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(71) Applicant: **Deco Industrie S. Coop. P.A.**  
**48012 Bagnacavallo (RA) (IT)**

(72) Inventors:  

- FABBRI, Samanta**  
**48012 BAGNACAVALLO (RA) (IT)**
- EGENOLF, Francesca**  
**48012 BAGNACAVALLO (RA) (IT)**
- DI CHIARO, Vito**  
**48012 BAGNACAVALLO (RA) (IT)**

(74) Representative: **Studio Torta S.p.A.**  
**Via Viotti, 9**  
**10121 Torino (IT)**

### (54) PRODUCT FOR WASHING MACHINES

(57) A product for washing machines; the product (1) comprises a substantially water-soluble sheet (2); a collecting chamber (3), delimited by the sheet (2); and an inner composition (4), which is substantially liquid and

two-phase, is arranged inside the collecting chamber (3) and comprises an organic solvent, a nonionic surfactant, a sequestering component, a detergent enzymatic component and from 0% to 20% of water.

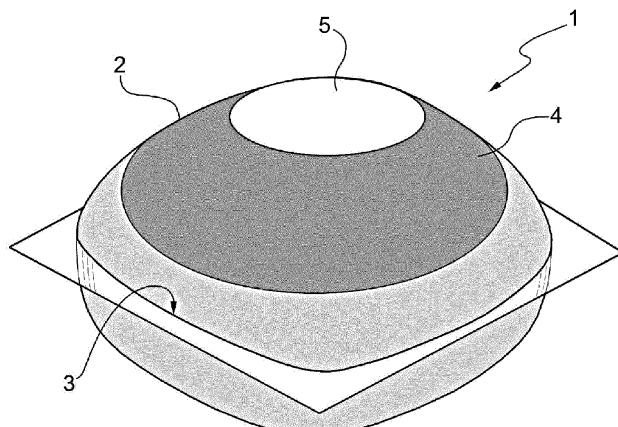


FIG.1

**Description**TECHNICAL FIELD

5 [0001] The present invention concerns a product for washing machines and uses of said product.

CROSS-REFERENCE TO RELATED APPLICATIONS

10 [0002] This patent application claims priority from Italian patent application no. 102021000002048 filed on February 1, 2021.

BACKGROUND TO THE INVENTION

15 [0003] Anti-scale products for washing machines are liquid products at high dilution ( $H_2O > 80\%$ ), preferably with pH varying from 4 to 7, which are added directly in the washing machine detergent drawer together with the detergent at every wash. Anti-scale products therefore cooperate with the detergent by sequestering the limescale present, thus improving the washing performance of the detergent. They therefore perform their action during the washing phase.

20 [0004] The formulations currently on the market consist of a pool of sequestering agents and dispersing agents. These products are generally sold in bottles of various volumes (500-1500ml) with measuring cap. Normally, 25-100ml of product are used per wash.

[0005] Anti-scale products for washing machines have various drawbacks, including the following: they are contained in bottles made of non bio-degradable plastic material (and therefore have a negative environmental impact), they are relatively difficult to measure out (making washing machine filling operations more complex and inaccurate - they also increase the risk of wastage) and do not allow for satisfactory improvement of the detergent action on all types of dirt.

25 [0006] Liquid detergents sold in water-soluble single-dose capsules are also known. However, they are not able to perform the functions of the above-mentioned anti-scale and washing machine care products and so far have been produced only in single-phase version.

[0007] In relation to this aspect, it is observed that users increasingly demand two-phase products for use in washing machines.

30 [0008] These products, in addition to having greater aesthetic appeal, give users the impression that the product has several components and can, therefore, function more effectively. However, up to now two-phase compositions have been proposed only with a high water content. These compositions are obviously not compatible with water-soluble packaging.

35 [0009] The object of the present invention is to provide a product for washing machines and uses of said product which overcome, at least partially, the drawbacks of the known art and if possible are, at the same time, easy and inexpensive to produce.

SUMMARY

40 [0010] According to the present invention a product for washing machines and uses of said product are provided as claimed in the following independent claim and, preferably, in any one of the claims depending directly or indirectly on the independent claim.

BRIEF DESCRIPTION OF THE FIGURES

45 [0011] The invention is described below with reference to the attached drawings, which illustrate a non-limiting embodiment example thereof, in which:

50 - figure 1 is a perspective view of a product according to the present invention arranged horizontally;  
- figure 2 is a plan view of the product of figure 1; and  
- figure 3 is a front view of the product of figure 1 arranged vertically.

DETAILED DISCLOSURE

55 [0012] In figure 1 the number 1 indicates overall a product for washing machines. The product 1 is for washing laundry and reducing the formation of scale in washing machines. In other words, the product 1 acts simultaneously as a detergent for laundry (it washes the laundry) and as an anti-scale product (it protects the washing machine).

[0013] The product 1 comprises a substantially water-soluble (in particular, biodegradable) sheet 2; a collecting cham-

ber 3, at least partially delimited by the sheet 2; and an inner composition 4, which is substantially liquid, is arranged inside the collecting chamber 3 and comprises 0% to 20% by weight, with respect to the total weight of said inner composition 4, of water; at least one non-ionic surfactant; an organic solvent, selected from the group consisting of: alcohols, diols, triols, polyols and a combination thereof; a detergent enzymatic component; and a sequestering component.

[0014] The inner composition 4 has at least two phases (more in particular it is two-phase - as illustrated in the figures).

[0015] In other words, the inner composition 4 has a first phase, which comprises the non-ionic surfactant (in particular and predominantly, also the detergent enzymatic component and/or if necessary an anionic surfactant - described in further detail below); and a second phase, which comprises the organic solvent (water if necessary), the sequestering component (and if necessary an alkalizing agent and/or a polymer component - described in further detail below). More precisely but not necessarily, the first and the second phase are (substantially) immiscible (between each other). In particular (since the inner composition 4 is substantially liquid), the first phase and the second phase are substantially liquid.

[0016] More in particular, in the first (upper) phase (portion - illustrated in darker grey in the attached figures) of the inner composition 4, the non-ionic surfactant is collected (is arranged - predominantly) (in particular, also the enzymatic component and/or if necessary the anionic surfactant); in the second (lower) phase (portion - shown in lighter grey in the attached figures) of the inner composition 4, the organic solvent (water if necessary) is collected (is arranged - predominantly), together with the sequestering component and if necessary the alkalizing agent and/or the polymer component.

[0017] In this context, advantageously but not necessarily, the inner composition 4 comprises a dye (a first organic pigment) which is arranged predominantly together with the non-ionic surfactant thus visually distinguishing, even more evidently, the division between the two phases.

[0018] Alternatively or additionally, the inner composition 4 comprises a further dye (a second organic pigment having a colour different, if possible, from the first organic pigment) which is arranged predominantly together with the organic solvent. In practice, the inner composition 4 can be coloured only in the first phase (upper portion); or the inner composition 4 can be coloured only in the second phase (lower portion); or the first phase and the second phase of the inner composition 4 can have two different colours.

[0019] In other words, the inner composition 4 comprises at least a dye so that the first and the second phase have different colours from each other.

[0020] It should be noted that when a component of the inner composition 4 is said to be arranged "predominantly" in a phase (portion), it means that the quantity of said component in that phase is higher than (in particular, is at least double) the quantity of the same component throughout the rest of the inner composition 4.

[0021] Advantageously but not necessarily, the inner composition comprises 5% to 60% (in particular, 57%) by weight, with respect to the total weight of the inner composition 4, of the organic solvent.

[0022] According to some preferred but non-limiting embodiments, the inner composition 4 comprises up to a maximum of 15% (in particular, up to a maximum of 10%) by weight, with respect to the total weight of the inner composition 4, of water. It has been experimentally observed that the lower the concentration of water, the lower the risk of the sheet 2 being damaged.

[0023] Advantageously but not necessarily, the inner composition 4 comprises 1% to 50% by weight, with respect to the total weight of the inner composition 4, of a non-ionic surfactant.

[0024] Referring in particular to the attached figures, it should be noted that, according to some non-limiting embodiments, inside the chamber 3 a portion of air 5 (an air bubble) can also be arranged, which tends to locate above the afore-mentioned first phase (upper).

[0025] Advantageously but not necessarily, according to some non-limiting embodiments, the inner composition 4 comprises at least 0.001% (in particular, up to 5%) by weight, with respect to the total weight of said inner composition 4, of the detergent enzymatic component. More precisely but not necessarily, the inner composition 4 comprises 0.01% (in particular, 0.06%; more in particular 0.1%) to 2% (in particular, 1%) by weight, with respect to the total weight of said inner composition 4, of the detergent enzymatic component.

[0026] According to some non-limiting embodiments, as indicated above, said enzymatic component is collected (is arranged - predominantly) in the first (upper) phase (portion - illustrated in darker grey in the attached figures) of the inner composition 4.

[0027] In particular, the detergent enzymatic component comprises at least an enzyme selected from the group consisting of: protease enzymes, amylase enzymes, lipase enzymes, mannanase enzymes, cellulase enzymes, pectinase enzymes and licheninase enzymes.

[0028] More in particular, the detergent enzymatic component comprises at least one enzyme selected from the group consisting of: protease enzymes, amylase enzymes, lipase enzymes, mannanase enzymes and cellulase enzymes.

[0029] Even more in particular, the detergent enzymatic component comprises at least one enzyme selected from the group consisting of: protease enzymes, mannanase enzymes, amylase enzymes. Even more in particular, the detergent

enzymatic component comprises at least one enzyme selected from the group consisting of: protease enzymes, amylase enzymes.

[0030] According to some non-limiting embodiments, the detergent enzymatic component comprises at least one protease enzyme (protease enzymes).

5 [0031] Alternatively or additionally, the detergent enzymatic component comprises at least one amylase enzyme (amylase enzymes).

[0032] Alternatively or additionally, the detergent enzymatic component comprises at least one mannanase enzyme (mannanase enzymes).

10 [0033] According to specific non-limiting embodiments, the detergent enzymatic component comprises (is composed of) at least one protease enzyme (protease enzymes) and at least one amylase enzyme (amylase enzymes).

[0034] According to further specific non-limiting embodiments, the detergent enzymatic component comprises (is composed of) at least one protease enzyme (protease enzymes) and at least one mannanase enzyme (mannanase enzymes).

15 [0035] Advantageously but not necessarily, the detergent enzymatic component comprises at least 0.001% (in particular, at least 0.03%; more in particular, at least 0.04%; even more in particular, at least 0.1%) by weight, with respect to the total weight of said inner composition 4, of at least one protease enzyme (protease enzymes).

[0036] According to some non-limiting embodiments, the detergent enzymatic component comprises up to (a maximum of) 3% (in particular, up to 1%; more in particular, up to 0.5%; more in particular, up to 0.3%) by weight, with respect to the total weight of said inner composition 4, of at least one protease enzyme (protease enzymes).

20 [0037] According to specific non-limiting embodiments, the protease enzyme comprises (in particular, is) subtilisin (CAS number: 9014-01-1).

[0038] Advantageously but not necessarily, the detergent enzymatic component comprises at least 0.001% (in particular, at least 0.01%; in particular, at least 0.03%), with respect to the total weight of said inner composition 4, of at least one amylase enzyme (amylase enzymes).

25 [0039] According to some non-limiting embodiments, the detergent enzymatic component comprises up to (a maximum of) 1% (in particular, up to 0.1%; more in particular, up to 0.05%) by weight, with respect to the total weight of said inner composition 4, of at least one amylase enzyme (amylase enzymes).

[0040] According to specific non-limiting embodiments, the amylase enzyme comprises (in particular, is) an enzyme selected from the group consisting of:  $\alpha$ -amylase (EC number: 3.2.1.1; e.g. CAS NUMBER: 9000-90-2),  $\beta$ -amylase (EC number: 3.2.1.2),  $\gamma$ -amylase (EC number: 3.2.1.3) (and a combination thereof). Even more precisely but not necessarily, the amylase enzyme comprises (in particular, is) an  $\alpha$ -amylase (EC number: 3.2.1.1; e.g. CAS number: 9000-90-2).

30 [0041] It should be noted that when reference is made in this text to a combination of several components (e.g. of several enzymes) a mixture thereof is intended.

[0042] Advantageously but not necessarily, the detergent enzymatic component comprises at least 0.0005% (in particular, at least 0.001%), with respect to the total weight of said inner composition 4, of at least one mannanase enzyme (mannanase enzymes).

[0043] According to some non-limiting embodiments, the detergent enzymatic component comprises up to (a maximum of) 0.1% (in particular, up to 0.01%; more in particular, up to 0.002%) by weight, with respect to the total weight of said inner composition 4, of at least one mannanase enzyme (mannanase enzymes; e.g. CAS number: 37288-54-3).

35 [0044] In particular, the mannanase enzyme comprises (is) a Beta-mannosidase enzyme (EC number: 3.2.1.25).

[0045] Advantageously but not necessarily, the detergent enzymatic component comprises at least 0.0005% (in particular, at least 0.001%), with respect to the total weight of said inner composition 4, of at least one cellulase enzyme (cellulase enzymes).

40 [0046] According to some non-limiting embodiments, the detergent enzymatic component comprises up to (a maximum of) 0.1% (in particular, up to 0.01%; more in particular, up to 0.002%) by weight, with respect to the total weight of said inner composition 4, of at least one cellulase enzyme (cellulase enzymes; e.g. CAS number: 9012-54-8).

[0047] Advantageously but not necessarily, the detergent enzymatic component comprises at least 0.0005% (in particular, at least 0.001%), with respect to the total weight of said inner composition 4, of at least one pectinase enzyme (pectinase enzymes).

45 [0048] According to some non-limiting embodiments, the detergent enzymatic component comprises up to (a maximum of) 0.1% (in particular, up to 0.01%; more in particular, up to 0.002%) by weight, with respect to the total weight of said inner composition 4, of at least one pectinase enzyme (pectinase enzymes; e.g. CAS number: 9032-75-1).

[0049] Advantageously but not necessarily, the detergent enzymatic component comprises at least 0.0005% (in particular, at least 0.001%), with respect to the total weight of said inner composition 4, of at least one licheninase enzyme (licheninase enzymes).

50 [0050] According to some non-limiting embodiments, the detergent enzymatic component comprises up to (a maximum of) 0.1% (in particular, up to 0.01%; more in particular, up to 0.002%) by weight, with respect to the total weight of said inner composition 4, of at least one licheninase enzyme (licheninase enzymes; e.g. CAS number: 37288-51-0).

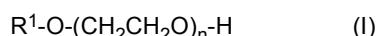
[0051] Examples of the detergent enzymatic component and of the different enzymes are, for example, provided in: Olsen, H.S., Falholt, P. The role of enzymes in modern detergency. *J Surfact Deterg* 1, 555-567 (1998). <https://doi.org/10.1007/s11743-998-0058-7>; and Kirk O, Borchert TV, Fuglsang CC. Industrial enzyme applications. *Curr Opin Biotechnol*. 2002 Aug;13(4):345-51. doi: 10.1016/s0958-1669(02)00328-2. PMID: 12323357.

5 [0052] According to some non-limiting embodiments, the non-ionic surfactant is selected from the group consisting of: alkoxylated alcohols (in particular C<sub>8</sub>-C<sub>38</sub>; more in particular, C<sub>12</sub>-C<sub>28</sub>), alkyl polyglucosides (in particular C<sub>9</sub>-C<sub>38</sub>; more in particular, C<sub>12</sub>-C<sub>28</sub>), ethanolamides (in particular C<sub>9</sub>-C<sub>27</sub>; more in particular, C<sub>18</sub>-C<sub>24</sub>) of fatty acids, glycerol ethoxylated esters (and a combination thereof).

10 [0053] More precisely but not necessarily, the non-ionic surfactant is selected from the group consisting of: ethoxylated alcohols (in particular C<sub>8</sub>-C<sub>38</sub>; more in particular, C<sub>12</sub>-C<sub>28</sub>), etho-propoxylated alcohols (in particular C<sub>8</sub>-C<sub>38</sub>; more in particular, C<sub>12</sub>-C<sub>28</sub>), alkyl polyglucosides (in particular C<sub>9</sub>-C<sub>38</sub>; more in particular, C<sub>12</sub>-C<sub>28</sub>), ethanolamides (in particular C<sub>9</sub>-C<sub>27</sub>; more in particular, C<sub>18</sub>-C<sub>24</sub>) of fatty acids, glycerol ethoxylated esters (and a combination thereof).

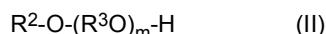
15 [0054] In some specific non-limiting cases, the non-ionic surfactant is selected from the group consisting of: ethoxylated alcohols (in particular C<sub>8</sub>-C<sub>38</sub>; more in particular, C<sub>12</sub>-C<sub>28</sub>), etho-propoxylated alcohols (in particular C<sub>8</sub>-C<sub>38</sub>; more in particular, C<sub>12</sub>-C<sub>28</sub>) (and a combination thereof).

[0055] In particular, the alcohol-ethoxylates have the following structural formula (I):



20 in which R<sup>1</sup> is an aliphatic (in particular, an alkyl) C<sub>9</sub>-C<sub>18</sub>; n is an integer from 1 to 9.

[0056] In particular, the alcohol-ethopropoxylates have the following structural formula (II):



25 in which R<sup>2</sup> is a C<sub>9</sub>-C<sub>18</sub> aliphatic (in particular, an alkyl); m is an integer from 1 to 9; and each R<sup>3</sup> is selected, independently of the others, from -(CH<sub>2</sub>)<sub>3</sub>- and -(CH<sub>2</sub>)<sub>2</sub>-.

[0057] According to some non-limiting embodiments, R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> are linear.

[0058] In the present text, "C<sub>x</sub>-C<sub>y</sub>" refers to a group and/or a compound which is understood to have x to y atoms of carbon.

30 [0059] In the present text, the term "aliphatic" indicates a nonaromatic and non-substituted hydrocarbon (unless specified otherwise), saturated or unsaturated, linear, branched and/or cyclic. Non-limiting examples of aliphatic groups are: t-butyl, ethenyl, 1- or 2-propenyl, cyclohexyl.

[0060] In the present text, the term "alkyl" indicates a saturated aliphatic (namely an aliphatic group without double or triple carbon-carbon bonds). Non-limiting examples of alkyls are: methyl, n-propyl, t-butyl, cyclohexyl.

35 [0061] Advantageously but not necessarily, the inner composition 4 comprises from 1% (in particular, 10%) to 30% (in particular, 25%) by weight, with respect to the total weight of the inner composition 4, of the above-mentioned non-ionic surfactant.

[0062] According to some preferred embodiments, the inner composition 4 comprises at least one anionic surfactant.

40 [0063] More precisely but not necessarily, the inner composition 4 comprises at least 1% (in particular, at least 2%; more in particular, at least 4%; even more in particular, at least 10%; even more in particular, at least 15%) by weight with respect to the total weight of the inner composition 4, of the anionic surfactant.

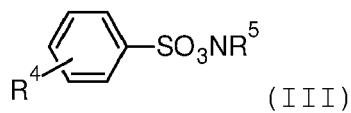
[0064] According to some non-limiting embodiments, the inner composition 4 comprises up to 45% (in particular up to 40%; more in particular, up to 35%) by weight with respect to the overall weight of the inner composition 4, of the anionic surfactant.

45 [0065] According to some non-limiting embodiments, the anionic surfactant is selected from the group consisting of: alkyl ethoxylate sulphates (in particular C<sub>8</sub>-C<sub>38</sub>; more in particular, C<sub>12</sub>-C<sub>28</sub>), alkyl sulphates (in particular C<sub>8</sub>-C<sub>18</sub>; more in particular, C<sub>12</sub>-C<sub>16</sub>), dodecylbenzene sulfonates (dodecylbenzenesulfonic acid salts), alkylbenzene sulfonates (in particular C<sub>9</sub>-C<sub>27</sub>; more in particular, C<sub>18</sub>-C<sub>24</sub>), alkyl sulfonates (in particular C<sub>9</sub>-C<sub>21</sub>; more in particular, C<sub>12</sub>-C<sub>18</sub>), soaps (in particular C<sub>9</sub>-C<sub>21</sub>; more in particular, C<sub>12</sub>-C<sub>18</sub>).

50 [0066] In the present text the term "sulphates" and/or "sulfonates" of organic compounds indicates both the relative acids (sulphuric acids and sulfonic acids, respectively) and the relative salts (for example sodium salts) and the anions (completely dissociated from the counterions).

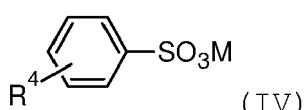
[0067] According to some non-limiting embodiments, the surfactant is one or more alkylbenzene sulphonates (in particular C<sub>9</sub>-C<sub>27</sub>; more in particular, C<sub>18</sub>-C<sub>24</sub>).

55 [0068] In particular, the alkylbenzene sulphonates have the following structural formula (III):



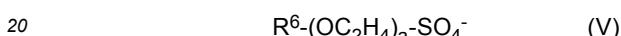
5 in which R<sup>4</sup> is a C<sub>9</sub>-C<sub>18</sub> aliphatic (in particular, an alkyl); R<sup>5</sup> is a C<sub>1</sub>-C<sub>4</sub> (in particular, C<sub>2</sub>-C<sub>3</sub>, more in particular C<sub>2</sub>) aliphatic (in particular, an alkyl). More precisely but not necessarily, R<sup>4</sup> is a linear aliphatic (in particular, an alkyl); R<sup>5</sup> is a linear aliphatic (in particular, an alkyl).

10 [0069] Alternatively or additionally, in particular, the alkylbenzene sulphonates have the following structural formula (IV):



15 in which R<sup>4</sup> is a C<sub>9</sub>-C<sub>18</sub> aliphatic (in particular, an alkyl); M is hydroxyamine or a metal selected from sodium and potassium. More precisely but not necessarily, R<sup>4</sup> is a linear aliphatic (in particular, an alkyl).

[0070] In particular, the alkyl ethoxylate sulphates have the following structural formula (V):



in which R<sup>6</sup> is a C<sub>9</sub>-C<sub>18</sub> aliphatic (in particular, an alkyl); a is an integer from 1 to 9.

[0071] In particular, the alkyl sulphates have the following structural formula (VI):



in which R<sup>7</sup> is a C<sub>9</sub>-C<sub>18</sub> aliphatic (in particular, an alkyl).

[0072] Advantageously but not necessarily, the inner composition 4 comprises one or more further surfactants selected from the group consisting of: cationic surfactants, amphoteric surfactants (and a combination thereof).

30 [0073] Advantageously but not necessarily, the non-ionic character of any mixture of surfactants is predominant. In particular, in the inner composition 4, the non-ionic surfactant is in a quantity (weight) greater than the other surfactants.

[0074] It is not necessary for the non-ionic surfactant to be in a quantity greater than other types of surfactant (the quantity of another single surfactant or the sum of the quantities of other surfactants in the inner composition 4 can be higher than that of the non-ionic surfactant).

35 [0075] According to some non-limiting embodiments (as mentioned above), the inner composition 4 comprises (in particular, from 1% to 30%; more in particular from 5% to 15%; even more in particular, up to 10% by weight, with respect to the total weight of the inner composition 4) the above-mentioned further surfactant, which can be a mixture of different cationic surfactants and/or amphoteric surfactants or composed of a single cationic surfactant or a single amphoteric surfactant.

40 [0076] According to some non-limiting embodiments, the further surfactant is selected from the group consisting of: amine ethoxylates (in particular C<sub>12</sub>-C<sub>18</sub>), quaternary ammonium salts (in particular C<sub>9</sub>-C<sub>21</sub>; more in particular, C<sub>12</sub>-C<sub>18</sub>), betaines (in particular C<sub>9</sub>-C<sub>27</sub>; more in particular, C<sub>12</sub>-C<sub>16</sub>), amine oxide (in particular C<sub>9</sub>-C<sub>21</sub>; more in particular, C<sub>12</sub>-C<sub>16</sub>) (and a combination thereof).

45 [0077] Advantageously but not necessarily, the inner composition 4 comprises from 0.5% to 50% by weight, with respect to the total weight of the inner composition 4, of the sequestering component (for the metallic ions; in particular for the calcium and magnesium ions). In particular, the sequestering component is collected (is arranged - predominantly) in the second (lower) phase (portion - shown in lighter grey in the attached figures).

50 [0078] Advantageously but not necessarily, the inner composition 4 comprises at least 1% (in particular, at least 2%; more in particular, at least 5%) by weight, with respect to the total weight of the inner composition 4, of the sequestering component.

[0079] According to some non-limiting embodiments, the inner composition 4 comprises up to (less than or equal to) 40% (in particular, up to 30%; more in particular, up to 15%) by weight, with respect to the total weight of the inner composition 4, of the sequestering component.

55 [0080] Please note, that it has been experimentally observed that the sequestering component acts synergically together with the surfactant/s so as to improve the cleaning action of the surfactant/s.

[0081] Advantageously but not necessarily, the sequestering component comprises at least one weak acid and/or at least one component with chelating action (on the metallic cations; in particular, on the calcium and magnesium cation).

[0082] According to some non-limiting embodiments, the sequestering component comprises (is) the component with

chelating action.

[0083] Alternatively or additionally, the sequestering component comprises (is) the weak acid.

[0084] In the present text, the term weak acid indicates the acid as such (not dissociated) and/or a salt thereof (for example sodium citrate) and/or the anion (completely dissociated from the counterion). This applies to any embodiment and/or example of said weak acid.

[0085] Please note that it has been experimentally observed that the weak acid and the organic solvent surprisingly act synergically, producing an inner composition 4 which simultaneously has a low concentration of water (therefore mildly aggressive for the sheet 2) and is able to perform (once the sheet 2 has been dissolved) a sequestering action on the limescale.

[0086] Advantageously but not necessarily, the weak acid has a  $pK_a$  in water (in particular, measured at ambient temperature and pressure - 25°C and 1 bar) higher than 1 (in particular, higher than or equal to 2) up to 9 (in particular, up to 6; more in particular, up to 5; even more in particular up to 4).

[0087] The  $pK_a$  and the  $pK_b$  are determined according to one of the known methods (if necessary using the most suitable method of those described, for example, in Reijenga et al, Developments of Methods for the Determination of  $pK_a$  Values, Analytical Chemistry Insights 2013:8 53-17). In particular, the  $pK_a$  and the  $pK_b$  are determined according to the potentiometric method (see X. Subirats et al., Methods for  $pK_a$  Determination (I): Potentiometry, Spectrophotometry, and Capillary Electrophore, Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, (2015), DOI: 10.1016/B978-0-12-409547-2.11559-8; and Serjeant, E.P. Potentiometry and Potentiometric Titrations; Wiley: New York, 1984).

[0088] According to some non-limiting embodiments, the weak acid is selected from the group consisting of: carboxylic acids (in particular,  $C_1-C_9$ ; with, in particular, 1 to 4 - more precisely 1 to 3 - carboxylic groups), phosphoric acid (and a combination thereof).

[0089] In other words, the weak acid can be a mixture of different carboxylic acids (with or without the phosphoric acid) or composed of a single carboxylic acid.

[0090] In some specific non-limiting cases, the weak acid is selected from the group consisting of: citric acid, lactic acid, formic acid, phosphoric acid (and a combination thereof). More precisely but not necessarily, weak acid is selected from the group consisting of: citric acid, lactic acid, formic acid (and a combination thereof). In some preferred non-limiting cases, the weak acid is citric acid.

[0091] Advantageously but not necessarily, the chelating component is selected from the group consisting of: glutamate diacetate (e.g. tetrasodium glutamate diacetate), phosphonates.

[0092] According to some non-limiting embodiments, the phosphonates have a molecular weight ranging from 50 g/mol to 5000 g/mol (more in particular from 100g/mol to 1000 g/mol).

[0093] According to some specific and non-limiting embodiments, the phosphonates are selected from the group consisting of: ATMP (aminotris (methylene phosphonic acid) - CAS number: 6419-19-8), HEDP (1-hydroxyethane 1,1-diphosphonic acid - CAS number: 2809-21-4), EDTMPA (ethylenediamine tetra (methylene phosphonic) acid - CAS number: 1429-50-1), HDTMPA (hexamethylenediamine tetra (methylene phosphonic) acid - CAS number: 23605-74-5), DTPMPA (diethylenetriamine penta (methylene phosphonic) acid - CAS number: 15827-60-8), (and combinations thereof).

[0094] In the present text, the terms glutamate diacetate and phosphonates indicate the relative acids, the relative salts (for example sodium salts) and the anions (completely dissociated from the counterions).

[0095] According to some non-limiting embodiments, the sequestering component is selected from the group consisting of: citric acid, lactic acid, formic acid, phosphoric acid, glutamate diacetate, ATMP, HEDP, EDTMPA, HDTMPA, DTPMPA (and a combination thereof). In particular, the sequestering component is selected from the group consisting of: citric acid, lactic acid, formic acid, phosphoric acid, glutamate diacetate, ATMP, HEDP, EDTMPA, HDTMPA, DTPMPA (and a combination thereof).

[0096] Advantageously but not necessarily, the organic solvent is selected from the group consisting of alcohols, diols, triols, polyols (and a combination thereof). According to some non-limiting embodiments, the alcohols, diols, triols and polyols are, each independently of one another,  $C_2-C_8$  (in particular,  $C_3-C_6$ ). In other words, the organic solvent can be a mixture of different alcohols (and/or diols and/or triols and/or polyols) or composed of one single alcohol (or diol or triol or polyol).

[0097] According to some non-limiting embodiments, the alcohols, diols, triols and polyols have, each one independently of the others, a number of hydroxyls equal to the number of carbons. In particular, each carbon of the alcohols, diols, triols and polyols is bound to a respective single (sole) hydroxyl group.

[0098] In some non-limiting cases, the cited alcohols, diols, triols and polyols are linear (namely, they have a linear chain of carbons bound to one another).

[0099] Advantageously but not necessarily, the organic solvent is selected from the group consisting of: glycerin, sorbitol (and a combination thereof).

[0100] According to some non-limiting embodiments, the organic solvent comprises (in particular, is) glycerin.

[0101] Alternatively or additionally, the organic solvent comprises (in particular, is) sorbitol.

[0102] Advantageously but not necessarily, the inner composition 4 comprises at least 5% (in particular, at least 10%, more in particular at least 15%) by weight, with respect to the total weight of the inner composition 4, of the organic solvent.

[0103] Alternatively or additionally, the inner composition 4 comprises up to (less than or equal to) 50% (in particular, up to 45%; more in particular, up to 35%) by weight, with respect to the total weight of the inner composition 4, of the organic solvent.

[0104] Advantageously but not necessarily, the inner composition 4 comprises from 1% to 40% by weight, with respect to the total weight of the inner composition 4, of an alkalinizing agent having a  $PK_b$ , in water at 25°C and at 1 bar, from 2 (in particular, from 3) to 9 (in particular, to 8; more in particular, to 7; even more in particular, to 5). In particular, the alkalinizing agent is arranged together with the organic solvent (in the lower part of the chamber 3).

[0105] The alkalinizing agent, surprisingly, allows improved solubilization of the above-mentioned weak acid and, at the same time, regulates the pH, reducing the risk, for example, of inactivating the detergent enzymes.

[0106] According to some non-limiting embodiments, the inner composition 4 comprises at least 2% (in particular, at least 5%) by weight, with respect to the total weight of the inner composition 4, of the alkalinizing agent.

[0107] Alternatively or additionally, the inner composition 4 comprises up to (less than or equal to) 35% (in particular, up to 25%; more in particular, up to 20%; even more in particular, up to 15%; even more in particular, up to 10%) by weight, with respect to the total weight of the inner composition 4, of the alkalinizing agent.

[0108] Advantageously but not necessarily, the alkalinizing agent is selected from the group consisting of: C<sub>1</sub>-C<sub>8</sub> hydroxy-amine (in particular, with one single amine functionality; in particular, C<sub>2</sub>-C<sub>6</sub>), ammonia, potassium hydroxide (and a combination thereof). In other words, the alkalinizing agent can be a mixture of different hydroxy-amines or composed of one single hydroxy-amine.

[0109] More precisely but not necessarily, the alkalinizing agent is selected from the group consisting of: monoethanolamine, diethanolamine, triethanolamine (potassium hydroxide) (and a combination thereof).

[0110] Advantageously but not necessarily, the inner composition 4 comprises from 1% to 20% (in particular 10%; more in particular, 8%) by weight, with respect to the total weight of the inner composition 4, of a polymer component (in particular, comprising - consisting of - a plurality of polymers selected from the group consisting of: acrylic homopolymers, acrylic-maleic copolymers - and a combination thereof). In other words, for example, the polymer component can be a mixture of different acrylic homopolymers (and/or acrylic-maleic copolymers) or composed of a single acrylic homopolymer. In particular, the polymer component is arranged together with the organic solvent (in the lower part of the chamber 3).

[0111] The polymer component is able to sequester calcium and magnesium and, acting synergically with the weak acid, allows limescale to be reduced.

[0112] The polymer component comprises polymers with a mean molecular weight ranging from 1000 g/mol (in particular, 3000 g/mol) to 20000 g/mol (in particular, 10000 g/mol; more in particular, 6000 g/mol).

[0113] The mean molecular weight of the polymers is measured by static light scattering methods (as described, for example, in ASTM D4001 - 13).

[0114] Advantageously but not necessarily, once the product 1 is dissolved in demineralized water - namely, osmotized and/or distilled (99 ml of water for each ml of the inner composition 4), the product 1 (in particular, the inner composition 4) has a pH from 4 to 8.

[0115] According to some non-limiting embodiments, the sheet has a thickness ranging from approximately 20 $\mu$ m to approximately 300 $\mu$ m (in particular, approximately 150 $\mu$ m).

[0116] Advantageously but not necessarily, the sheet 2 (is made of a material such that it) dissolves in water at 25°C within 10 minutes from immersion.

[0117] According to some non-limiting embodiments, the sheet 2 is (mainly) made of polyvinyl alcohol (PVOH).

[0118] According to some non-limiting embodiments (like those illustrated in the figures), the collecting chamber 3 is completely delimited by the sheet 2. In other words, in these cases, the sheet 2 fully envelops the inner composition 4.

[0119] Alternatively, the product 1 comprises a container having a substantially non water-soluble portion and the sheet 2. For example, the non water-soluble portion is shaped like a cup, inside which the inner composition 4 is arranged. In these cases, the cup-shaped portion has an opening which is (completely) covered (closed) by the sheet 2. According to specific non-limiting embodiments, the non water-soluble portion is (mainly) made of PE, PP, PET, PS, PVC (and a combination thereof).

[0120] In particular, the sheet 2 is limp. In other words, for example, when the sheet 2 completely delimits the collecting chamber 3 and the collecting chamber 3 is full, the collecting chamber 3 assumes an expanded shape different from (and volumetrically larger than) the shape assumed by the collecting chamber 3, when the collecting chamber 3 is empty.

[0121] Advantageously but not necessarily, the product 1 comprises from approximately 5 ml (in particular, from approximately 15 ml) to approximately 30 ml (in particular, to approximately 25 ml) of the inner composition 4.

[0122] In particular, the above-mentioned product 1 is for washing at least one item (in particular, a plurality of items) predominantly made of fabric (more in particular, clothes and/or linen) and reducing the formation of limescale inside

the washing machine.

[0123] It has been experimentally observed that the product 1 (as defined above) has various advantages with respect to the state of the art. Among these are the following: surprisingly, it is possible to obtain a two-phase inner composition 4; the product 1 has a reduced environmental impact (in particular, the sheet 2, since it is water-soluble and biodegradable, does not leave residues); the product 1 has reduced overall dimensions (therefore, among other things, great ease of transport and reduced need for packaging); it is easy to dose (thus also reducing waste); the washing action is improved for some types of dirt; for use, and therefore for performing its function, it requires less energy, water and time.

[0124] According to one aspect of the present invention, the use of the above defined product 1 in a washing machine is provided.

[0125] Advantageously but not necessarily, during use, inside the washing machine there is at least one item (in particular, a plurality of said items) made of fabric (more in particular, clothes and/or linen).

[0126] According to some non-limiting embodiments, the use comprises a treatment phase during which the product 1 comes into contact with the water (in particular, having a temperature below 40°C) inside the washing machine and the sheet 2 dissolves (at least partially).

[0127] Advantageously but not necessarily, during the treatment phase, inside the washing machine there is at least one above-mentioned item (in particular, a plurality of said items).

[0128] Advantageously but not necessarily, the use entails a washing cycle (in particular, during which inside the washing machine there is at least one above-mentioned item - more in particular, a plurality of said items). More precisely but not necessarily, the washing cycle comprises the above-mentioned treatment phase and (optionally) a washing phase, during which the item/s is/are washed.

[0129] In addition or alternatively to the above, a use is provided of a product 1 as described above for washing in a washing machine at least one item (in particular, a plurality of items), predominantly made of fabric (more in particular, clothing and/or linen), and reducing the formation of scale (in particular, limescale) inside the washing machine. In other words, during use, the product 1 contributes to washing (washes) at least one item (in particular, a plurality of items), which is predominantly made of fabric (more in particular, clothes and/or linen) and is inside a washing machine, and reduces (contributes to reducing) the formation of scale (in particular, limescale) inside the washing machine.

[0130] One of the main problems to be overcome in development of the product 1 was to produce a two-phase composition compatible with the water-soluble sheet 2. This implies that, unlike the normal products, which use high percentages of water, alternative solvents are employed that are able to solubilize the active ingredients and at the same time allow (together with other compounds, in particular the non-ionic surfactants, previously not identified for this purpose) a two-phase inner composition 4 to be obtained. This is far from simple since some ingredients, e.g. the weak acid, have good dissolvability in water but poor dissolvability in other media.

[0131] Unless explicitly indicated otherwise, the contents of the references (articles, books, patent applications etc.) cited in this text are fully referred to here. In particular the mentioned references are incorporated here for reference.

[0132] Further characteristics of the present invention will become clear from the following description of merely illustrative and non-limiting examples.

### Example 1

[0133] This example describes the production of some products in accordance with the present invention.

[0134] 20 millilitres of each of the inner compositions having one of the formulations from A to C were inserted between two sheets of MonoSol material (marketed by Kuraray WS Fil Division), the perimeter edges of which were overlapped and subsequently heat-welded so as to enclose the formulations from A to E. To facilitate the welding, a very thin layer of water was applied between the edges before overlapping them. These activities were carried out by a machine called Hydroforma supplied by the company Cloud Packaging Europe (L-8366 Hagen, Luxembourg).

[0135] In this way, three different (single-dose) products were obtained, each of which (as described above) has a collecting chamber, delimited by a sheet 2 (obtained from the MonoSol material) and inside which an inner composition 4 is arranged having a respective formulation of the formulations from A to D.

Formulation A

Single dose components	% by weight
Glycerol	41.534
Alkylbenzene sulfonic acid, monoethanolamine salt	19.0
Alcohol ethoxylate	15.0
Monopropylene glycol	10.0

(continued)

<b>Single dose components</b>		<b>% by weight</b>
5	Coconut fatty acids, monoethanolamine salt	5.0
10	Ethopropoxylated alcohol	20
15	Water	4.5
20	Polycarboxylate polymer	3.2
25	Tetrasodium glutamate diacetate	1.5
30	Diethylenetriamine pentamethylene phosphonic acid, sodium salt	0.20
35	Protease enzyme (subtilisin)	0.050
40	Amylase enzyme	0.015
45	Dye	0.015
	<b>Total</b>	100

## Formulation B

<b>Single dose components</b>		<b>% by weight</b>
25	Glycerol	43.08
30	Alcohol ethoxylate	21.0
35	Monoethanolamine citrate	13.3
40	Alkylbenzene sulfonic acid, monoethanolamine salt	5.0
45	Water	4.9
	Ethyl alcohol	4.5
	Monopropylene glycol	3.6
	Coconut fatty acids, monoethanolamine salt	2.5
	Polycarboxylate polymer	1.0
	Diethylenetriamine pentamethylene phosphonic acid, sodium salt	0.50
	Fragrance	0.45
	Protease enzyme (subtilisin)	0.080
	Amylase enzyme	0.040
	Disodium distyrylbiphenyl disulfonate	0.040
	Dye	0.010
	<b>Total</b>	100

## Formulation C

<b>Single dose components</b>		<b>% by weight</b>
50	Sorbitol	27.869
55	Alcohol ethoxylate	18.0
	Dipropylene glycol	14.0
	Monoethanolamine citrate	10.3
	Alkylbenzene sulfonic acid, monoethanolamine salt	13.2

(continued)

Single dose components	% by weight
Water	7.6
Ethyl alcohol	4.0
Cocamidopropyl betaine	4.1
Tetrasodium glutamate diacetate	0.40
Polycarboxylate polymer	1.0
Diethylenetriamine pentamethylene phosphonic acid, sodium salt	0.50
Fragrance	0.40
Protease enzyme (subtilisin)	0.080
Amylase enzyme	0.10
Disodium distyrylbiphenyl disulfonate	0.030
Dye	0.0010
<b>Total</b>	100

[0136] The products containing the compositions with the formulations A, B and C were prepared mainly as washing machine products. These products are two-phase.

[0137] The formulations described above were tested for laundry washing and proved to be more efficient in washing some types of dirt than commercial detergents (which also have higher concentrations, in use).

[0138] The formulations described above also proved to be effective in reducing limescale.

[0139] The two-phase formulation, compared to a traditional single-phase formulation, is effective in reducing limescale. In fact, the single-phase formulations only show detergent properties vis-à-vis the fabrics and do not prove effective in removing scale.

## Claims

1. A product for washing machines, for washing laundry and reducing the formation of deposits in washing machines; the product (1) comprises a substantially water-soluble sheet (2); a collecting chamber (3), which is at least partially delimited by said sheet (2); and an inner composition (4), which is substantially liquid, is arranged inside the collecting chamber (3) and comprises 0% to 20% by weight, with respect to the total weight of said inner composition (4), of water; at least one non-ionic surfactant; an organic solvent chosen from the group consisting of: alcohols, diols, triols, polyols and a combination thereof; a detergent enzymatic component; and a sequestering agent; said inner composition (4) has a first phase, in which said non-ionic surfactant is predominantly arranged, and at least a second phase, in which said organic solvent and said sequestering agent are predominantly arranged.
2. The product according to claim 1, wherein said inner composition (4) comprises 1% to 50% by weight, with respect to the total weight of said inner composition (4), of said non-ionic surfactant; 5% to 60% by weight, with respect to the total weight of said inner composition (4), of said organic solvent; at least 0.001% by weight, with respect to the total weight of said inner composition (4), of said detergent enzymatic component; and 0.5% to 50% by weight, with respect to the total weight of said inner composition (4), of said sequestering agent.
3. The product according to claim 1 or 2, wherein said detergent enzymatic component comprises at least one enzyme selected from the group consisting of: protease enzymes, amylase enzymes, lipase enzymes, mannanase enzymes, cellulase enzyme, pectinase enzymes and licheninase enzymes; the sequestering agent comprises at least one weak acid and/or at least one chelating component.
4. The product according to any one of the preceding claims, wherein the detergent enzymatic component comprises at least one enzyme selected from the group consisting of: protease enzymes, mannanase enzymes, amylase

5 enzymes; the sequestering agent comprises at least one weak acid, which has a  $\text{pK}_a$  in water, measured at 25°C and 1 bar, greater than 1 and up to 9, and/or at least one chelating component chosen from the group consisting of: glutamate diacetate, phosphonates having a molecular weight from 50 g/mol to 5000 g/mol and a combination thereof; in particular, the detergent enzymatic component comprises at least one protease enzyme and at least one amylase enzyme.

10 5. The product according to any one of the preceding claims, wherein said sequestering agent is selected from the group consisting of: citric acid, lactic acid, formic acid, phosphoric acid, glutamate diacetate, ATMP, HEDP, EDTMPA, HDTMPA, DTPMPA and a combination thereof.

15 6. The product according to any one of the preceding claims, wherein, said sequestering agent comprises at least one chelating component;

15 said alcohols, diols, triols and polyols are, each one independently of the other ones,  $\text{C}_2\text{-C}_8$ ;  
in particular, the inner composition (4) comprises at least one dye, so that the first phase and the second phase have different colours.

20 7. The product according to any one of the preceding claims, wherein said sequestering agent comprises at least one chelating component chosen (in particular, said sequestering agent is chosen) from the group consisting of: glutamate diacetate, ATMP, HEDP, EDTMPA, HDTMPA, DTPMPA and a combination thereof;

25 said alcohols, diols, triols and polyols are linear and have, each one independently of the other ones, a number of hydroxyl groups which is the same as the number of carbons;  
wherein said non-ionic surfactant is selected from the group consisting of:  $\text{C}_8\text{-C}_{38}$  alcohol ethoxylates,  $\text{C}_8\text{-C}_{38}$  etho-propoxylated alcohols and a combination thereof;  
the inner composition (4) comprises less than 10% by weight, with respect to the total weight of said inner composition (4), of water.

30 8. The product according to any one of the preceding claims, wherein said sequestering agent comprises at least one chelating component selected (in particular, said sequestering agent is selected) from the group consisting of: glutamate diacetate, etidronate, diethylenetriamine pentamethylene phosphonate and a combination thereof;  
said organic solvent is selected from among the group consisting of: glycerin, sorbitol and a combination thereof.

35 9. The product according to any one of the preceding claims, wherein said inner composition (4) comprises at least 1% by weight, with respect to the total weight of said inner composition (4), of an anionic surfactant, which is predominantly arranged in the first phase of the inner composition (4); in particular, said inner composition (4) comprises 2% to 45% by weight, with respect to the total weight of said inner composition (4), of said anionic surfactant.

40 10. The product according to claim 9, wherein said anionic surfactant is selected from the group consisting of: alkyl ethoxylate sulphates (in particular,  $\text{C}_8\text{-C}_{38}$ ; more in particular,  $\text{C}_{12}\text{-C}_{28}$ ), alkyl sulphates (in particular,  $\text{C}_8\text{-C}_{18}$ ; more in particular,  $\text{C}_{12}\text{-C}_{16}$ ), salts of the dodecylbenzenesulfonic acid, alkylbenzene sulfonates (in particular,  $\text{C}_9\text{-C}_{27}$ ; more in particular,  $\text{C}_{18}\text{-C}_{24}$ ), alkyl sulfonates (in particular,  $\text{C}_9\text{-C}_{21}$ ; more in particular,  $\text{C}_{12}\text{-C}_{18}$ ), soaps (in particular,  $\text{C}_9\text{-C}_{21}$ ; more in particular,  $\text{C}_{12}\text{-C}_{18}$ ).

45 11. The product according to any one of the preceding claims, wherein said inner composition (4) comprises 0% to 15% by weight, with respect to the total weight of said inner composition (4), of water; 10% to 50% by weight, with respect to the total weight of said inner composition (4), of said organic solvent; 10% to 25% by weight, with respect to the total weight of said inner composition (4), of said non-ionic surfactant, which is selected from the group consisting of:  $\text{C}_8\text{-C}_{38}$  alcohol ethoxylates,  $\text{C}_8\text{-C}_{38}$  etho-propoxylated alcohols, alkyl polyglycosides, ethanolamides of fatty acids and a combination thereof; 0.01% to 5% by weight, with respect to the total weight of said inner composition (4), of said detergent enzymatic component; and 1% to 30% (in particular, up to 15%) by weight, with respect to the total weight of said inner composition (4), of said sequestering agent.

55 12. The product according to any one of the preceding claims, wherein said inner composition (4) comprises 1% to 20% by weight, with respect to the total weight of said inner composition (4), of a polymer component chosen from the group consisting of: acrylic homopolymers, acrylic-maleic copolymers and a combination thereof.

13. The product according to claim 12, wherein the acrylic homopolymers and the acrylic-maleic copolymers have, each

one independently of the other ones, a mean molecular weight ranging from 1000 g/mol to 20000 g/mol.

5            14. A use of a product according to any one of the preceding claims in a washing machine; in particular, during the use, inside the washing machine there is at least one item (in particular, a plurality of items) predominantly made of fabric (more in particular, clothes and/or linen).

10            15. The use according to claim 14 and comprising a treatment step, during which the product comes into contact with water at a temperature below 40°C inside said home appliance and said sheet (2) at least partially dissolves; inside the home appliance there is at least one aforesaid item (in particular, a plurality of said items).

15            16. A use of a product according to any one of the claims from 1 to 13 in a washing machine for washing at least one item (in particular, a plurality of items) predominantly made of fabric (more in particular, clothes and/or linen) and for reducing the formation of limescale inside the washing machine.

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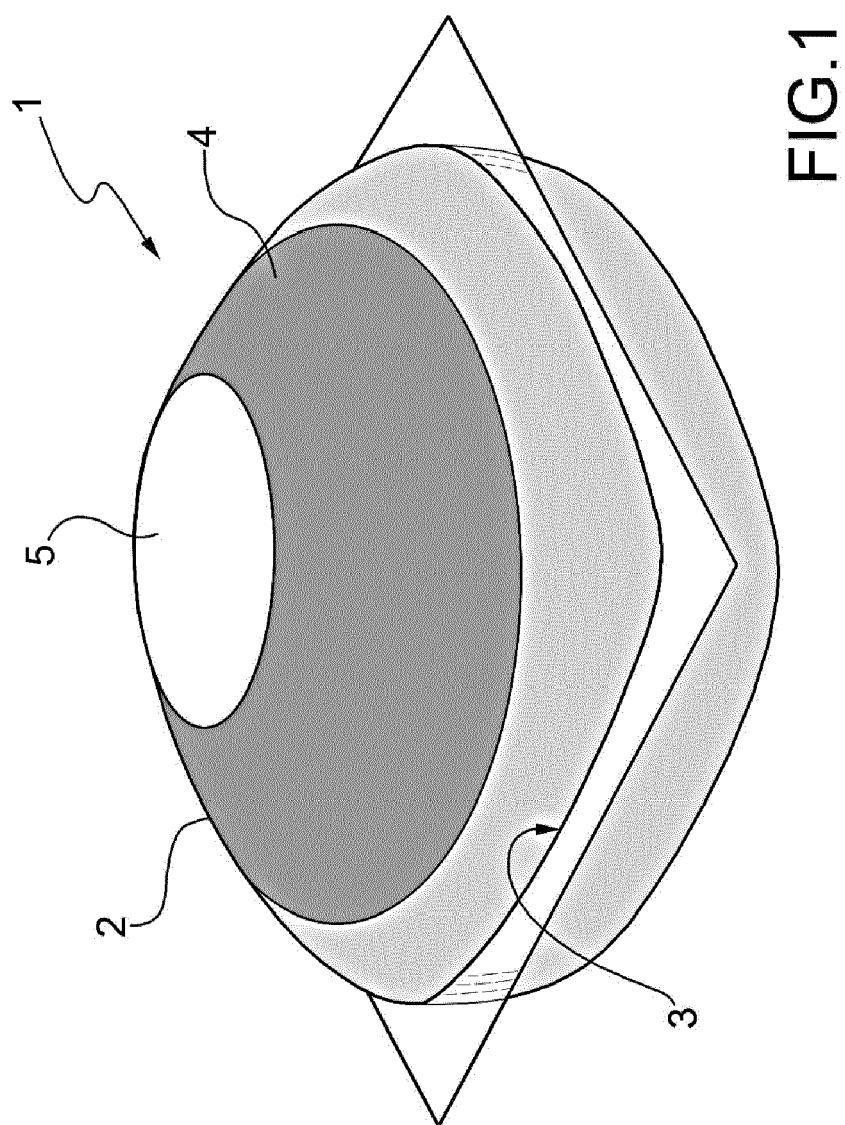


FIG.1

FIG.2

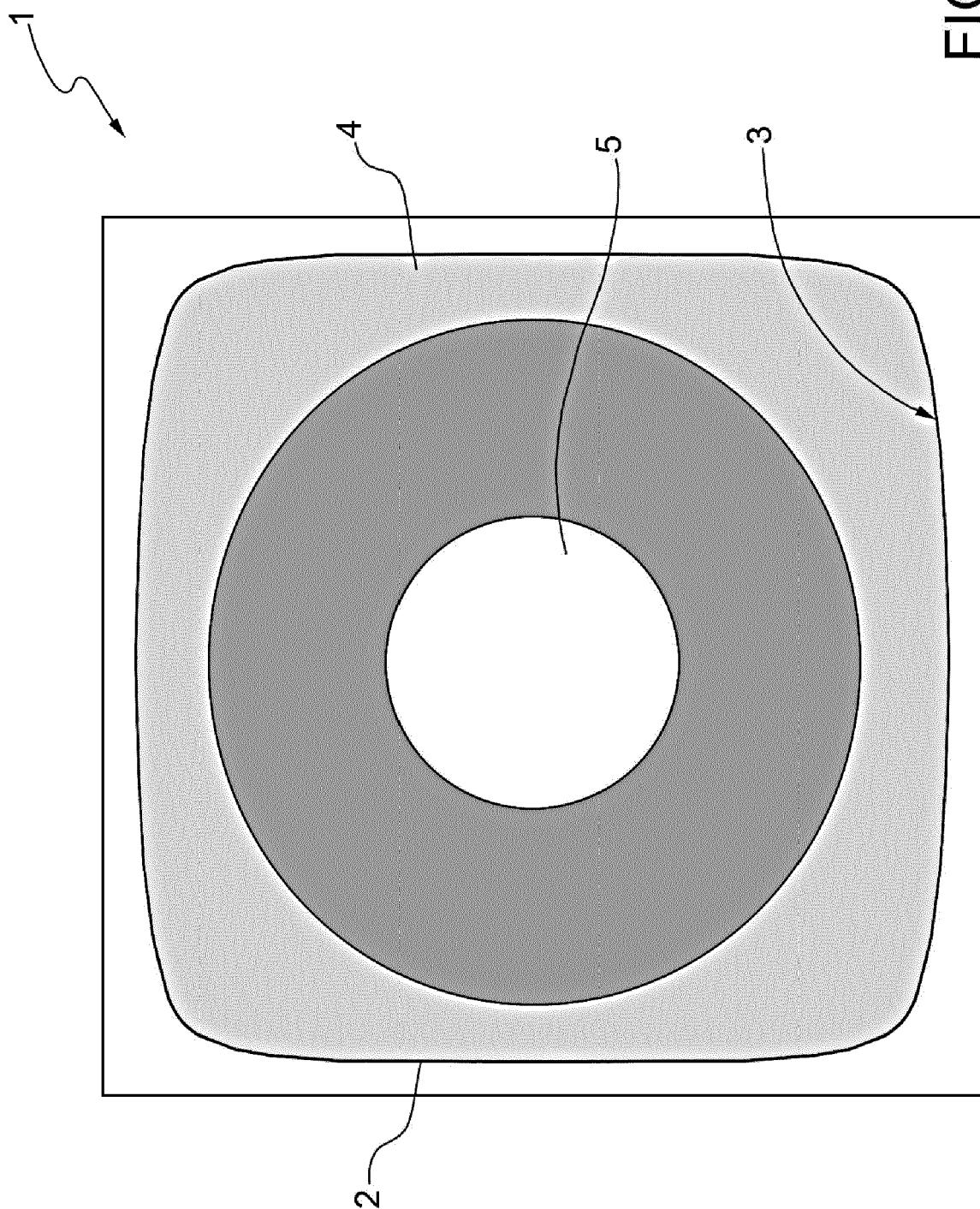
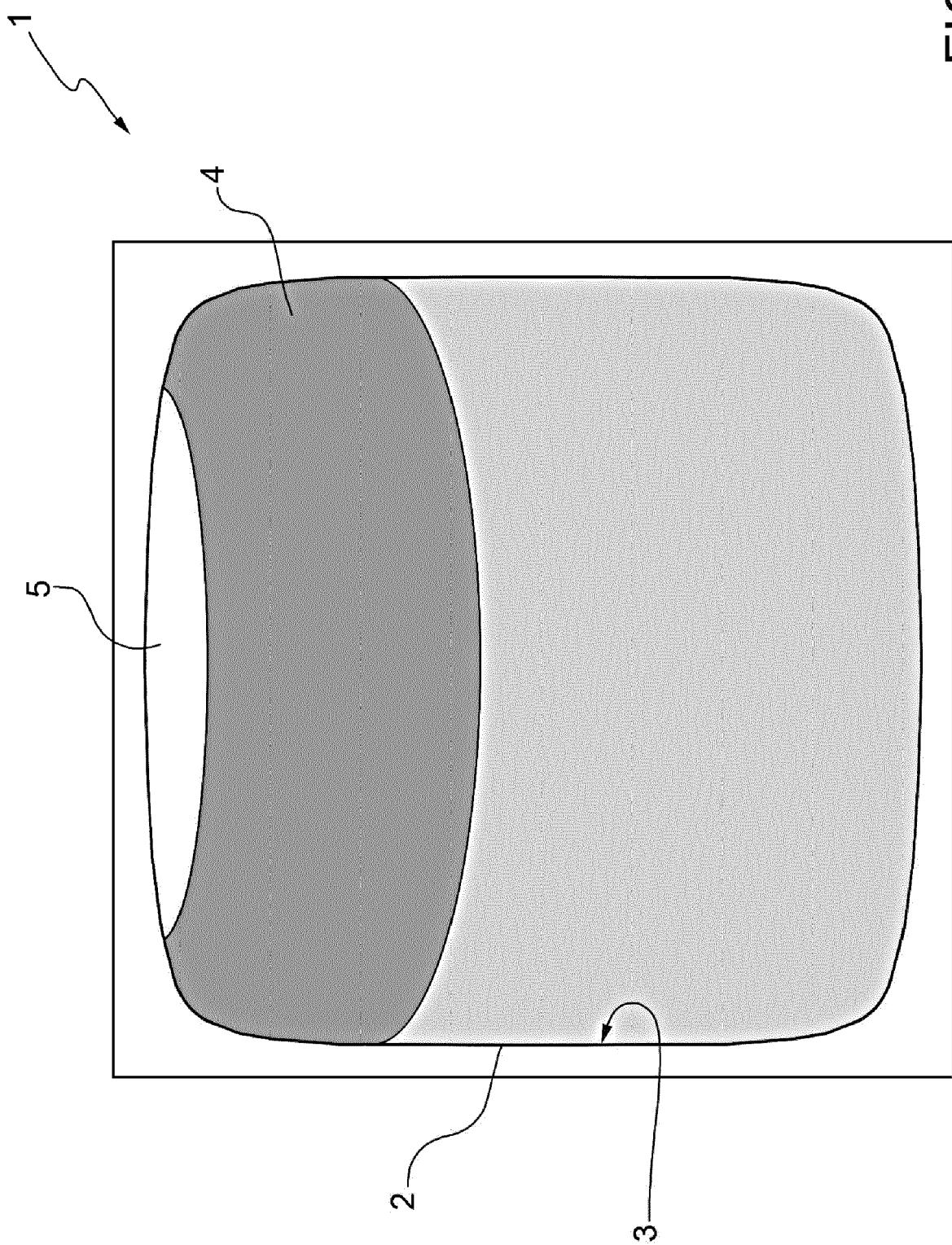


FIG.3





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Application Number

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50	The present search report has been drawn up for all claims		
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Place of search		Date of completion of the search	Examiner
The Hague		27 July 2022	Richards, Michael
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			
EPO FORM 1503 03/82 (P04C01)			

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ON EUROPEAN PATENT APPLICATION NO.

EP 22 15 4434

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