally applicable to the APB per se. These adjuncts are added to the APB after base
30 and if applicable bleaching treatment.

- 6 -

The most preferred APB are not strongly coloured. The colour of the raw, i.e., before any bleaching, hueing or fluorescer step, milled material is measured using a reflectometer and expressed as the CIE LAB values is preferably L* at least
5 60, preferably at least 70. The b* value from 0 to 35 preferably 0 to 25 and the a* value from -10 and +10.

To lighten the colour of the APB a further bleaching step may be included in the treatment of the materials. Preferred
10 bleaches are hydrogen peroxide; hydrogen peroxide activated by a transition metal catalyst, preferably the manganese catalyst of 1,4,7-trimethyl-1,4,7-triazacyclononane (EP 458397); hydrogen peroxide activated by an organic precursor to give a peracid, particularly peracetic acid. Chlorine
15 dioxide may also be used for bleaching but is not preferred and is preferably avoided. The APB is preferably not subjected to a hypohalite (e.g. hypochlorite) bleaching step to avoid the formation of high levels undesirable organo-chlorine compounds. If a chlorine bleach is used it is
20 preferably used at a level of less than 10 wt % of the APB being treated, most preferably less than 1 wt %.

The APB is preferably uncoated per se by an encapsulating coat. The ABP may however be coated with a fine particulate
25 matter that makes up the granule per se. In particular, the APB has not been subjected to a plasma coating per USP 6,677,290 which encapsulates the particle.

The size of the APB is measured using graded sieves and is
30 that the is retained or passes through such sieves.

- 7 -

The APB is sized preferably from 100 to 1000 microns, most preferably from 200 to 800 microns.

5 Preferably the agricultural waste products are dried and milled such that particles are produced which are smaller than 1mm, preferably 0.2 to 0.8 mm.

The following are examples of APBs:

- 10 1. The stones and seeds of fruits, preferably olive, peaches, avocado's, plums, most preferably olives.
2. The shells of nuts, preferably peanut, walnuts, hazelnuts, almonds, coconut most preferably coconuts and peanuts.
3. The stems, cobs and husks from cereal production, preferably wheat, corn, sorghum, barley and rye, most
15 preferably wheat and corn cobs.
4. The stems and husks from rice production
5. The remnants of the plant and seeds from edible oil production, preferably sunflower, soybean, rapeseed, cottonseed, canola, most preferably sunflower and
20 soybeans.
6. The plant remnants from sugarbeet and sugarcane.
7. The skin and pith of fruits and vegetables, preferably the pith of citrus fruit, preferably the pith of oranges.

25 With respect to the above nut allergies must be considered. In this regard, nut APBs are least preferred.

The pith and chaff portions have a low bulk density which means that for a given volume of product, the weight is
30 relatively low. In general, high volume and low weight translates to high freight costs for finished products. For some products, we increase the bulk density, by compressing

- 8 -

the pith and chaff into pellets. The pellets are then reprocessed into various particle sizes.

SURFACTANT

5 The composition comprises between 2 to 70 wt % of a surfactant, most preferably 10 to 30 wt %. In general, the nonionic and anionic surfactants of the surfactant system may be chosen from the surfactants described "Surface Active Agents" Vol. 1, by Schwartz & Perry, Interscience 1949, Vol. 10 2 by Schwartz, Perry & Berch, Interscience 1958, in the current edition of "McCutcheon's Emulsifiers and Detergents" published by Manufacturing Confectioners Company or in "Tenside-Taschenbuch", H. Stache, 2nd Edn., Carl Hauser Verlag, 1981. Preferably the surfactants used are saturated.

15 Suitable nonionic detergent compounds which may be used include, in particular, the reaction products of compounds having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols 20 with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Specific nonionic detergent compounds are C₆ to C₂₂ alkyl phenol-ethylene oxide condensates, generally 5 to 25 EO, i.e. 5 to 25 units of ethylene oxide per molecule, and the condensation products 25 of aliphatic C₈ to C₁₈ primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 40 EO.

Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic 30 sulphates and sulphonates having alkyl radicals containing from about 8 to about 22 carbon atoms, the term alkyl being used to include the alkyl portion of higher acyl radicals.

- 9 -

Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C₈ to C₁₈ alcohols, produced for example from tallow or coconut oil, sodium and potassium
5 alkyl C₉ to C₂₀ benzene sulphonates, particularly sodium linear secondary alkyl C₁₀ to C₁₅ benzene sulphonates; and sodium alkyl glyceryl ether sulphates, especially those ethers of the higher alcohols derived from tallow or coconut oil and synthetic alcohols derived from petroleum. The
10 preferred anionic detergent compounds are sodium C₁₁ to C₁₅ alkyl benzene sulphonates and sodium C₁₂ to C₁₈ alkyl sulphates. Also applicable are surfactants such as those described in EP-A-328 177 (Unilever), which show resistance to salting-out, the alkyl polyglycoside surfactants
15 described in EP-A-070 074, and alkyl monoglycosides.

Preferred surfactant systems are mixtures of anionic with nonionic detergent active materials, in particular the groups and examples of anionic and nonionic surfactants
20 pointed out in EP-A-346 995 (Unilever). Especially preferred is surfactant system that is a mixture of an alkali metal salt of a C₁₆ to C₁₈ primary alcohol sulphate together with a C₁₂ to C₁₅ primary alcohol 3 to 7 EO ethoxylate.

25 The nonionic detergent is preferably present in amounts greater than 10%, e.g. 25 to 90 wt % of the surfactant system. Anionic surfactants can be present for example in amounts in the range from about 5% to about 40 wt % of the surfactant system.

30

Soaps and non-ionic detergents derived from plant/renewable sources may be used.

- 10 -

BALANCE CARRIERS AND ADJUNCT INGREDIENTS

The composition in addition to above comprises the balance carriers and adjunct ingredients to 100 wt % of the composition.

These may be, for example, other surfactants, builders, foam agents, anti-foam agents, solvents, fluorescers, enzymes and bleaching agents e.g., peroxides. The use and amounts of these components are such that the composition performs depending upon economics, environmental factors and use of the composition. Preferably the composition comprises a builder, in particular sodium carbonate in the range from 2 to 40 wt %.

BUILDER

The composition of the present invention preferably comprises one or more detergency builders. The total amount of detergency builder in the compositions will preferably range from 2 to 80 wt%, more preferably from 10 to 60 wt%.

Inorganic builders that may be present include sodium carbonate, if desired in combination with a crystallisation seed for calcium carbonate, as disclosed in GB 1 437 950 (Unilever); 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); and layered silicates as disclosed in EP 164 514B (Hoechst). Inorganic phosphate builders, for example, sodium orthophosphate,

- 11 -

pyrophosphate and tripolyphosphate are also suitable for use with this invention.

The compositions of the invention preferably contain an
5 alkali metal, preferably sodium, aluminosilicate builder. Sodium aluminosilicates may generally be incorporated in amounts of from 10 to 70% by weight (anhydrous basis), preferably from 25 to 50 wt%.

10 The alkali metal aluminosilicate may be either crystalline or amorphous or mixtures thereof, having the general formula: $0.8-1.5 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 0.8-6 \text{ SiO}_2$.

These materials contain some bound water and are required to
15 have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO_2 units (in the formula above). Both the amorphous and the crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply
20 described in the literature. Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1 429 143 (Procter & Gamble). The preferred sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and
25 mixtures thereof.

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite
30 builder incorporated in the compositions of the invention is maximum aluminium zeolite P (zeolite MAP) as described and claimed in EP 384 070A (Unilever). Zeolite MAP is defined as

- 12 -

an alkali metal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.

5

Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per g of anhydrous material.

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 and trisuccinates, carboxymethyloxy succinates, carboxymethyloxymalonates, dipicolinates, hydroxyethyliminodiacetates, alkyl- and alkenylmalonates and succinates; and sulphonated fatty acid salts. This list is not intended to be exhaustive.

20

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%.

25

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

30 HUEING AGENT

Hueing agents are well known and are used provide a perception of whiteness. The presence of blue or violet dye

- 13 -

or pigments are preferred, violet is most preferred. Dyes and Pigments which are have very low substantivity to textiles, may be used to enhance the whiteness of the detergent products. Examples of such dyes and pigments, are
5 acid violet 43, acid blue 80, food black 1, food black 2, pigment violet 23, pigment blue 64, pigment blue 60, pigment blue 66, pigment violet 66, pigment violet 19, pigment blue 29. The non-substantive dyes and pigments may also be used to impart color to the product.

10

Non-Substantive Hueing dye levels are in the range 0.00005 to 0.1 wt %.

Dyes which are substantive to textiles may also be used.

15

Preferred dyes are direct violet 9 and solvent violet 13. Substantive Hueing dye levels are in the range 0.00005 to 0.01 wt %.

FLUORESCENT AGENT

20

The composition preferably comprises a fluorescent agent (optical brightener). Fluorescent agents are well known and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the
25 sodium salts. The total amount of the fluorescent agent or agents used in the composition is generally from 0.005 to 2 wt %, more preferably 0.01 to 0.1 wt %. Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid
30 compounds, e.g. Tinopal DMS pure Xtra and Blankophor (Trade Mark) HRH, and Pyrazoline compounds, e.g. Blankophor SN. Preferred fluorescers are: sodium 2 (4-styryl-3-

- 14 -

sulfophenyl)-2H-naphthol[1,2-d]trazole, disodium 4,4'-bis{[(4-anilino-6-(N methyl-N-2 hydroxyethyl) amino 1,3,5-triazin-2-yl)]amino}stilbene-2-2' disulfonate, disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate, and disodium 4,4'-bis(2-sulfoslyryl)biphenyl.

PERFUME

Preferably the composition comprises a perfume. The perfume is preferably in the range from 0.001 to 3 wt %, most preferably 0.1 to 1 wt %. Many suitable examples of perfumes are provided in the CTFA (Cosmetic, Toiletry and Fragrance Association) 1992 International Buyers Guide, published by CFTA Publications and OPD 1993 Chemicals Buyers Directory 80th Annual Edition, published by Schnell Publishing Co.

EXPERIMENTAL

Example 1

The following range of agricultural waste products were obtained:

straw (stalk of wheat plant)

wood shavings

The materials were dried, then chopped in a food processor and passed through a grinder. This produced powder like materials with a wide range of particle sizes (up to 2-4mm). Ground olive stones (120-250 micron particle size), were also obtained.

The materials were left open to air, in 2 molar NaOH solution for 14 hours at room temperature. They were then rinsed and dried.

- 15 -

The materials were used to make washing products, such that in the wash solution there was 0.28g/L linear alkyl benzene sulfonate, 0.46g/L sodium sulphate, 0.37g/L sodium carbonate and 4g/L of the agricultural waste product. Agricultural
5 waste products that had no treatment and that been treated with NaOH were compared.

The products were used to wash an AS9 oily detergency test cloth (ex CFT, Vlaardingen, Netherlands), at a liquor:cloth
10 ratio of 80:1, 40°C for 30 minutes in 12° French hard water (Ca only), rinsed dried and the reflectance spectrum of the cloth measured using a reflectometer. The results expressed as the increase in the reflectance at 460nm compared to the original cloth are given in the table below.

- 16 -

Agricultural waste product	Delta R(460nm)
control	7.2
Olive stone	7.5
Treated Olive Stone	10.4
Straw	8.7
Treated Straw	10.5
Wood shavings	8.1
Treated Wood shavings	10.3

All tested materials led to an increase in soil removal as evidenced by the increase in delta R(460nm). The treated materials gave much greater soil removal. Control is washing system without addition of an agricultural waste product.

In similar experiment NaOH treated ground corn cob also gave enhanced performance. Benefits were also found when dosed at 0.7g/L.

- 17 -

We Claim:

1. A granular laundry detergent composition comprising
from 2 and 70 wt % of a surfactant, 2 to 40 wt % of
5 sodium carbonate, and from 5 to 80 wt % of an insoluble
agricultural plant by-product, the insoluble
agricultural plant by-product is in the form of a
particulate having a particle size of 1 mm or below,
wherein the insoluble agricultural plant by-product has
10 been treated with an aqueous solution, the aqueous
solution having a pH of at least 12, and subjected to a
drying step.
2. A granular laundry detergent composition according to
15 claim 1, wherein the composition comprises from 20 to
40 wt % of an insoluble agricultural plant by-product.
3. A granular laundry detergent composition according to
20 claim 1 or 2, wherein the by-product has only been
subjected to one or more steps selected from bleaching,
the application of a hueing agent, and a fluorescent
agent.
4. A granular laundry detergent composition according to
25 claim 1, wherein the plant products has been bleached.
5. A granular laundry detergent composition according to
any preceding claim, wherein the plant by-product
comprises from 0.005 to 2 wt % of a fluorescent agent.

30

- 18 -

6. A granular laundry detergent composition according to any preceding claim, wherein the plant by-product comprises from 0.00005 to 0.01 wt % of a hueing dye.
- 5 7. A granular laundry detergent composition according to any preceding claim, wherein the raw plant by-product has an L* value of at least 60, a b* value from 0 to 35 and an a* value from -10 to +10.
- 10 8. A granular laundry detergent composition according to any preceding claim, wherein the by-product is selected from: remnants of stems, cobs and husks from cereal production.
- 15 9. A granular laundry detergent composition according to claim 9, wherein the by-product is selected from: remnants of wheat, corn, sorghum, barley and rye.
10. A granular laundry detergent composition according to
20 any one of claims 1 to 8, wherein the by-product is selected from: remnants of stems and husks from rice production.
11. A granular laundry detergent composition according to
25 any one of claims 1 to 8, wherein the by-product is selected from: remnants of plant and seeds from edible oil production.
12. A granular laundry detergent composition according to
30 claim 12, preferably sunflower, soybean, rapeseed, cottonseed, canola, most preferably sunflower and soybeans.

- 19 -

13. A method of treating a textile comprising the following steps:

- 5 (i) treating a textile with the composition as defined in any preceding claim in an aqueous medium, wherein the aqueous medium comprises from 0.2 g/L to 5 g/L of a surfactant, the aqueous medium having a pH in the range 4 to 11; and,
- 10 (ii) rinsing the textile with water; and,
- (iii) drying the textile.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/055064

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11D3/382 C11D3/10

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)
C11D A23K

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 004 111 A (PROCTER & GAMBLE) 19 September 1979 (1979-09-19) page 2, line 24 - page 3, line 6 page 13, line 1 - page 14, line 24 page 23, lines 10-23 examples I-VI page 27, lines 1-10	1-13
A	US 4 056 400 A (DIAMANTOGLLOU MICHAEL ET AL) 1 November 1977 (1977-11-01) column 2, line 63 - column 3, line 5 column 10; example 24; table 3 column 11; example 28; table 4 ----- -/--	1-13

☒ Further documents are listed in the continuation of Box C.

☒ See patent family 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.
- *G* document member of the same patent family

Date of the actual completion of the international search

29 August 2007

Date of mailing of the international search report

05/09/2007

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

Bertran Nadal, Josep

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/055064

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 830 445 A (BOUILLON GUENTER ET AL) 3 November 1998 (1998-11-03) column 3, lines 39-54 example 1 claims 1,2,5 -----	1-13
A	US 4 594 260 A (VAQUEIRO M CRISTINA ET AL) 10 June 1986 (1986-06-10) column 6, lines 8-26 column 9, lines 1-4,22-44 -----	1-13
A	US 5 916 610 A (WITT PAUL R ET AL) 29 June 1999 (1999-06-29) example 1 -----	1-13
A	US 7 008 912 B1 (RETENMAIER JOSEF OTTO ET AL) 7 March 2006 (2006-03-07) column 2, lines 8-28 column 4, lines 54-64 claims 1,2 -----	1-13
A	WO 00/77153 A (UNILEVER) 21 December 2000 (2000-12-21) page 3, line 31 - page 4, line 15 examples -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2007/055064

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0004111	A	19-09-1979	BE 54 T1	11-04-1980
			CA 1121560 A1	13-04-1982
			DE 2952822 A1	25-09-1980
			FR 2443499 A1	04-07-1980
			GB 2043130 A	01-10-1980
			IT 1148228 B	26-11-1986
			JP 54160897 A	19-12-1979
			NL 7915012 A	30-05-1980
			US 4178254 A	11-12-1979
US 4056400	A	01-11-1977	DE 2436843 A1	12-02-1976
			FR 2280674 A1	27-02-1976
			JP 51039755 A	02-04-1976
US 5830445	A	03-11-1998	NONE	
US 4594260	A	10-06-1986	MX 7630 E	06-04-1990
US 5916610	A	29-06-1999	NONE	
US 7008912	B1	07-03-2006	AT 205875 T	15-10-2001
			WO 9840462 A1	17-09-1998
			DE 19709991 A1	17-09-1998
			DK 970181 T3	28-01-2002
			EP 0970181 A1	12-01-2000
			ES 2165155 T3	01-03-2002
			PT 970181 T	28-12-2001
WO 0077153	A	21-12-2000	AU 5531200 A	02-01-2001
			BR 0011396 A	05-03-2002
			CA 2372186 A1	21-12-2000
			CN 1371414 A	25-09-2002
			EP 1185608 A1	13-03-2002
			TR 200103557 T2	22-04-2002
			TW 490484 B	11-06-2002
			US 6486118 B1	26-11-2002
			ZA 200108764 A	24-10-2002