

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 June 2010 (24.06.2010)

PCT

(10) International Publication Number
WO 2010/069742 A1

- (51) **International Patent Classification:**
C11D 3/386 (2006.01) *C11D 3/28* (2006.01)
C11D 3/20 (2006.01)
- (21) **International Application Number:**
PCT/EP2009/066037
- (22) **International Filing Date:**
30 November 2009 (30.11.2009)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
08172196.1 18 December 2008 (18.12.2008) EP
- (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, MT, MW, MY, NA, NG, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, US, VC, ZA, ZM, ZW): **UNILEVER NV** [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).
- (71) **Applicant** (for AE, AG, AU, BB, BH, BW, BZ, CA, CY, EG, GB, GD, GH, GM, IE, IL, KE, KN, LC, LK, LS, MT, MW, MY, NA, NG, NZ, OM, PG, SC, SD, SG, SL, SZ, TT, TZ, UG, VC, ZA, ZM, ZW only): **UNILEVER PLC** [GB/GB]; a company registered in England and Wales, under company no.41424 of Unilever House, 100 Victoria Embankment, London Greater London EC4Y 0DY (GB).
- (71) **Applicant** (for IN only): **HINDUSTAN UNILEVER LIMITED** [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Maharashtra, Mumbai 400 020 (IN).
- (72) **Inventors; and**
- (75) **Inventors/Applicants** (for US only): **O'KEEFFE, Joanne** [GB/GB]; Unilever R & D Port Sunlight, Quarry

Road East, Bebington Merseyside CH63 3JW (GB). **PARRY, Neil, James** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington Merseyside CH63 3JW (GB). **SMITH, Ian, Karl** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington Merseyside CH63 3JW (GB). **TAYLOR, David** [GB/GB]; Unilever R & D Port Sunlight, Quarry Road East, Bebington, Wirral Merseyside CH63 3JW (GB).

(74) **Agent:** **KAN, Jacob, H**; Unilever Patent Group, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, 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, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, 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, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))



WO 2010/069742 A1

(54) **Title:** LAUNDRY DETERGENT COMPOSITION

(57) **Abstract:** Potential malodour problems are reduced in laundry detergent compositions comprising (i) at least one surfactant, (ii) at least one furanone compound or lactam analogue thereof, and (iii) a microbial cell wall degrading enzyme.

LAUNDRY DETERGENT COMPOSITION

TECHNICAL FIELD

5 The present invention relates to the field of laundry detergent compositions. More in particular, it relates to a laundry detergent composition comprising one or more surfactants, a furanone compound or lactam analogue thereof, and an enzyme.

10 BACKGROUND OF THE INVENTION

Modern laundry detergent compositions have become very effective at cleaning soiled fabrics. One of the remaining challenges is malodour, which may occur under certain circumstances, especially when reduced wash times and lower
15 temperatures are used. It is believed that such conditions may be ineffective at removing microbes and ultimately preventing their metabolism on the fabric and/or in the wash process itself i.e. parts of a washing system. The microbes can then be retained on fabric or can be distributed across garments in the
20 washing process and they can subsequently contribute to malodour being generated on the garment during wear or storage.

Suitable solutions to prevent microbial activity and or achieve microbial kill have traditionally involved the application of
25 strong chemicals such as bleaches. However, there are many formulations that are bleach free and in some products it is beneficial to remove such chemicals. It is also important to develop laundry detergent systems that have a reduced environmental impact.

30

There is a constant need for new or alternative laundry detergent compositions and processes having a reduced tendency for malodour. It is therefore an object of the present

invention to provide such laundry detergent compositions and processes. It is a further object of the invention to provide a process for the preparation of such laundry detergent compositions providing reduced malodour.

5

It has been surprisingly found that this and further objects of the invention may be achieved by the laundry detergent composition according to the invention, comprising

- (i) at least one surfactant,
- 10 (ii) at least one furanone compound or lactam analogue thereof, and
- (iii) a microbial cell wall degrading enzyme.

Furanones are heterocyclic compounds having a five-membered
15 ring containing an oxygen atom. Some furanones have been reported to possess activity as biofilm blocking substances, see for instance WO-A-2006/117113 (Henkel KGaA). Further suitable furanone compounds and their lactam analogues are described in WO-A-2008/040097 (Biosignal Ltd.).

20

It was surprisingly found that such furanones are particularly compatible with other laundry ingredients such as builders and surfactants and that they can act synergistically with an enzyme against microbes present on fabrics and those
25 encountered in the washing process, which results in a reduction of malodour.

DEFINITION OF THE INVENTION

30 According to a first aspect of the invention, there is provided a laundry detergent composition comprising

- (i) at least one surfactant,

- (ii) at least one furanone compound or lactam analogue thereof, and
- (iii) a microbial cell wall degrading enzyme.

5 According to a second aspect of the invention, there is provided a process for laundering textile fabrics by machine or hand, characterised in that it comprises the step of immersing the fabrics in a wash liquor comprising water in which the composition according to the invention is dissolved or
10 dispersed.

According to a third aspect of the invention, there is provided a process for manufacturing a laundry detergent composition according to the invention.

15

DETAILED DESCRIPTION OF THE INVENTION

The laundry detergent composition of the invention comprises, as a first ingredient, at least one surface active ingredients
20 or surfactants. Depending on the physical type of detergent, the surfactants are present in an amount of 0.1 to 60 % by weight of the composition. Typically, an aqueous liquid detergent composition comprises from 5% to 50%, commonly at least 10% and up to 40% by weight of one or more surfactants.
25 Fabric washing powders usually comprise from 20% to 45% by weight of one or more surfactants.

Surfactants are well-known to those skilled in the art. Many suitable detergent-active compounds are available and are fully
30 described in the literature, for example, in "Surface-Active Agents and Detergents", Volumes I and II, by Schwartz, Perry and Berch.

Examples of surfactants include alkylbenzene sulphonates, branched or linear alkyl benzene sulphonates, primary and secondary alcohol sulphates, particularly C₈-C₁₆ primary
5 alcohol sulphates; alkyl ether sulphates, olefin sulphonates, including alpha olefin sulphonates, alkane sulphonates, alkyl xylene sulphonates, dialkyl sulphosuccinates, and alkyl carboxylates. These may be present as sodium, potassium, calcium or magnesium salts or mixtures of these. Sodium salts
10 are generally preferred.

The surfactant is preferably a sulphonate or sulphate anionic surfactant or a combination thereof. More preferably, the anionic surfactant is linear alkylbenzene sulphonate or primary
15 alkyl sulphate. Most preferably the other surfactant is linear alkylbenzene sulphonate. The linear alkyl benzene sulphonate may be present as sodium, potassium, or alkaline earth metal salts, or mixtures of these salts. Sodium salts are generally preferred.

20

The surfactant may also comprise a nonionic surfactant, preferably an ethoxylated alcohol nonionic surfactant with an average degree of ethoxylation ranging from about 3 to 9, preferably from about 3 to 7. The alcohol may be derived from
25 natural or synthetic feedstock. Preferred alcohol feedstocks are coconut and palm kernel, predominantly C₁₂-C₁₄, and oxo C₁₂-C₁₅ alcohols.

The nonionic surfactant is suitably present in an amount of
30 from 1 to 20 wt.%, preferably from 1 to 10, more preferably from 2 to 6 wt.%, most preferably from 3 to 5 wt.%, based on the weight of the total composition.

Additional surfactants may comprise other nonionics such as alkylpolyglucosides, polyhydroxyamides (glucamide), methyl ester ethoxylates and glycerol monoethers. Also cationic, 5 amphoteric surfactants and/or zwitterionic surfactants may be present. Preferred cationic surfactants are quaternary ammonium salts of the general formula $R_1R_2R_3R_4N^+ X^-$, for example where R_1 is a C_{12} - C_{14} alkyl group, R_2 and R_3 are methyl groups, R_4 is a 2-hydroxyethyl group, and X^- is a chloride ion. This material 10 is available commercially as Praepagen (Trade Mark) HY from Clariant GmbH, in the form of a 40 wt.% aqueous solution.

Preferred amphoteric surfactants are amine oxides, for example coco dimethyl amine oxide. Preferred zwitterionic surfactants 15 are betaines, and especially amidobetaines. Preferred betaines are C_8 to C_{18} alkyl amidoalkyl betaines, for example coco amido betaine. These may be included as co-surfactants, preferably present in an amount of from 0 to 10 wt.%, more preferably 1 to 5 wt.%, based on the weight of the total composition.

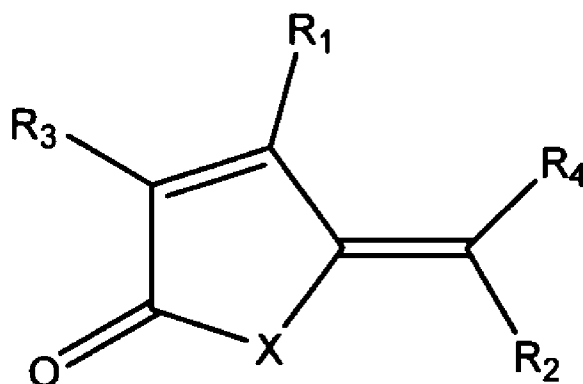
20

The laundry detergent may also contain a biological based surfactant, as sourced and generated via microbial fermentation. Such biosurfactants that could be used are described in Pattanathu *et al.* Biotechnology 7 (2) 360-370 25 (2008) and Muthusamy *et al.* Current Science Vol. 94 N°6 736-747 (2008).

The laundry detergent composition of the invention comprises, as a second ingredient, one or more furanone compounds or their 30 lactam analogues. As mentioned above, furanones are heterocyclic compounds having a five-membered ring containing

an oxygen atom. Suitable furanone compounds and their lactam analogues are described in WO-A-2008/040097 (Biosignal Ltd.).

Preferably, the furanone compound has the general formula



I

5 I

w

herein X is selected from -O- or -N(R5)-; wherein R5 is selected from H, alkyl, aryl and arylalkyl; R1 is selected from H, halo, alkyl, aryl and heteroaryl; R2 and R4 are each independently selected from hydrogen, aryl and heteroaryl with
 10 the proviso that both R2 and R4 cannot be hydrogen; and R3 is selected from H, alkyl, heteroaryl and aryl. R4 and R3 are preferably H. It is preferred that wherein R2 is aryl or heteroaryl. The aryl is preferably a phenyl group, optionally substituted with one or more substituents selected from the
 15 group consisting of CF₃, OCF₃, cyano (CN), halo, F, alkoxy and methoxy. The heteroaryl is preferably a five-membered heteroaromatic ring containing one or more heteroatoms selected from O, N and S. Preferably, the five-membered heteroaromatic ring is a thiophene.

20

In there formula I, R1 is preferably aryl, heteroaryl or halo, wherein halo is Br. The aryl is preferably a phenyl group

optionally substituted with one or more substituents selected from the group consisting of CF₃, OCF₃, cyano (CN), halo and F. The heteroaryl is preferably a five-membered heteroaromatic ring containing one or more heteroatoms selected from O, N and S. In an especially preferred embodiment the five-membered heteroaromatic ring is a thiophene. Hereby, each of R₁ and R₂ are preferably the same substituent selected from aryl and heteroaryl.

10 Alternatively, one may employ the lactam analogues of such furanones, which are also described in WO-A-2008/040097.

Highly preferred compounds are:

Compound	Name
113	3-Bromo-4-hexyl-5-(bromomethylene)-2(5H)-furanone
265	4-(4-Trifluoromethyl)phenyl)-2(5H)-furanone
295	5-methylene-4-(4'-bromophenyl)-dihydropyrrol-2-one
310	5-methylene-4-(2'-fluorophenyl)-dihydropyrrol-2-one
313	5-Hydroxy-5-methyl-4-(2'-fluorophenyl)-dihydropyrrol-2-one
350	5-(Thiophen-3-ylmethylene)furan-(2H)-one

15 The furanone compound or its lactam analogue would generally be present in an amount of 0.0001 to 20 wt.% of the composition. The desired in use concentration of the furanone is generally from 0.1 to 1000ppm, more preferably from 0.5 to 500ppm, most
20 preferably from 1 to 50ppm.

The laundry detergent composition of the invention comprises, as a third ingredient, one or more other microbial cell wall degrading enzymes. By the term "microbial cell wall degrading

enzyme" we mean in the context of the present invention, any enzyme that can effect or assist in the degradation of microbial cell walls. The enzymes are capable, directly or indirectly through their activity, of modifying the surrounding
5 matrix or environment around the microbial entity or of modifying the cell wall of the microbe itself. The enzymes are suitably selected from the group consisting of glycosyl hydrolases (mannanase, glucanase, hemicellulase, cellulase, amylase, glycosidase, lysozyme, exopolysaccharidase, chitinase,
10 ligninase), lactonase, transferase, amidase, protease, lipase, phospholipase, esterase, cutinase, polyesterase, oxidoreductases (laccase, peroxidase, pyranose oxidase, haloperoxidase), lysostaphin, perhydrolase.

15 Preferred microbial cell wall degrading enzymes are protease, lipase, esterase (cutinase and polyesterase) and glycosyl hydrolases such as mannanase and amylase.

Suitable members of these enzyme classes are described in
20 Enzyme nomenclature 1992: recommendations of the Nomenclature Committee of the International Union of Biochemistry and Molecular Biology on the nomenclature and classification of enzymes, 1992, ISBN 0-12-227165-3, Academic Press. The most recent information on the nomenclature of enzymes is available
25 on the Internet through the ExPaSy Molecular Biology Server (<http://us.expasy.org/>).

The compositions may also contain a lipase variant of the *Humicola lanuginosa* lipase with substitutions T231R + N233R,
30 commercially available as Lipex™ from Novozymes or another variant as described in WO-A-00/60063. Examples of commercially available bacterial lipase, cutinase or esterase are Lumafast™ and Lipomax™ or variants thereof.

The composition may contain commercial enzymes such as the new enzymes from Novozymes: Mannaway™, Natalase™, Renozyme™, Ovozyme™, CelluClean™, Polarzyme™, Stainzyme™, Coronase™, 5 Pectaaway™, Pectawash™, Termamyl Ultra™. And the new enzymes from Genencor: FN-3, FN-4, Purafect Prime™, Properase™.

The compositions of the invention may also contain maltogenic α -amylases as described in WO-A-02/02726 page 5, line 14 to 10 page 11 line 29. Commercially available maltogenic α -amylases are Novamyl™ and Maltogenase™ from Novozymes.

Enzymes capable of hydrolysing or removing biofilms are known in the art, e.g. Amylase WO2006031554 (Novozymes), 15 Oxidoreductases EP946207 (Novozymes), Endogalactonase WO2001023534 (VTT Biotechnology), Enzyme libraries for biofilm control WO20040606945 (Verenium Corp), Mannanases EP871596, exopolysaccharidases EP820516 (Betzadearborn), Carbohydrase / protease WO2001053010 (University Madrid). As such, these and 20 other enzyme families can be used as the third ingredient in the invention. The enzyme may be a single enzyme or a mixture of enzymes.

Optional ingredients

25 The laundry detergent composition of the invention may additionally comprise a number of the following optional ingredients which provide cleaning performance, fabric care and/or sanitation benefits.

30 Detergency builder

The compositions of the invention may contain a detergency builder. Preferably the builder is present in an amount of from

1 to less than 80 wt.% based on the weight of the total composition. More preferably the amount of builder is from 1 to 60 wt.%. Builders are well-known to those skilled in the art. Many suitable builder compounds are available. Examples are 5 zeolites, sodium tripolyphosphate, layered silicate, sodium carbonate, sodium bicarbonate, burkeite, sodium silicate and mixtures thereof.

The optional builder may be selected from strong builders such 10 as phosphate builders, aluminosilicate builders and mixtures thereof. However, strong builders are preferably present in an amount not exceeding 5 wt.%, and most preferably strong builders are absent. One or more weak builders such as calcite/carbonate, beryllium/carbonate, citrate or polymer 15 builders may be additionally or alternatively present.

The phosphate builder (if present) may for example be selected from alkali metal, preferably sodium, pyrophosphate, orthophosphate and tripolyphosphate, and mixtures thereof. 20

The aluminosilicate (if present) may be, for example, selected from one or more crystalline and amorphous aluminosilicates, for example, zeolites as disclosed in GB 1 473 201 (Henkel), amorphous aluminosilicates as disclosed in GB 1 473 202 25 (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)

The alkali metal aluminosilicate may be either crystalline or 30 amorphous or mixtures thereof, having the general formula: $0.8 \text{ Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 0.8 \text{ SiO}_2$.

These materials contain some bound water and are required to have a calcium ion exchange capacity of at least 50 mg CaO/g. The preferred sodium aluminosilicates contain 1.5-3.5 SiO₂ units (in the formula above). Both the amorphous and the
5 crystalline materials can be prepared readily by reaction between sodium silicate and sodium aluminate, as amply 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
10 sodium aluminosilicates of this type are the well known commercially available zeolites A and X, and mixtures thereof.

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according
15 to a preferred embodiment of the invention, the zeolite 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 an alkali metal aluminosilicate of the zeolite P type having a silicon to
20 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.

Suitably zeolite MAP may be used, having a silicon to aluminium
25 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.

Bleaches

30 Detergent compositions according to the invention may suitably contain a bleach system. The bleach system is preferably based on peroxy bleach compounds, for example, inorganic persalts or

organic peroxyacids, capable of yielding hydrogen peroxide in aqueous solution. Suitable peroxy bleach compounds include organic peroxides such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, 5 perphosphates, persilicates and persulphates. Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate. Especially preferred is sodium percarbonate having a protective coating against destabilisation by moisture. Sodium percarbonate having a 10 protective coating comprising sodium metaborate and sodium 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.%. The peroxy 15 bleach compound may be used in conjunction with a bleach activator (bleach precursor) to improve bleaching action at low wash temperatures. The bleach precursor is suitably present in an amount of from 1 to 8 wt.%, preferably from 2 to 5 wt.%.

20 Preferred bleach precursors are peroxy-carboxylic acid precursors, more especially peracetic acid precursors and peroxybenzoic acid precursors; and peroxy-carbonic acid precursors. An especially preferred bleach precursor suitable for use in the present invention is N,N,N',N'-tetracetyl 25 ethylenediamine (TAED). Also of interest are peroxybenzoic acid precursors, in particular, N,N,N-trimethylammonium toluoyloxy benzene sulphonate.

A bleach stabiliser (heavy metal sequestrant) may also be 30 present. Suitable bleach stabilisers include ethylenediamine tetraacetate (EDTA) and the polyphosphonates such as Dequest (Trade Mark), EDTMP.

Alternatively the present invention may be used in a formulation that is used to bleach via air, or an air bleach catalyst system. In this regard the bleaching composition substantially devoid of a peroxygen bleach or a peroxy-based or
5 peroxy-generating bleach system.

The term "substantially devoid of a peroxygen bleach or a peroxy-based or peroxy-generating bleach system" should be construed within spirit of the invention. It is preferred that
10 the composition has as low a content of peroxy species present as possible. It is preferred that the bleaching formulation contains less than 1 % wt./wt. total concentration of peracid or hydrogen peroxide or source thereof, preferably the bleaching formulation contains less than 0.3 % wt./wt. total
15 concentration of peracid or hydrogen peroxide or source thereof, most preferably the bleaching composition is devoid of peracid or hydrogen peroxide or source thereof. In addition, it is preferred that the presence of alkyl hydroperoxides is kept to a minimum in a bleaching composition comprising the ligand
20 or complex of the present invention.

In order to function as an air bleaching composition the bleaching composition comprises an organic substance that forms a complex with a transition metal for bleaching a substrate
25 with atmospheric oxygen.

The bleach catalyst per se may be selected from a wide range of transition metal complexes of organic molecules (ligands). In typical washing compositions the level of the organic substance
30 is such that the in-use level is from 0.05 μM to 50 mM, with preferred in-use levels for domestic laundry operations falling in the range 1 to 100 μM . Higher levels may be desired and applied in industrial textile bleaching processes.

Suitable organic molecules (ligands) for forming complexes and complexes thereof are found, for example in: WO-A-98/39098; WO-A-98/39406, WO 9748787, WO 0029537; WO 0052124, and WO0060045
5 the complexes and organic molecule (ligand) precursors of which are herein incorporated by reference. An example of a preferred catalyst is a transition metal complex of MeN₄Py ligand (N,N-bis(pyridin-2-yl-methyl)-1,1-bis(pyridin-2-yl)-1-aminoethane).

10 Further enzymes

The laundry detergent composition of the invention may comprise one or more further enzymes other than microbial cell wall degrading enzymes, which provide cleaning performance, fabric care and/or sanitation benefits.

15

In the compositions of the invention, all enzymes are usually employed in granular form in amounts of from about 0.1 to about 10.0 wt.%, preferably from about 0.2 to about 3% by weight, more preferably from about 0.2 to about 1% by weight.

20

Further optional ingredients

The detergent compositions of the invention may further comprise one or more of the following optional ingredients selected from soap, sequestrants, cellulose ethers and esters,
25 cellulosic polymers, other antiredeposition agents, sodium chloride, calcium chloride, sodium bicarbonate, other inorganic salts, fluorescers, photobleaches, polyvinyl pyrrolidone, other dye transfer inhibiting polymers, foam controllers, foam boosters, acrylic and acrylic/maleic polymers, citric acid,
30 soil release polymers, silicone, fabric conditioning compounds, coloured speckles such as blue speckles, and perfume. This list is not intended to be exhaustive.

of BASF Aktiengesellschaft, D-6700 Ludwigshaven, Germany describes organic polymers which are useful. Preferably, the polycarboxylate polymer is selected from the group consisting of sodium polyacrylate, sodium acrylate maleate and mixtures
5 thereof. Examples of suitable polymers include Sokalan CP5, ex BASF polyacrylate, namely maleic acid-acrylic acid copolymer, with a sodium salt.

Form of the composition

10 The laundry detergent composition of the invention may be in any convenient dry form, e.g., a bar, a tablet, a powder, a particle or a paste. It may also be a liquid detergent, in particular low-content aqueous (less than 70% by weight) or
15 non-aqueous liquid detergent. If it is in a powder form, it preferably has a mean particle size between 200 and 800 micrometer. Alternatively, the compositions may be in tablet form. The compositions can be formulated for use as hand wash or machine wash detergents.

20 Preparation of the compositions

The granular compositions of the invention may be prepared by any suitable process. Powders of low to moderate bulk density may be prepared by spray-drying a slurry, and optionally
25 postdosing (dry-mixing) further ingredients. "Concentrated" or "compact" powders may be prepared by mixing and granulating processes, for example, using a high-speed mixer/granulator, or other non-tower processes.

Tablets may be prepared by compacting powders, especially
30 "concentrated" powders. The choice of processing route may be in part dictated by the stability or heat-sensitivity of the

surfactants involved, and the form in which they are available. In all cases, all ingredients may be added separately.

The invention will now be further illustrated by the following, 5 non-limiting Examples, in which parts and percentages are by weight, unless indicated otherwise.

In the Figures:

10 Figure 1 shows a two-day biofilm treated with furanone compounds, with and without one of two enzymes (polyesterase or protease), in a laundry detergent base formulation.

Figure 2 shows a two-day biofilm treated with furanone compounds, with and without one of two enzymes (polyesterase or 15 protease), in sterile distilled water.

Figure 3 shows Images obtained after treatment of attached bacterial cells with a dilute laundry liquid base (LLB).

Figure 4 shows the darkness (%) levels assigned to each image of Figure 3.

20

EXAMPLE 1

METHOD AND MATERIALS

25 **Bacterial Cultures**

Bacteria were established as overnight cultures on tryptone soya agar (TSA) at 37°C. Colonies from these agar plates were suspended in tryptone diluent. The optical density (measured in McFarland units) was established using a Densimat (BioMeriux).

30 The resulting bacterial suspension should read between 1.5 - 1.7 which equates to a suspension containing $1-5 \times 10^8$ cfu/ml.

Biofilm Development

A 1:10 dilution of the bacterial suspension was prepared in 25% Tryptone Soya Broth (TSB). This bacteria and media solution was then added (100µl) to the wells of a PreSens microplate and incubated at 28°C for 48h in static, moist conditions.

5

Test Formulations

Stocks:

The Liquid Laundry Base (LLB) had the following composition:

		As total formulation		
Name	Active (%)	as 100%	as received	Weight
		(%)	(%)	(g)
demin water	100.0		37.16	1486.27
Tinopal 5BM-GX	68.0	0.10	0.15	5.88
MPG	100.0	7.43	7.43	297.20
Glycerol	100.0	4.13	4.13	165.20
NaOH	47.0	2.23	4.74	189.79
TEA	100.0	2.67	2.67	106.80
Citric acid	50.0	0.81	1.62	64.80
Neodol 25-7E	100.0	16.59	16.59	663.60
LAS acid	97.1	11.06	11.39	455.61
prifac 5908	100.0	3.94	3.94	157.60
SLES 3EO	70.0	5.53	7.90	316.00
Dequest 2066	32.0	0.41	1.28	51.25
Savinase Ultra 16L	100.0	1.00	1.00	40.00
			100.00	4000.00

10

It was diluted to 2.3g/L in sterile distilled water.

Furanone compounds were:

Compound	Name
113	3-Bromo-4-hexyl-5-(bromomethylene)-2(5H)-furanone
265	4-(4-Trifluoromethyl)phenyl)-2(5H)-furanone
295	5-methylene-4-(4'-bromophenyl)-dihydropyrrol-2-one
310	5-methylene-4-(2'-fluorophenyl)-dihydropyrrol-2-one
313	5-Hydroxy-5-methyl-4-(2'-fluorophenyl)-dihydropyrrol-2-one
350	5-(Thiophen-3-ylmethylene)furan-(2H)-one

Stock solutions of each compound were prepared in neat mono propylene glycol to 500 ppm (0.01g of each into 20ml MPG).

5 Enzymes: Supplied as 1mg/ml or 1000 ppm in PBS (phosphate buffered saline).

Mixes:

Using the stock for each compound, a 1:10 dilution was prepared
 10 in SDW and the laundry base, thereby resulting in 50ppm of each compound in each base. This was repeated, but using a 1:5 dilution to achieve 100 ppm levels of each compound in each base. Enzymes were diluted 1:100 in SDW or dilute laundry base, resulting in 10 ppm levels. If furanones and enzymes were
 15 mixed, the furanone samples at 100 ppm samples were used in mixing with the 10 ppm levels of enzyme (1:1 dilution), resulting in a final concentration of 50 ppm furanone and 5 ppm enzyme in either the SDW base or the dilute laundry base. All test formulations were prepared at the time of assessment.

20

Treatment

Following 48h incubation of the biofilm plate, the wells were rinsed three times with PBS (120µl) using a multi-channel pipette. The test samples were then added (100µl) for 2h

(static at room temperature) then removed. Following treatment, the wells were rinsed again three times with PBS (120µl) using a multi-channel pipette.

5 **Detecting respiration from the remaining viable cells**

Following treatment and rinsing, neat TSB was introduced into the wells (200µl) and a sterile, gas permeable sheet was placed on top of the plate. Plates were then incubated at 37°C for 20h. Bacterial respiration within each well was determined using a Genios plate reader and the Tecan workstation was employed to transfer the plates between the plate reader and the incubator. The data generated was represented as time required to detect bacterial respiration (mid way through the exponential phase of the "growth" curve for the control i.e. no treatment).

The results are shown in Figures 1 and 2. The combination of furanones and a microbial cell wall degrading enzyme (polyesterase or protease) is very effective in delaying bacterial growth.

EXAMPLE 2

25 The level of bacterial removal was established after treating attached bacterial cells with a dilute laundry liquid base (LLB) with and without an enzyme, with and without a furanone compound.

30 Glass slides (2cm²) were cleaned using ethanol and left to dry, then rinsed in sterile distilled water (SDW) and dried at 37°C lay flat on a tray. Bacterial suspensions of *P. aeruginosa* and *F. odoratum* were prepared (1-1.5 x 10⁸ cfu/ml) in phosphate buffered saline and an aliquot (500µl) of each suspension added

to 9ml tryptone soya agar and mixed gently. Aliquots (100µl) of the bacterial suspension were placed onto each slide and the inocula spread to the edge using the pipette tip. The tray was then placed into a large sterile bag (un-sealed) and placed 5 into 37°C incubator overnight. The slides were re-inoculated the day afterwards using a fresh bacterial suspension and returned to the incubator.

Treatment

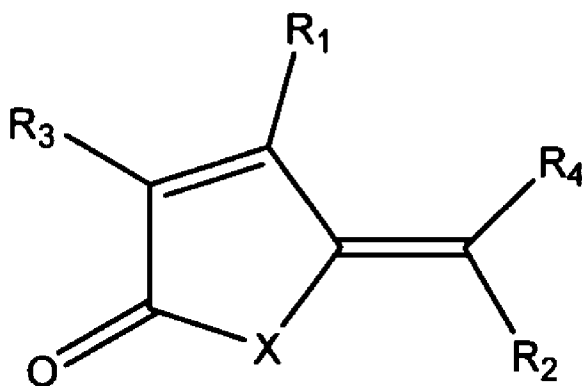
- 10 Dilute test solutions (3ml) were placed into the wells of a 12 well MTP and the glass slides placed vertically into the test solution for 30 min at room temperature (no agitation). The slides were removed and rinsed lightly with SDW using a wash bottle. The slides were then placed flat onto the tray and 15 incubated (37°C) to dry. Ethanol (70%) was sprayed onto the slides to fix, and then the slides were stained using crystal violet solution. Representative images were obtained using x100 oil immersion lens (Figure 3).
- 20 Crude quantitative analysis was performed on the images as a way to enumerate the level of surface coverage by the bacteria. This was done by opening each image in IrfanView and *greyscaling* the image. The *Enhanced colours* option was then selected and the *contrast scale* slid fully to the right 25 (maximum). This produced images that consisted of black and white pixels. The images were then opened in PaintShop Pro and the Histogram option was selected. This enabled a quantitative assignment of the percentage "darkness" that was on each image, which is representative of the level of bacterial coverage post 30 treatment. See Figure 4 and Table 1 below.

Table 1: Darkness (%) levels assigned to each image.

	Image darkness (%)
LLB (no enzyme)	24.7
LLB (no enzyme) Furanone (2ppm)	9.9
LLB (no enzyme) Furanone (5ppm)	6.0
LLB (with enzyme)	15.8
LLB (with enzyme) Furanone (2ppm)	0.6
LLB (with enzyme) Furanone (5ppm)	0.9
Untreated	77.9

Claims

1. A laundry detergent composition comprising
 - (i) at least one surfactant,
 - (ii) at least one furanone compound or lactam analogue thereof, and
 - (iii) a microbial cell wall degrading enzyme.
2. A laundry detergent composition according to claim 1, wherein the furanone compound has the general formula

**I**

I:

wherein X is selected from -O- or -N(R₅)-; wherein R₅ is selected from H, alkyl, aryl and arylalkyl; R₁ is selected from H, halo, alkyl, aryl and heteroaryl; R₂ and R₄ are each independently selected from hydrogen, aryl and heteroaryl with the proviso that both R₂ and R₄ cannot be hydrogen; and R₃ is selected from H, alkyl, heteroaryl and aryl.

3. A laundry detergent composition according to any one of the preceding claims, wherein R₄ is H.

4. A laundry detergent composition according to any one of the preceding claims, wherein R3 is H.
5. A laundry detergent composition according to any one of the preceding claims, wherein R2 is aryl or heteroaryl.
6. A laundry detergent composition according to any one of the preceding claims, wherein the microbial cell wall degrading enzyme is selected from the group consisting of glycosyl hydrolases (mannanase, glucanase, hemicellulase, cellulase, amylase, glycosidase, lysozyme, exopoly-saccharidase, chitinase, ligninase), lactonase, Transferase, amidase, protease, lipase, phospholipase, esterase, cutinase, polyesterase, oxidoreductases (laccase, peroxidase, pyranose oxidase, haloperoxidase), lysostaphin, perhydrolase.
7. A laundry detergent composition according to any one of the preceding claims, wherein the cell wall degrading enzymes is selected from the group consisting of protease, lipase, esterase (cutinase and polyesterase) and glycosyl hydrolases such as mannanase and amylase.
8. A laundry detergent composition according to any one of the preceding claims, wherein the enzymes are capable, directly or indirectly through its activity, in modifying the surrounding matrix or the environment around the microbial entity or in modifying the cell wall of the microbe itself.
9. A laundry detergent composition according to any one of the preceding claims detergent composition according to any one of the preceding claims, comprising a builder in an amount of

from 1 to 60%, preferably from 1 to 40% by weight.

10. A laundry detergent composition according to claim 8, wherein said builder selected from the group consisting of zeolite, sodium tripolyphosphate, layered silicate, sodium carbonate, sodium bicarbonate, burkeite, sodium silicate and mixtures thereof.

11. Process for laundering textile fabrics by machine or hand, characterised in that it comprises the step of immersing the fabrics in a wash liquor comprising water in which the composition according to the invention is dissolved or dispersed.

12. Process for manufacturing a granular detergent composition according to any one of the preceding claims.

Fig.1.

S. epidermidis: 2 day biofilm treated with furanone compounds, with and without one of two enzymes (Polyesterase or Protease) in a Laundry Detergent Base

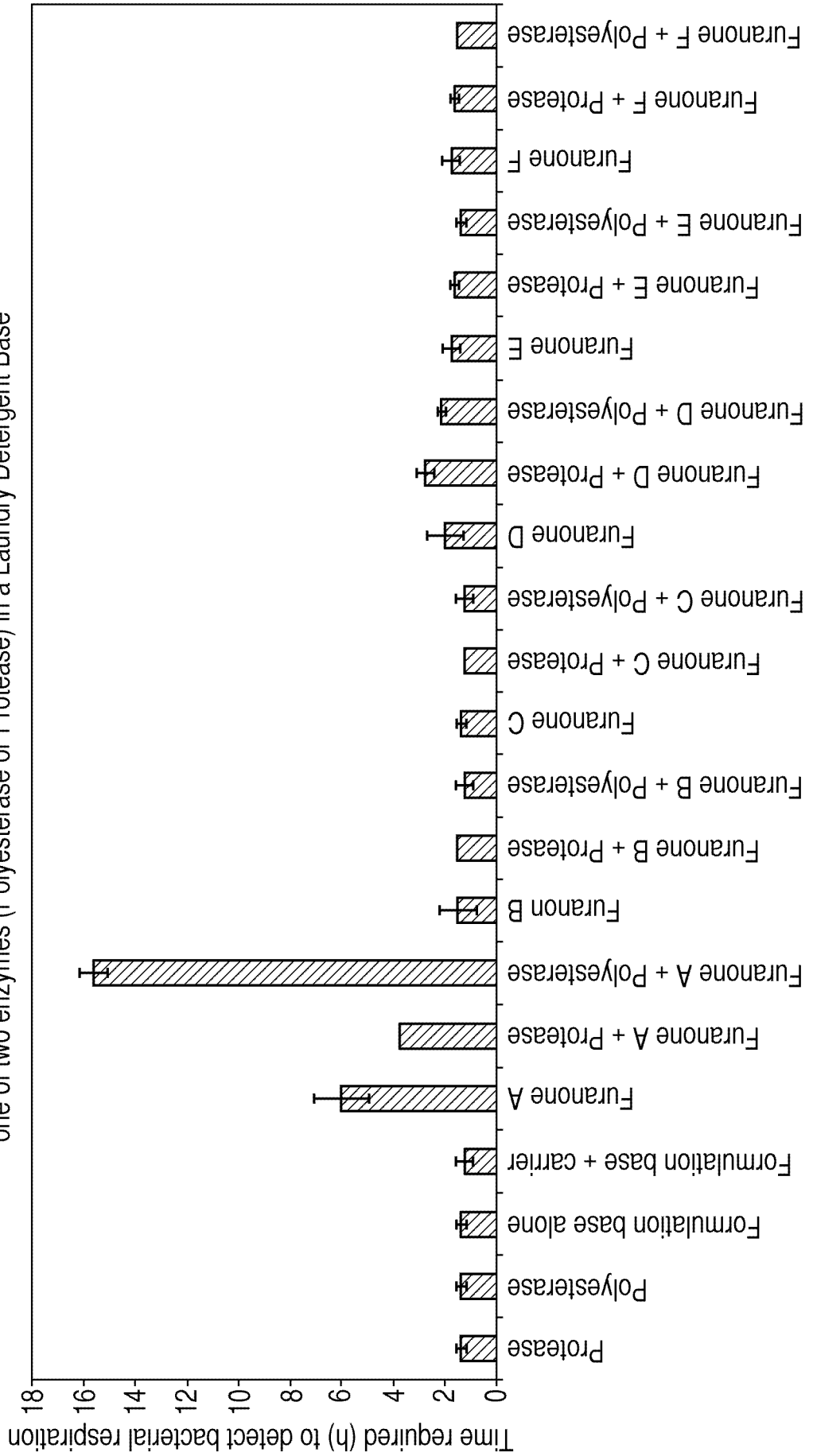


Fig.2.

S. epidermidis: 2 day biofilm treated with furanone compounds, with and without one of two enzymes (Polyesterase or Protease) in Sterile Distilled Water

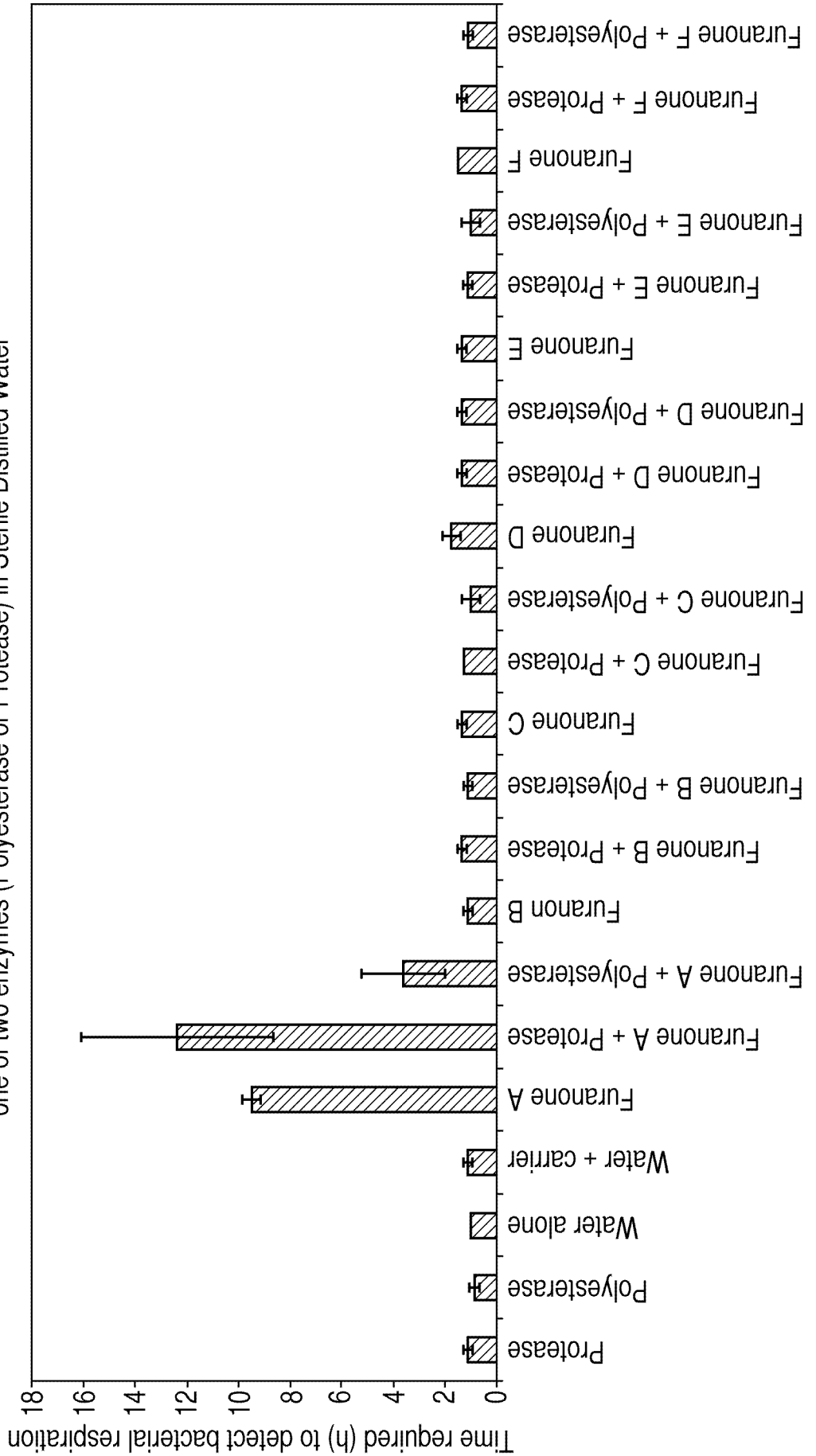
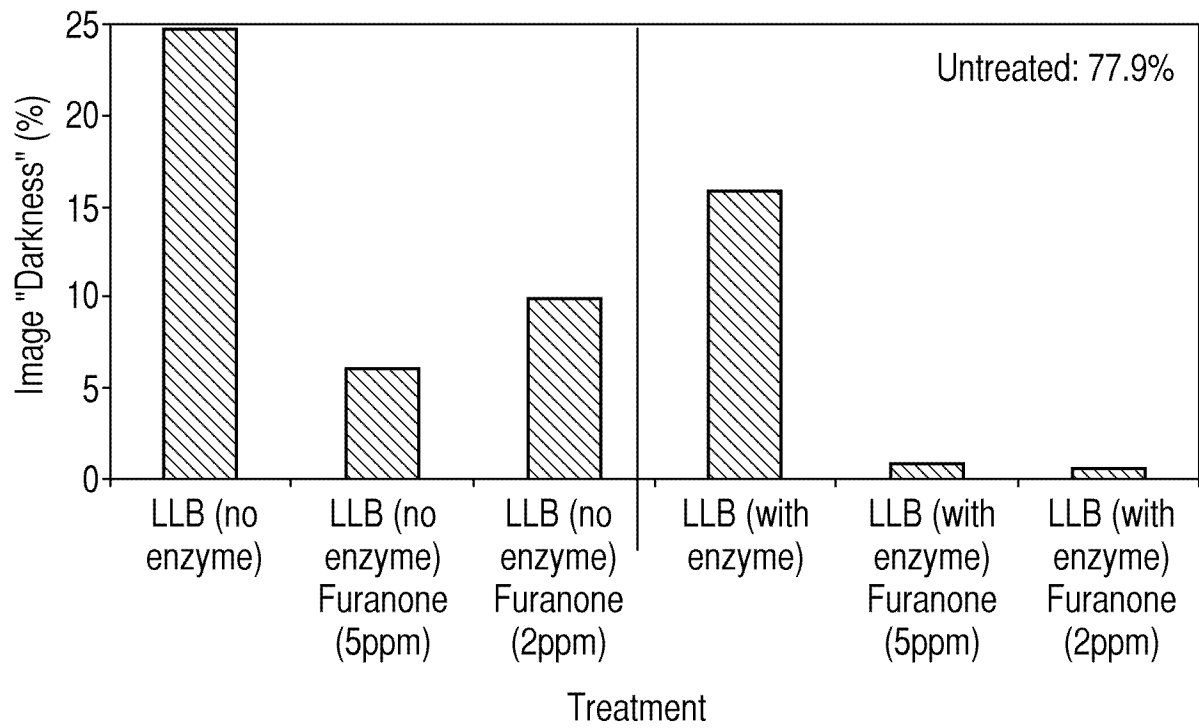


Fig.4.



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/066037

A. CLASSIFICATION OF SUBJECT MATTER INV. C11D3/386 C11D3/20 C11D3/28		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C11D A01N		
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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 98/26807 A (NOVONORDISK AS [DK]) 25 June 1998 (1998-06-25) claims	1-12
Y	WO 2008/040097 A (BIOSIGNAL LTD [AU]; KUMAR NARESH [AU]; ISKANDER GEORGE [AU]) 10 April 2008 (2008-04-10) claims	1-12
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> 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	"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	
"E" earlier document but published on or after the international filing date	"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	
"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)	"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.	
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
26 February 2010	17/03/2010	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Culmann, J	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2009/066037

Patent document cited in search report	Publication date	Patent family member(s)	Publication date		
WO 9826807	A	25-06-1998	AT 207367 T 15-11-2001		
			AU 5310298 A 15-07-1998		
			CA 2275157 A1 25-06-1998		
			DE 69707701 D1 29-11-2001		
			DE 69707701 T2 01-08-2002		
			EP 0946207 A1 06-10-1999		
			ES 2167022 T3 01-05-2002		
			JP 4191253 B2 03-12-2008		
			JP 2001508677 T 03-07-2001		
			PT 946207 E 29-04-2002		
			US 6100080 A 08-08-2000		
			WO 2008040097	A	10-04-2008
CN 101646664 A 10-02-2010					
US 2010035948 A1 11-02-2010					