(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 441 820 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
18.04.2012 Bulletin 2012/16

(21) Application number: **10187517.7**

(22) Date of filing: **14.10.2010**

(51) Int Cl.:
C11D 1/37 $^{(2006.01)}$
C11D 1/825 $^{(2006.01)}$
C11D 1/83 $^{(2006.01)}$
C11D 3/04 $^{(2006.01)}$
C11D 3/10 $^{(2006.01)}$
C11D 3/395 $^{(2006.01)}$

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME

(71) Applicant: **Unilever PLC, A Company Registered in England and
Wales under Company no. 41424
London EC4Y 0DY
Greater London (GB)**

(72) Inventors:
- **Chapple, Andrew Paul**
  Wirral, Merseyside CH63 3JW (GB)
- **Roseblade, Jennifer Sian**
  Dursley,
  Gloucestershire, GL11 5UU (GB)

(74) Representative: **Avila, David Victor
Unilever Patent Group
Colworth House
Sharnbrook
Bedford
MK44 1LQ (GB)**

(54) Laundry detergent particles

(57) The present invention provides lenticular or disc detergent particle.

Printed by Jouve, 75001 PARIS (FR)

Description

Field of Invention

[0001] The present invention relates to large laundry detergent particles.

Background of Invention

[0002] WO9932599 describes a method of manufacturing laundry detergent particles, being an extrusion method in which a builder and surfactant, the latter comprising as a major component a sulphated or sulphonated anionic surfactant, are fed into an extruder, mechanically worked at a temperature of at least 40 °C, preferably at least 60°C, and extruded through an extrusion head having a multiplicity of extrusion apertures. In most examples, the surfactant is fed to the extruder along with builder in a weight ratio of more than 1 part builder to 2 parts surfactant. The extrudate apparently required further drying. In Example 6, PAS paste was dried and extruded. Such PAS noodles are well known in the prior art. The noodles are typically cylindrical in shape and their length exceeds their diameter, as described in example 2.

[0003] US 7,022,660 discloses a process for the preparation of a detergent particle having a coating.

[0004] The use of bleaching catalysts for stain removal has been developed over recent years. The recent discovery that some catalysts are capable of bleaching effectively in the absence of an added peroxyl source has recently become the focus of some interest, for example: WO9965905; WO0012667; WO0012808; WO0029537, and, WO0060045. These catalysts are predominantly capable of also bleaching with peroxyl species.

Summary of the Invention

[0005] We have found that the present invention reduces the unwanted fabric contact with the transition metal catalysts whist allowing dissolution.

[0006] In one aspect the present invention provides a coated detergent particle having perpendicular dimensions x, y and z, wherein x is from 1 to 2 mm, y is from 2 to 8mm (preferably 3 to 8 mm), and z is from 2 to 8 mm (preferably 3 to 8 mm), wherein the particle comprises:

(i) from 40 to 90 wt %, preferably 50 to 90 wt%, surfactant selected from: anionic surfactant; and, non-ionic surfactant;
(ii) from 1 to 40 wt %, preferably 20 to 40 wt%, water soluble inorganic salts; and,
(iii) from 0.0001 to 0.3 wt %, preferably 0.015 to 0.03%, of a transition metal catalyst, wherein the transition metal is selected from iron and manganese, wherein the inorganic salts are present on the laundry detergent particle as a coating and the surfactant and the transition metal catalyst are present as a core.

[0007] Unless otherwise stated all wt % refer to the total percentage in the particle as dry weights.

[0008] In a further aspect, the present invention provides a coated detergent particle that is a concentrated formulation with more surfactant than inorganic solid. Only by having the coating encasing the surfactant which is soft can one have such a particulate concentrate where the unit dose required for a wash is reduced. Adding solvent to the core would result by converting the particle into a liquid formulation. On the other hand, having a greater amount of inorganic solid would result in a less concentrated formulation; a high inorganic content would take one back to conventional low surfactant concentration granular powder. The coated detergent particle of the present invention sits in the middle of the two conventional (liquid and granular) formats.

Detailed Description of the Invention

SHAPE

[0009] Preferably the coated laundry detergent particle is curved.

[0010] The coated laundry detergent particle may be lenticular (shaped like a whole dried lentil), an oblate ellipsoid, where z and *y* are the equatorial diameters and x is the polar diameter; preferably y = z.

[0011] The coated laundry detergent particle may be shaped as a disc.

[0012] Preferably the coated laundry detergent particle does not have hole; that is to say, the coated laundry detergent particle does not have a conduit passing there though that passes through the core, i.e., the coated detergent particle has a topologic genus of zero.

CORE

SURFACTANT

[0013] The coated laundry detergent particle comprises between 40 to 90 wt%, preferably 50 to 90 wt% of a surfactant, most preferably 70 to 90 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. 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.

Anionic Surfactants

[0014] Suitable anionic detergent compounds which may be used are usually water-soluble alkali metal salts of organic 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. Examples of suitable synthetic anionic detergent compounds are sodium and potassium alkyl sulphates, especially those obtained by sulphating higher C_8 to C_{18} alcohols, produced for example from tallow or coconut oil, sodium and potassium alkyl C_9 to C_{20} benzene sulphonates, particularly sodium linear secondary alkyl C_{10} to C_{15} 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. Most preferred anionic surfactants are sodium lauryl ether sulfate (SLES), particularly preferred with 1 to 3 ethoxy groups, sodium C_{10} to C_{15} alkyl benzene sulphonates and sodium C_{12} to C_{18} 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 described in EP-A-070 074, and alkyl monoglycosides. The chains of the surfactants may be branched or linear.

[0015] Soaps may also be present. The fatty acid soap used preferably contains from about 16 to about 22 carbon atoms, preferably in a straight chain configuration. The anionic contribution from soap is preferably from 0 to 30 wt% of the total anionic.

[0016] Preferably, at least 50 wt % of the anionic surfactant is selected from: sodium C_{11} to C_{15} alkyl benzene sulphonates; and, sodium C_{12} to C_{18} alkyl sulphates. Even more preferably, the anionic surfactant is sodium C_{11} to C_{15} alkyl benzene sulphonates.

[0017] Preferably the anionic surfactant is present in the coated laundry detergent particle at levels between 15 to 85 wt%, more preferably 50 to 80wt% on total surfactant.

Nonionic Surfactants

[0018] 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 with alkylene oxides, especially ethylene oxide either alone or with propylene oxide. Preferred nonionic detergent compounds are C_6 to C_{22} 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 of aliphatic C_8 to C_{18} primary or secondary linear or branched alcohols with ethylene oxide, generally 5 to 50 EO. Preferably, the non-ionic is 10 to 50 EO, more preferably 20 to 35 EO. Alkyl ethoxylates are particularly preferred.

[0019] Preferably the nonionic surfactant is present in the coated laundry detergent particle at levels between 5 to 75 wt% on total surfactant, more preferably 10 to 40 wt% on total surfactant.

[0020] Cationic surfactant may be present as minor ingredients at levels preferably between 0 to 5 wt% on total surfactant.

[0021] Preferably all the surfactants are mixed together before being dried. Conventional mixing equipment may be used. The surfactant core of the laundry detergent particle may be formed by extrusion or roller compaction and subsequently coated with an inorganic salt.

Calcium Tolerant Surfactant System

[0022] In another aspect the surfactant system used is calcium tolerant and this is a preferred aspect because this reduces the need for builder.

[0023] Surfactant blends that do not require builders to be present for effective detergency in hard water are preferred. Such blends are called calcium tolerant surfactant blends if they pass the test set out hereinafter. However, the invention may also be of use for washing with soft water, either naturally occurring or made using a water softener. In this case, calcium tolerance is no longer important and blends other than calcium tolerant ones may be used.

[0024] Calcium-tolerance of the surfactant blend is tested as follows:

> The surfactant blend in question is prepared at a concentration of 0.7 g surfactant solids per litre of water containing sufficient calcium ions to give a French hardness of 40 (4 x 10^{-3} Molar Ca^{2+}). Other hardness ion free electrolytes such as sodium chloride, sodium sulphate, and sodium hydroxide are added to the solution to adjust the ionic strength to 0.05M and the pH to 10. The adsorption of light of wavelength 540 nm through 4 mm of sample is measured 15 minutes after sample preparation. Ten measurements are made and an average value is calculated. Samples that give an absorption value of less than 0.08 are deemed to be calcium tolerant.

[0025] Examples of surfactant blends that satisfy the above test for calcium tolerance include those having a major part of LAS surfactant (which is not of itself calcium tolerant) blended with one or more other surfactants (co-surfactants) that are calcium tolerant to give a blend that is sufficiently calcium tolerant to be usable with little or no builder and to pass the given test. Suitable calcium tolerant co-surfactants include SLES 1-7EO, and alkyl-ethoxylate nonionic surfactants, particularly those with melting points less than 40°C.

[0026] A LAS/SLES surfactant blend has a superior foam profile to a LAS nonionic surfactant blend and is therefore preferred for hand washing formulations requiring high levels of foam. SLES may be used at levels of up to 30 wt% of the surfactant blend.

Water Soluble Inorganic Salts

[0027] The water-soluble inorganic salts are preferably selected from sodium carbonate, sodium chloride, sodium silicate and sodium sulphate, or mixtures thereof, most preferably, 70 to 100 wt% sodium carbonate on total water-soluble inorganic salts. The water-soluble inorganic salt is present as a coating on the particle. The water-soluble inorganic salt is preferably present at a level that reduces the stickiness of the laundry detergent particle to a point where the particles are free flowing.

[0028] It will be appreciated by those skilled in the art that while multiple layered coatings, of the same or different coating materials, could be applied, a single coating layer is preferred, for simplicity of operation, and to maximise the thickness of the coating. The amount of coating should lay in the range 1 to 40 wt% of the particle, preferably 20 to 40 wt%, more preferably 25 to 35 wt% for the best results in terms of anti-caking properties of the detergent particles.

[0029] The coating is preferably applied to the surface of the surfactant core, by deposition from an aqueous solution of the water soluble inorganic salt. In the alternative coating can be performed using a slurry. The aqueous solution preferably contains greater than 50g/L, more preferably 200 g/L of the salt. An aqueous spray-on of the coating solution in a fluidised bed has been found to give good results and may also generate a slight rounding of the detergent particles during the fluidisation process. Drying and/or cooling may be needed to finish the process.

[0030] A preferred calcium tolerant coated laundry detergent particle comprises 15 to 100 wt% on surfactant of anionic surfactant of which 20 to 30 wt% on surfactant is sodium lauryl ether sulphate.

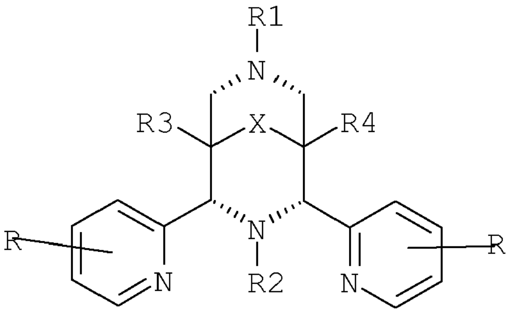
Transition metal catalyst

[0031] Preferred transition metal catalysts are described below.

BISPIDON

[0032] The bispidon class are preferably in the form of an iron transition metal catalyst.

[0033] The bispidon ligand is preferably of the form:



(I)

wherein each R is independently selected from: hydrogen, F, Cl, Br, hydroxyl, C1-C4-alkylO-, -NH-CO-H, -NH-CO-C1-C4-alkyl, -NH2, -NH-C1-C4-alkyl, and C1-C4-alkyl;
R1 and R2 are independently selected from:
C1-C24-alkyl,
C6-C10-aryl, and,
a group containing a heteroatom capable of coordinating to a transition metal;
R3 and R4 are independently selected from hydrogen, C1-C8 alkyl, C1-C8-alkyl-O-C1-C8-alkyl, C1-C8-alkyl-O-C6-C10-aryl, C6-C10-aryl, C1-C8-hydroxyalkyl, and $-(CH2)_nC(O)OR5$
wherein R5 is independently selected from: hydrogen, C1-C4-alkyl, n is from 0 to 4, and mixtures thereof; and,
X is selected from C=O, $-[C(R6)_2]_y-$ wherein Y is from 0 to 3 each R6 is independently selected from hydrogen, hydroxyl, C1-C4-alkoxy and C1-C4-alkyl.

[0034] Preferably R3 = R4 and selected from -C(O)-O-CH3, -C(O)-O-CH2CH3, -C(O)-O-CH2C6H5 and CH2OH.

[0035] Preferably the heteroatom capable of coordinating to a transition metal is pyridin-2-ylmethyl optionally substituted by -C0-C4-alkyl.

[0036] Preferably X is C=O or C(OH)2.

[0037] Preferred groups for R1 and R2 are CH3, -C2H5, -C3H7, benzyl, -C4H9, -C6H13, -C8H17, -C12H25, and -C18H37 and pyridin-2-yl. A preferred class of bispidon is one in which at least one of R1 or R2 is pyridin-2-ylmethyl or benzyl, preferably pyridin-2-ylmethyl.

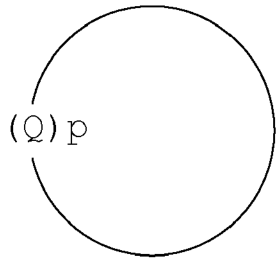
[0038] A preferred bispidon is dimethyl 2,4-di-(2-pyridyl) -3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate (N2py3o-C1) and the iron complex thereof FeN2py3o-C1 which was prepared as described in W002/48301. Other preferred bispidons are one in which instead of having a methyl group (C1) at the 3 position have longer alkyl chains, namely isobutyl, (n-hexyl) C6, (n-octyl) C8, (n-dodecyl) C12, (n-tetradecyl) C14, (n-octadecyl) C18, which were prepared in an analogous manner.

[0039] Preferred tetradentate bispidons are also illustrated in WO00/60045 and preferred pentadentate bispidons are illustrated in W002/48301 and WO03/104379.

ME3-TACN AND RELATED COMPOUNDS

[0040] A preferred transition metal catalyst is described in EP 0458397 and WO06/125517; both of these patents disclose the use of manganese 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me3-TACN) as related compounds as complexes. The PF_6^- ligand of Me3-TACN has been commercialised in laundry detergent powders and dish wash tablets. It is preferred that the preformed transition metal of Me3-TACN and related compounds is in the form of a salt such that it has a water solubility of at least 50 g/l at 20 °C. Preferred salts are those of chloride, acetate, sulphate, and nitrate. Most preferred are the acetate and sulphate salts.

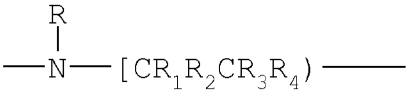
[0041] The catalyst is most preferably a mononuclear or dinuclear complex of a Mn II-V transition metal catalyst, the ligand of the transition metal catalyst of formula (II):



(I)

,

wherein:

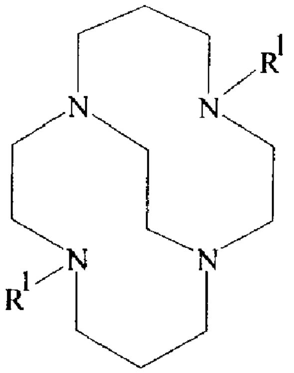
Q = 

$$Q = -N(R)-[CR_1R_2CR_3R_4)-$$

;

p is 3;
R is independently selected from: hydrogen, C1-C6-alkyl, C2OH, C1COOH, and pyridin-2-ylmethyl or one of R is linked to the N of another Q via an ethylene bridge;
R1, R2, R3, and R4 are independently selected from: H, C1-C4-alkyl, and C1-C4-alkylhydroxy.
R is preferably independently selected from: hydrogen, CH3, C2H5, CH2CH2OH and CH2COOH.
R, R1, R2, R3, and R4 are preferably independently selected from: H and Me.
1,4,7-Trimethyl-1,4,7-triazacyclononane (Me3-TACN) and 1,2,-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me4-DTNE) are most preferred.

[0042] A preferred cross-bridged ligand is of the form:



.

(III)

wherein "R^1" is independently selected from H, and linear or branched, substituted or unsubstituted C1 to C20 alkyl, alkylaryl, alkenyl or alkynyl; and all nitrogen atoms in the macropolycyclic rings are coordinated with the transition metal.

[0043] Preferably R1 = Me, which is the ligand 5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane of which the complex [Mn(Bcyclam)Cl_2] may be synthesised according to WO98/39098.

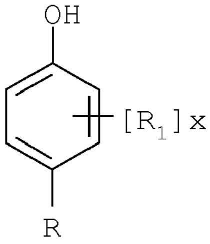
[0044] Other suitable crossed bridged ligands are also found in WO98/39098.

Antioxidant

[0045] Anti-oxidants are substances as described in Kirk-Othmers (Vol 3, pg 424) and in Uhlmans Encyclopedia (Vol 3, pg 91).

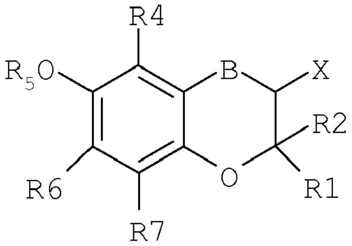
[0046] Preferably the core comprises from 0.0001 to 2 wt % of an antioxidant.

[0047] One class of anti-oxidants suitable for use in the present invention is alkylated phenols having the general formula:



wherein R is C1-C22 linear or branched alkyl, preferably methyl or branched C3-C6 alkyl; C3-C6 alkoxy, preferably methoxy; R1 is a C3-C6 branched alkyl, preferably tert-butyl; x is 1 or 2. Hindered phenolic compounds are preferred as antioxidant.

[0048] Another class of anti-oxidants suitable for use in the present invention is a benzofuran or benzopyran derivative having the formula:



wherein R1 and R2 are each independently alkyl or R1 and R2 can be taken together to form a C5-C6 cyclic hydrocarbyl moiety; B is absent or CH2; R4 is C1-C6 alkyl; R5 is hydrogen or -C(O)R3 wherein R3 is hydrogen or C1-C19 alkyl; R6 is C1-C6 alkyl; R7 is hydrogen or C1-C6 alkyl; X is -CH2OH, or - CH2A wherein A is a nitrogen comprising unit, phenyl, or substituted phenyl. Preferred nitrogen comprising A units include amino, pyrrolidino, piperidino, morpholino, piperazino, and mixtures thereof.

[0049] Other suitable antioxidants are found as follows. A derivative of α-tocopherol, beta-tocopherol, gamma-tocopherol, delta-tocopherol, 6-hydroxy-2,5,7,8-tetra-methylchroman-2-carboxylic acid (Trolox™).

The coated laundry detergent particle

[0050] Preferably, the coated laundry detergent particle comprises from 10 to 100 wt %, more preferably 50 to 100 wt %, even more preferably 80 to 100 wt %, most preferably 90 to 100 wt % of a laundry detergent formulation in a package.

[0051] The package is that of a commercial formulation for sale to the general public and is preferably in the range of 0.01 kg to 5 kg, preferably 0.02 kg to 2 kg, most preferably 0.5 kg to 2 kg.

[0052] Preferably, the coated laundry detergent particle is such that at least 90 to 100 % of the coated laundry detergent particles in the in the x, y and z dimensions are within a 20 %, preferably 10%, variable from the largest to the smallest coated laundry detergent particle.

Water content

[0053] The particle preferably comprises from 0 to 15 wt % water, more preferably 0 to 10 wt %, most preferably from 1 to 5 wt % water, at 293K and 50% relative humidity. This facilitates the storage stability of the particle and its mechanical properties.

Other Adjuncts

[0054] The adjuncts as described below may be present in the coating or the core. These may be in the core or the coating.

Fluorescent Agent

[0055] The coated laundry detergent particle 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 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 %. Suitable Fluorescer for use in the invention are described in chapter 7 of Industrial Dyes edited by K.Hunger 2003 Wiley-VCH ISBN 3-527-30426-6.

[0056] Preferred fluorescers are selected from the classes distyrylbiphenyls, triazinylaminostilbenes, bis(1,2,3-triazol-2-yl)stilbenes, bis(benzo[b]furan-2-yl)biphenyls, 1,3-diphenyl-2-pyrazolines and courmarins. The fluorescer is preferably sulfonated.

[0057] Preferred classes of fluorescer are: Di-styryl biphenyl compounds, e.g. Tinopal (Trade Mark) CBS-X, Di-amine stilbene di-sulphonic acid 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-sulfophenyl)-2H-napthol[1,2-d]triazole, 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-sulfostyryl)biphenyl.

[0058] Tinopal® DMS is the disodium salt of disodium 4,4'-bis{[(4-anilino-6-morpholino-1,3,5-triazin-2-yl)]amino} stilbene-2-2' disulfonate. Tinopal® CBS is the disodium salt of disodium 4,4'-bis(2-sulfostyryl)biphenyl.

Perfume

[0059] 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.

[0060] It is commonplace for a plurality of perfume components to be present in a formulation. In the compositions of the present invention it is envisaged that there will be four or more, preferably five or more, more preferably six or more or even seven or more different perfume components.

[0061] In perfume mixtures preferably 15 to 25 wt% are top notes. Top notes are defined by Poucher (Journal of the Society of Cosmetic Chemists 6(2):80 [1955]). Preferred top-notes are selected from citrus oils, linalool, linalyl acetate, lavender, dihydromyrcenol, rose oxide and cis-3-hexanol.

[0062] It is preferred that the coated laundry detergent particle does not contain a peroxygen bleach, e.g., sodium percarbonate, sodium perborate, and peracid.

Polymers

[0063] The composition may comprise one or more further polymers. Examples are carboxymethylcellulose, poly (ethylene glycol), poly(vinyl alcohol), polyethylene imines, ethoxylated polyethylene imines, water soluble polyester polymers polycarboxylates such as polyacrylates, maleic/acrylic acid copolymers and lauryl methacrylate/acrylic acid copolymers.

Enzymes

[0064] One or more enzymes are preferred present in a composition of the invention.

[0065] Preferably the level of each enzyme is from 0.0001 wt% to 0.5 wt% protein on product.

[0066] Especially contemplated enzymes include proteases, alpha-amylases, cellulases, lipases, peroxidases/oxidases, pectate lyases, and mannanases, or mixtures thereof.

[0067] Suitable lipases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful lipases include lipases from *Humicola* (synonym *Thermomyces),* e.g. from *H. lanuginosa (T. lanuginosus*) as described in EP 258 068 and EP 305 216 or from *H. insolens* as described in WO 96/13580, a *Pseudomonas* lipase, e.g. from *P. alcaligenes* or P. *pseudoalcaligenes* (EP 218 272), *P. cepacia* (EP 331 376), *P. stutzeri* (GB 1,372,034), *P. fluorescens, Pseudomonas* sp. strain SD 705 (WO 95/06720 and WO 96/27002), *P. wisconsinensis* (WO 96/12012), a *Bacillus* lipase, e.g. from *B. subtilis* (Dartois et al. (1993), Biochemica et Biophysica Acta, 1131, 253-360), *B. stearothermophilus* (JP 64/744992) or *B. pumilus* (WO 91/16422).

[0068] Other examples are lipase variants such as those described in WO 92/05249, WO 94/01541, EP 407 225, EP 260 105, WO 95/35381, WO 96/00292, WO 95/30744, WO 94/25578, WO 95/14783, WO 95/22615, WO 97/04079 and WO 97/07202, WO 00/60063, WO 09/107091 and WO09/111258.

[0069] Preferred commercially available lipase enzymes include Lipolase™ and Lipolase Ultra™, Lipex™ (Novozymes A/S) and Lipoclean™.

[0070] The method of the invention may be carried out in the presence of phospholipase classified as EC 3.1.1.4 and/or EC 3.1.1.32. As used herein, the term phospholipase is an enzyme which has activity towards phospholipids. Phospholipids, such as lecithin or phosphatidylcholine, consist of glycerol esterified with two fatty acids in an outer (sn-1) and the middle (sn-2) positions and esterified with phosphoric acid in the third position; the phosphoric acid, in turn, may be esterified to an amino-alcohol. Phospholipases are enzymes which participate in the hydrolysis of phospholipids. Several types of phospholipase activity can be distinguished, including phospholipases A_1 and A_2 which hydrolyze one fatty acyl group (in the sn-1 and sn-2 position, respectively) to form lysophospholipid; and lysophospholipase (or phospholipase B) which can hydrolyze the remaining fatty acyl group in lysophospholipid. Phospholipase C and phospholipase D (phosphodiesterases) release diacyl glycerol or phosphatidic acid respectively.

[0071] Suitable proteases include those of animal, vegetable or microbial origin. Microbial origin is preferred. Chemically modified or protein engineered mutants are included. The protease may be a serine protease or a metallo protease, preferably an alkaline microbial protease or a trypsin-like protease. Preferred commercially available protease enzymes include Alcalase™, Savinase™, Primase™, Duralase™, Dyrazym™, Esperase™, Everlase™, Polarzyme™, and Kannase™, (Novozymes A/S), Maxatase™, Maxacal™, Maxapem™, Properase™, Purafect™, Purafect OXP™, FN2™, and FN3™ (Genencor International Inc.).

[0072] The method of the invention may be carried out in the presence of cutinase. classified in EC 3.1.1.74. The cutinase used according to the invention may be of any origin. Preferably cutinases are of microbial origin, in particular of bacterial, of fungal or of yeast origin.

[0073] Suitable amylases (alpha and/or beta) include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Amylases include, for example, alpha-amylases obtained from *Bacillus,* e.g. a special strain of *B. licheniformis,* described in more detail in GB 1,296,839, or the *Bacillus* sp. strains disclosed in WO 95/026397 or WO 00/060060. Commercially available amylases are Duramyl™, Termamyl™, Termamyl Ultra™, Natalase™, Stainzyme™, Fungamyl™ and BAN™ (Novozymes A/S), Rapidase™ and Purastar™ (from Genencor International Inc.).

[0074] Suitable cellulases include those of bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Suitable cellulases include cellulases from the genera *Bacillus, Pseudomonas, Humicola, Fusarium, Thielavia, Acremonium,* e.g. the fungal cellulases produced from *Humicola insolens, Thielavia terrestris, Myceliophthora thermophila,* and *Fusarium oxysporum* disclosed in US 4,435,307, US 5,648,263, US 5,691,178, US 5,776,757, WO 89/09259, WO 96/029397, and WO 98/012307. Commercially available cellulases include Celluzyme™, Carezyme™, Endolase™, Renozyme™ (Novozymes A/S), Clazinase™ and Puradax HA™ (Genencor International Inc.), and KAC-500(B)™ (Kao Corporation).

[0075] Suitable peroxidases/oxidases include those of plant, bacterial or fungal origin. Chemically modified or protein engineered mutants are included. Examples of useful peroxidases include peroxidases from *Coprinus,* e.g. from C. *cinereus,* and variants thereof as those described in WO 93/24618, WO 95/10602, and WO 98/15257. Commercially available peroxidases include Guardzyme™ and Novozym™ 51004 (Novozymes A/S).

[0076] Further enzymes suitable for use are disclosed in WO2009/087524, WO2009/090576, WO2009/148983 and WO2008/007318.

Enzyme Stabilizers

[0077] Any enzyme present in the composition may be stabilized using conventional stabilizing agents, e.g., a polyol such as propylene glycol or glycerol, a sugar or sugar alcohol, lactic acid, boric acid, or a boric acid derivative, e.g., an aromatic borate ester, or a phenyl boronic acid derivative such as 4-formylphenyl boronic acid, and the composition may be formulated as described in e.g. WO 92/19709 and WO 92/19708.

[0078] Where alkyl groups are sufficiently long to form branched or cyclic chains, the alkyl groups encompass branched, cyclic and linear alkyl chains. The alkyl groups are preferably linear or branched, most preferably linear.

[0079] The indefinite article "a" or "an" and its corresponding definite article "the" as used herein means at least one, or one or more, unless specified otherwise. The singular encompasses the plural unless otherwise specified.

[0080] Sequesterants may be present in the coated laundry detergent particles.

[0081] It is preferred that the coated detergent particle has a core to shell ratio of from 3 to 1:1, most preferably 2.5 to 1.5:1; the optimal ratio of core to shell is 2:1.

EXPERIMENTAL

Example 1: (particle manufacture)

[0082] Dimethyl 2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate (N2py3o-C1) and the iron(II) complex thereof [Fe(N2py3o-C1)Cl]Cl was prepared as described in WO0248301.

[0083] A coated laundry detergent particle colour were created containing [Fe(N2py3o-C1)Cl]Cl in the core.:

> The particles were oblate elipisoids which had the following dimensions x= 1.1 mm y= 4.0 mm z= 5.0 mm. The particles weighed ~0.013g each.

Preparation of core

[0084] 1960.8g of dried, milled surfactant blend (LAS/PAS/NI 68/17/15 by weight) was thoroughly mixed with 37.4g of perfume oil and 1.8 g of [Fe(N2py3o-C1)Cl]Cl. The mixture was then extruded using a ThermoFisher 24HC twin screw extruder, operated at a rate of 8kg/hr. Inlet temperature of the extruder was set at 20°C, rising to 40°C just prior to the die-plate. The die-plate used was drilled with 6 circular orifices of 5mm diameter.

[0085] The extruded product was cut after the die-plate using a high speed cutter set up to produce particle with a thickness of ~1.1 mm.

Coating of Particle

[0086] 764g of the extrudates above were charged to the fluidising chamber of a Strea 1 laboratory fluid bed drier (Aeromatic-Fielder AG) and spray coated using 1069g of a solution containing 320.7g of sodium carbonate in 748.3g of water, using a top-spray configuration.

[0087] The coating solution was fed to the spray nozzle of the Strea 1 via a peristaltic pump (Watson-Marlow model 101 U/R) at an initial rate of 3.3g/min, rising to 9.1g/min during the course of the coating trial.

[0088] The Fluid bed coater was operated with an initial air inlet air temperature of 55°C increasing to 90 °C during the course of the coating trial whilst maintaining the outlet temperature in the range 45-50°C throughout the coating process.

Example 2: (particle manufacture)

[0089] A coated laundry detergent particle colour were created containing [Fe(N2py3o-C1)Cl]Cl in the core.:

> The particles were oblate elipisoids which had the following dimensions x= 1.1 mm y= 4.0 mm z= 5.0 mm. The particles weighed ~0.013g each.

Source of Catalyst

[0090] 30g of a granular catalyst sample (composition by weight 6% [Fe(N2py3o-C1)Cl]Cl, 12% Sokalan CP13S polymer and xx% Sodium Sulphate) was finely ground in a pestle and mortar.

Preparation of core

[0091] 1932.6.8g of dried, milled surfactant blend (LAS/PAS/NI 68/17/15 by weight) was thoroughly mixed with 37.4g of perfume oil and 30 g of the ground [Fe(N2py3o-C1)Cl]Cl containing catalyst granule (described above). The mixture was then extruded using a ThermoFisher 24HC twin screw extruder, operated at a rate of 8kg/hr. Inlet temperature of the extruder was set at 20°C, rising to 40°C just prior to the die-plate. The die-plate used was drilled with 6 circular orifices of 5mm diameter.

[0092] The extruded product was cut after the die-plate using a high speed cutter set up to produce particle with a thickness of ~1.1 mm.

Coating of Particle

[0093] 764g of the extrudates above were charged to the fluidising chamber of a Strea 1 laboratory fluid bed drier (Aeromatic-Fielder AG) and spray coated using 1069g of a solution containing 320.7g of sodium carbonate in 748.3g of water, using a top-spray configuration.

[0094] The coating solution was fed to the spray nozzle of the Strea 1 via a peristaltic pump (Watson-Marlow model 101 U/R) at an initial rate of 3.3g/min, rising to 9.1g/min during the course of the coating trial.

[0095] The Fluid bed coater was operated with an initial air inlet air temperature of 55°C increasing to 90°C during the course of the coating trial whilst maintaining the outlet temperature in the range 45-50°C throughout the coating process.

Claims

1. A coated detergent particle having perpendicular dimensions x, y and z, wherein x is from 1 to 2 mm, y is from 2 to 8mm, and z is from 2 to 8 mm, wherein the particle comprises:

    (i) from 40 to 90 wt % surfactant selected from: anionic surfactant; and, non-ionic surfactant;
    (ii) from 1 to 40 wt % water soluble inorganic salts; and,
    (iii) from 0.0001 to 0.3 wt % of a transition metal catalyst, wherein the transition metal is selected from iron and manganese,

    wherein the inorganic salts are present on the detergent particle as a coating and the surfactant and the transition metal catalyst are present as a core.

2. A coated detergent particle according to claim 1, wherein the ligand of the transition metal catalyst is selected from 1,4,7-Trimethyl-1,4,7-triazacyclononane (Me3-TACN); and 1,2,-bis-(4,7,-dimethyl-1,4,7,-triazacyclonon-1-yl)-ethane (Me4-DTNE).

3. A coated detergent particle according to claim 1, wherein the wherein the ligand of the transition metal catalyst is dimethyl 2,4-di-(2-pyridyl)-3-methyl-7-(pyridin-2-ylmethyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate.

4. A coated detergent particle according to claim 1, wherein the wherein the ligand of the transition metal catalyst is 5,12-dimethyl-1,5,8,12-tetraaza-bicyclo[6.6.2]hexadecane.

5. A coated detergent particle according to any one of the preceding claims, wherein the core comprises from 0.0001 to 2 wt % of an antioxidant.

6. A coated detergent particle according to any one of the preceding claims, wherein the inorganic salts act as a builder.

7. A coated detergent particle according to claim 6, wherein the inorganic salts comprises sodium carbonate.

8. A coated detergent particle according to any one of the preceding claims, wherein the coated detergent particle comprises from 15 to 85 wt % anionic surfactant on surfactant and from 5 to 75 wt % non-ionic surfactant on surfactant.

9. A coated detergent particle according to any one of claims 1 to 7, wherein the coated detergent particle comprises 15 to 100 wt % anionic surfactant on surfactant of which 20 to 30 wt % is sodium lauryl ether sulphate.

10. A coated detergent particle according to any one of the preceding claims, wherein the anionic surfactant is selected from alkyl benzene sulphonates; alkyl ether sulphates; alkyl sulphates.

11. A coated detergent particle according to claim 10, wherein the anionic surfactant is selected from sodium lauryl ether sulfate with 1 to 3 ethoxy groups, sodium C_{10} to C_{15} alkyl benzene sulphonates and sodium C_{12} to C_{18} alkyl sulphates.

12. A coated detergent particle according to any one of the preceding claims, wherein the non-anionic surfactant is 10 to 50 EO.

13. A coated detergent particle according to claim 12, wherein the non-ionic surfactant is the condensation products of aliphatic C_8 to C_{18} primary or secondary linear or branched alcohols with 20 to 35 ethylene oxide groups.

14. A coated detergent particle according to any one of the preceding claims, wherein the coated detergent particle comprises 20 to 40 wt % of inorganic builder salts as a coating.

15. A coated detergent particle according to claim 14, wherein the coated detergent particle comprises 25 to 35 wt % of inorganic builder salts as a coating.

16. A coated detergent particle according to any one of the preceding claims, wherein the particle comprises from 0 to 15 wt % water.

17. A coated detergent particle according to claim 16, wherein the particle comprises from 1 to 5 wt % water.

18. A coated detergent particle according to any one of the preceding claims, wherein the coated detergent particle comprises from 10 to 100 wt % of a detergent formulation in a package.

19. A coated detergent particle according to claim 18, wherein the coated detergent particle comprises from 50 to 100 wt % of a detergent formulation in a package.

20. A coated detergent particle according to claim 19, wherein the coated detergent particle comprises from 80 to 100 wt % of a detergent formulation in a package.

21. A coated detergent particle according to claim 20, wherein the coated detergent particle comprises from 90 to 100 wt % of a detergent formulation in a package.

22. A coated detergent particle according to any one of the preceding claims, wherein at least 90 to 100 % of the coated detergent particles in the in the x, y and z dimensions are within a 20 % variable from the largest to the smallest coated detergent particle.

Europäisches
Patentamt
European
Patent Office
Office européen
des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 10 18 7517

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 141 470 A2 (UNILEVER NV [NL]; UNILEVER PLC [GB]) 15 May 1985 (1985-05-15) * page 1, line 25 - page 2, line 1; claims 1-15; examples I-IV,VIII * * page 2, lines 21-23 * * page 4, lines 13-30 * * page 5, lines 1-20 * * page 6, lines 28-34 * * page 7, lines 6-18 * -----	1-22	INV. C11D1/37 C11D1/825 C11D1/83 C11D3/04 C11D3/10 C11D3/395
A	EP 1 081 219 A2 (COGNIS DEUTSCHLAND GMBH [DE]) 7 March 2001 (2001-03-07) * paragraphs [0001], [0004] - [0010], [0013] - [0017], [0032]; claims 1-4,9-15; table 1 * -----	1-22	
A	EP 1 881 059 A1 (PROCTER & GAMBLE [US]) 23 January 2008 (2008-01-23) * paragraphs [0002], [0003], [0020], [0021] - [0023], [0025]; claims 1-7 * * page 3, lines 28-32,52-55 * -----	1-22	

TECHNICAL FIELDS SEARCHED (IPC)
C11D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	28 March 2011	Klier, Erich

2

EPO FORM 1503 03.82 (P04C01)

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 10 18 7517

28-03-2011

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0141470 A2	15-05-1985	AU 549623 B2	06-02-1986
		AU 3499084 A	16-05-1985
		BR 8405679 A	10-09-1985
		CA 1234382 A1	22-03-1988
		DE 3484498 D1	29-05-1991
		DK 530284 A	09-05-1985
		ES 8600382 A1	01-01-1986
		FI 844337 A	09-05-1985
		GB 2149316 A	12-06-1985
		GR 80857 A1	07-02-1985
		IN 159938 A1	13-06-1987
		JP 60115700 A	22-06-1985
		NO 844414 A	09-05-1985
		PH 21422 A	15-10-1987
		PT 79465 A	01-12-1984
		US 4626373 A	02-12-1986
		ZA 8408703 A	30-07-1986
EP 1081219 A2	07-03-2001	AT 272105 T	15-08-2004
		DE 19941934 A1	15-03-2001
		ES 2224979 T3	16-03-2005
EP 1881059 A1	23-01-2008	BR PI0603808 A2	10-03-2009

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 9932599 A **[0002]**
- US 7022660 B **[0003]**
- WO 9965905 A **[0004]**
- WO 0012667 A **[0004]**
- WO 0012808 A **[0004]**
- WO 0029537 A **[0004]**
- WO 0060045 A **[0004] [0039]**
- EP 328177 A **[0014]**
- EP 070074 A **[0014]**
- WO 0248301 A **[0038] [0039] [0082]**
- WO 03104379 A **[0039]**
- EP 0458397 A **[0040]**
- WO 06125517 A **[0040]**
- WO 9839098 A **[0043] [0044]**
- EP 258068 A **[0067]**
- EP 305216 A **[0067]**
- WO 9613580 A **[0067]**
- EP 218272 A **[0067]**
- EP 331376 A **[0067]**
- GB 1372034 A **[0067]**
- WO 9506720 A **[0067]**
- WO 9627002 A **[0067]**
- WO 9612012 A **[0067]**
- JP 64744992 B **[0067]**
- WO 9116422 A **[0067]**
- WO 9205249 A **[0068]**
- WO 9401541 A **[0068]**
- EP 407225 A **[0068]**
- EP 260105 A **[0068]**
- WO 9535381 A **[0068]**
- WO 9600292 A **[0068]**
- WO 9530744 A **[0068]**
- WO 9425578 A **[0068]**
- WO 9514783 A **[0068]**
- WO 9522615 A **[0068]**
- WO 9704079 A **[0068]**
- WO 9707202 A **[0068]**
- WO 0060063 A **[0068]**
- WO 09107091 A **[0068]**
- WO 09111258 A **[0068]**
- GB 1296839 A **[0073]**
- WO 95026397 A **[0073]**
- WO 00060060 A **[0073]**
- US 4435307 A **[0074]**
- US 5648263 A **[0074]**
- US 5691178 A **[0074]**
- US 5776757 A **[0074]**
- WO 8909259 A **[0074]**
- WO 96029397 A **[0074]**
- WO 98012307 A **[0074]**
- WO 9324618 A **[0075]**
- WO 9510602 A **[0075]**
- WO 9815257 A **[0075]**
- WO 2009087524 A **[0076]**
- WO 2009090576 A **[0076]**
- WO 2009148983 A **[0076]**
- WO 2008007318 A **[0076]**
- WO 9219709 A **[0077]**
- WO 9219708 A **[0077]**

Non-patent literature cited in the description

- **SCHWARTZ ; PERRY.** Surface Active Agents. Interscience, 1949, vol. 1 **[0013]**
- **SCHWARTZ ; PERRY ; BERCH.** SURFACE ACTIVE AGENTS. Interscience, 1958, vol. 2 **[0013]**
- McCutcheon's Emulsifiers and Detergents. Manufacturing Confectioners Company **[0013]**
- Tenside-Taschenbuch. Carl Hauser Verlag, 1981 **[0013]**
- Uhlmans Encyclopedia. vol. 3, 91 **[0045]**
- Industrial Dyes. Wiley-VCH, 2003 **[0055]**
- International Buyers Guide. CFTA Publications, 1992 **[0059]**
- Chemicals Buyers Directory 80th Annual Edition. Schnell Publishing Co, 1993 **[0059]**
- **POUCHER.** *Journal of the Society of Cosmetic Chemists,* 1955, vol. 6 (2), 80 **[0061]**
- **DARTOIS et al.** *Biochemica et Biophysica Acta,* 1993, vol. 1131, 253-360 **[0067]**