



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
26.05.2021 Bulletin 2021/21

(51) Int Cl.:
C11D 7/50 (2006.01) **C11D 7/04** (2006.01)
C11D 11/00 (2006.01) **C11D 7/08** (2006.01)

(21) Application number: **20208761.5**

(22) Date of filing: **19.11.2020**

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

(72) Inventors:
• **FABBRI, Samanta**
48012 BAGNACAVALLLO (RA) (IT)
• **EGENOLF, Francesca**
48012 BAGNACAVALLLO (RA) (IT)

(30) Priority: **19.11.2019 IT 201900021549**

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

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

(54) **PRODUCT FOR THE TREATMENT OF AN ELECTRIC HOME APPLIANCE CONFIGURED FOR WASHING**

(57) Product (1) for the treatment of a washing appliance; the product (1) comprises a substantially water-soluble casing (2); a collecting chamber (3), which is delimited by said casing (2); and an inner composition (4), which is substantially liquid, is arranged inside the collecting chamber (3) and comprises 10% to 95% by weight of an organic solvent, 2% to 40% of a weak acid and 0% to 20% of water.

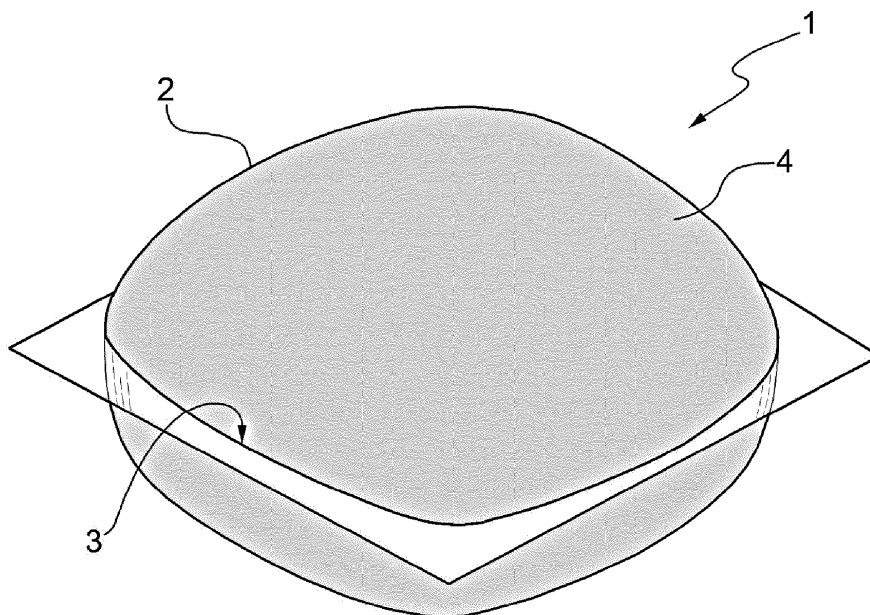


FIG.1

DescriptionCROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This patent application claims priority from Italian patent application no. 102019000021549 filed on 19/11/2019.

TECHNICAL SECTOR

[0002] The present invention relates to a product for the treatment of a washing appliance and to uses of said product.

BACKGROUND OF THE INVENTION

[0003] The products called dishwasher care are normally liquid products with high dilution (H_2O equal on average to 70%) with strongly acid characteristics ($pH=2$) and a strong degreasing power determined mainly by the presence of surfactants.

[0004] They have the purpose of removing dirt residues and limescale that periodically accumulate in the dishwasher, in particular in the filters and spray arms. Usually, monthly use is prescribed.

[0005] The method of use of this type of product envisages running a complete empty cycle by setting a high temperature programme. The empty cycle needs to be run because, given the highly acid pH of the product, the concomitant use with the classic detergents for dishwashers would cause the inactivation of the enzymes contained in the detergents, significantly worsening the performance of washing the crockery. The need to opt for an intensive programme, on the other hand, is determined by the fact that the dishwasher care products are generally packaged in bottles (typically 250ml) of water-resistant (non-biodegradable) plastic provided with a special cap consisting of a septum of meltable wax at temperatures above 45-50°C.

[0006] The product therefore starts its action in the central washing step when the temperature of the dishwasher is sufficient to melt the wax.

[0007] The dishwasher cares currently on the market come in a monophasic or biphasic version.

[0008] The washing machine care products are liquid products with high dilution ($H_2O>70\%$) with strongly acid pH, equal to about 2, and a fair degreasing power thanks to the presence of surfactants. They have the purpose of removing dirt residues and limescale that periodically accumulate in the appliance and are used in empty cycles, possibly at high temperatures to maximise the effect of the product. Considering the low pH, they cannot be used in the normal washing cycle together with the detergent because, similarly to the dishwasher cares, they would hinder the stain removal action of the enzymes normally contained in washing machine detergents. The sales formats currently available are 250ml bottles (disposable) of water-resistant (non-biodegradable) plastic to be poured into the detergent compartment.

[0009] The dishwasher care and washing machine care products have several drawbacks, among which we mention the following: to be used and, therefore, to exert their function, they require a lot of time, a lot of water and a lot of electricity (typically an entire washing cycle is necessary). It should also be noted that the packaging of these products (being in non-bio-degradable plastic) has a negative environmental impact. The washing machine care and anti-scale products for washing machines are also relatively difficult to dose (making the loading operations of appliances more complex and inaccurate - the risk of waste also increases).

[0010] Furthermore, it has been observed that the washing activities carried out even after the use of the dishwasher care and washing machine cares do not allow to satisfactorily improve the activity of the various detergents relatively to all types of dirt.

[0011] The anti-scale products for washing machines are liquid products with high dilution ($H_2O>80\%$) preferably with variable pH 4 to 7 which are added directly into the compartment of the washing machine together with the detergent at each wash. The anti-scale products therefore cooperate with the detergent by sequestering the limescale present, thus improving the cleaning performance of the detergent. They therefore start working in the actual washing step.

[0012] The formulations currently on the market consist of a pool of sequestrants and dispersants. The sales format of these products is generally in bottles of variable volume (500-750ml) with dosing cap. Normally, 50-75ml of product is used per wash.

[0013] Also the anti-scale products for washing machines have several drawbacks, among which we mention the following: they are contained in bottles of non-biodegradable plastic material (and therefore have a negative environmental impact), they are relatively difficult to dose (making the loading operations of appliances more complex and inaccurate - they also increase the risk of waste) and do not allow to satisfactorily improve the activity of the detergents relatively to all types of dirt.

[0014] Furthermore, liquid detergents sold in water-soluble single-dose capsules are known. However, they are unable to perform the functions of the aforementioned anti-scale, dishwasher care and washing machine care products and have so far been produced only in a monophasic version.

[0015] The object of the present invention is to provide a product for the treatment of a washing appliance and to uses of this product, which allow to overcome, at least partially, the drawbacks of the prior art and possibly are, at the same time, easy and economic to realise.

5 SUMMARY

[0016] According to the present invention, a product for the treatment of a washing appliance and uses of this product according to what is recited in the independent claim that follows and, preferably, in any of the claims directly or indirectly dependent on the independent claim are provided.

10 **[0017]** According to some non-limiting embodiments, the product may have two or more phases that are mutually immiscible.

BRIEF DESCRIPTION OF THE DRAWINGS

15 **[0018]** The invention will now be described with reference to the accompanying drawings, which illustrate some non-limiting examples of embodiments, wherein:

- Figure 1 is a perspective view of a product (arranged horizontally) in accordance with the present invention;
- Figure 2 is a plan view of the product of Figure 1;
- 20 - Figure 3 is a perspective view of a different embodiment of the product (arranged horizontally) of Figure 1; and
- Figure 4 is a plan view of the product of Figure 3.

DETAILED DESCRIPTION

25 **[0019]** In Figure 1, 1 denotes as a whole a product for the treatment of a washing appliance (for example, a dishwasher or a washing machine).

[0020] The product 1 is, for example, an appliance care product and/or an anti-scale product.

[0021] In some non-limiting cases, the product 1 is for the treatment of a dishwasher. Alternatively, the product 1 is for the treatment of a washing machine.

30 **[0022]** The product 1 comprises a substantially water-soluble (in particular, biodegradable) casing 2; a collecting chamber 3, which is delimited by said casing 2; and an inner composition 4, which is substantially liquid, is arranged inside the collecting chamber 3 and comprises 10% to 95% (in particular to 90%) by weight with respect to the total weight of the inner composition 4, of an organic solvent and 0% to 20% by weight, with respect to the total weight of the inner composition 4, of water.

35 **[0023]** According to some preferred but not limiting embodiments, the inner composition 4 comprises up to a maximum of 15% (in particular, up to a maximum of 10%; more in particular, up to a maximum of 5%) by weight, with respect to the total weight of the inner composition 4, of water. It should be noted that it has been experimentally observed that the lower the concentration of water, the lower the risk of the casing 2 being damaged.

[0024] Advantageously but not necessarily, the inner composition 4 comprises 2% to 40% by weight, with respect to the total weight of the inner composition 4, of a weak acid.

40 **[0025]** Within this text, weak acid refers to 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 such a weak acid.

[0026] In particular (since the inner composition 4 is substantially liquid), the weak acid is in the substantially liquid phase (for example, the weak acid is dissolved).

[0027] It should be noted that it has been experimentally observed that the weak acid and the organic solvent act surprisingly synergistically so to allow to obtain an inner composition 4 which is at the same time with a low concentration of water (therefore scarcely aggressive for the casing 2) and is able to exert (once the casing 2 has been dissolved) a sequestering action against limescale.

50 **[0028]** 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) greater than 1 (in particular, greater than or equal to 2) up to 9 (in particular, up to 6; more in particular, up to 5; still more particularly up to 4).

[0029] The pK_a and the pK_b are determined according to one of the known methods (possibly using the most suitable method among 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).

[0030] According to some non-limiting embodiments, the weak acid is selected from the group consisting of: carboxylic acids (in particular, C_1-C_8 ; in particular, with 1 to 4 - more precisely 1 to 3 carboxylic groups), phosphoric acid (and a combination thereof).

[0031] In other words, the weak acid can be a mixture of different carboxylic acids (with or without phosphoric acid) or composed of a single carboxylic acid.

[0032] In this text, " C_x-C_y " refers to a group and/or a compound which is intended as having x to y carbon atoms.

[0033] 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 specific non-limiting cases, the weak acid is the citric acid.

[0034] Advantageously but not necessarily, the inner composition 4 comprises at least 5% (in particular, at least 7%; more in particular, at least 20%) by weight, with respect to the total weight of the inner composition 4, of said weak acid.

[0035] According to some non-limiting embodiments, the inner composition 4 comprises up (less than or equal) to 35% (in particular, to 30%; more in particular, to 15%) by weight, with respect to the total weight of the inner composition 4, of the aforesaid weak acid.

[0036] According to some non-limiting embodiments, where the product 1 is for use as a dishwasher care, the inner composition 4 comprises from 5% (in particular, from 7%; more in particular, from 20%) to 40% (in particular, to 35%) by weight, with respect to the total weight of the inner composition 4, of said weak acid.

[0037] According to some non-limiting embodiments, where the product 1 is for use as an anti-scale product for washing machines and/or as a washing machine care, the inner composition 4 comprises from 5% (in particular, from 7%) to 40% (in particular, to 35%; more in particular, to 25%) by weight, with respect to the total weight of the inner composition 4, of said weak acid.

[0038] 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 one independently of the other ones, 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 a single alcohol (or diol etc.).

[0039] According to some non-limiting embodiments, the alcohols, diols, triols and polyols have, each one independently of the other ones, a number of hydroxyls which is the same as the number of carbons. In particular, each carbon of the alcohols, diols, triols and polyols is bound to a respective single (only) hydroxyl group.

[0040] In some limiting cases, the aforesaid alcohols, diols, triols and polyols are linear (i.e., they have a linear chain of carbons bound together).

[0041] Advantageously but not necessarily, the organic solvent is selected from the group consisting of: glycerin, sorbitol (and a combination thereof).

[0042] According to some non-limiting embodiments, the organic solvent comprises (in particular, is) glycerin.

[0043] Alternatively, or in addition, the organic solvent comprises (in particular, is) sorbitol.

[0044] Advantageously but not necessarily, the inner composition 4 comprises at least 25% (in particular, at least 40%, more in particular at least 50%) by weight, with respect to the total weight of the inner composition 4, of the organic solvent.

[0045] Alternatively, or in addition, the inner composition 4 comprises up (less than or equal) to 80% (in particular, up to 65%) by weight, with respect to the total weight of the inner composition 4, of the organic solvent.

[0046] Advantageously but not necessarily, the inner composition 4 comprises 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 1 bar, ranging from 2 (in particular, from 3) to 9 (in particular, to 8; more in particular, to 7; still more particularly, to 5).

[0047] The alkalinizing agent surprisingly allows to improve the solubilization of the aforesaid weak acid and, at the same time, regulates the pH reducing the risk, for example, of inactivating the enzymes of the detergents.

[0048] According to some non-limiting embodiments, the inner composition 4 comprises at least 2% (in particular, at least 10%) by weight, with respect to the total weight of the inner composition 4, of the alkalinizing agent. Alternatively, or in addition, the inner composition 4 comprises up (less than or equal) to 35% (in particular, up to 25%; more in particular, up to 20%; still more particularly, up to 15%; still more particularly, up to 6%) by weight, with respect to the total weight of said inner composition 4, of the alkalinizing agent.

[0049] According to some non-limiting embodiments, where the product 1 is for use as a dishwasher care, the inner composition 4 comprises 1% to 10% (in particular, to 6%; more in particular, to 4%) by weight, with respect to the total weight of said inner composition 4, of the alkalinizing agent.

[0050] Alternatively, where the product 1 is for use as an anti-scale product for washing machines and/or as a washing machine care, the inner composition 4 comprises from 1% (in particular, from 5%; more in particular, from 10%) to 40% (in particular, to 35%) by weight, with respect to the total weight of the inner composition 4, of the alkalinizing agent.

[0051] Advantageously but not necessarily, the alkalinizing agent is selected from the group consisting of: C_1-C_8

hydroxy-amines (in particular, with only one amino functionality; in particular, C₂-C₆), ammonia, potassium hydroxide (and a combination thereof). In other words, the alkalizing agent can be a mixture of different hydroxy-amines or composed of a single hydroxy-amine.

[0052] More precisely but not necessarily, the alkalizing agent is selected from the group consisting of: monoethanolamine, diethanolamine, triethanolamine (potassium hydroxide) (and a combination thereof).

[0053] Advantageously but not necessarily, the inner composition 4 comprises 1% to 10% (in particular, to 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.

[0054] The polymer component is able to sequester calcium and magnesium and, by acting synergistically with the weak acid, allows to reduce scale.

[0055] The polymer component comprises polymers with a mean molecular weight ranging from 1000 g/mol (in particular, from 3000 g/mol) to 20000 g/mol (in particular, to 10000 g/mol; more in particular, to 6000 g/mol).

[0056] The mean molecular weight of the polymers is measured through static light scattering methods (such as for example described in ASTM D4001 - 13).

[0057] 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 surfactant (in particular, selected from the group consisting of: anionic surfactants, cationic surfactants, amphoteric surfactants, non-ionic surfactants, and a combination thereof).

[0058] In other words, for example, the surfactant can be a mixture of different anionic surfactants (and/or cationic surfactants and/or amphoteric surfactants and/or non-ionic surfactants) or composed of a single anionic surfactant (or a single cationic surfactant or a single amphoteric surfactant or a single non-ionic surfactant).

[0059] According to some non-limiting embodiments, the surfactant is selected from the group consisting of: alkyl ethoxysulfates (in particular C₈-C₃₈; more in particular, C₁₂-C₂₈), alkyl sulfates (in particular C₈-C₁₈; more in particular, C₁₂-C₁₆), salts of the dodecylbenzenesulfonic acid, alkylbenzene sulfonates (in particular C₉-C₂₇; more in particular, C₁₈-C₂₄), alkyl sulfonates (in particular C₉-C₂₁; more in particular, C₁₂-C₁₈), soaps (in particular C₉-C₂₁; more in particular, C₁₂-C₁₈), amine ethoxylates (in particular C₁₂-C₁₈), quaternary ammonium salts (in particular C₉-C₂₁; more in particular, C₁₂-C₁₈), betaines (in particular C₉-C₂₇; more in particular, C₁₂-C₁₆), amine oxide (in particular C₉-C₂₁; more in particular, C₁₂-C₁₆), ethoxylated alcohols (in particular C₈-C₃₈; more in particular, C₁₂-C₂₈), etho-propoxylated alcohols (in particular C₈-C₃₈; more in particular, C₁₂-C₂₈), alkyl polyglucosides (in particular C₉-C₃₈; more in particular, C₁₂-C₂₈), ethanolamides (in particular C₉-C₂₇; more in particular, C₁₈-C₂₄) of fatty acids (and a combination thereof).

[0060] In this text, "sulfates" and/or "sulfonates" of organic compounds refer to either the relative acids (sulfuric acids and sulphonic acids, respectively) or the relative salts (for example of sodium) and the anions (completely dissociated from the counterions).

[0061] Advantageously but not necessarily, the surfactant mainly comprises (is) a non-ionic surfactant.

[0062] In this way, it is possible to obtain a biphasic inner composition 4 (Figures 3 and 4). In particular, the non-ionic surfactant is gathered (is - mainly - present) in the upper phase (portion) (shown in darker grey in the attached figures); the organic solvent (the possible water), the weak acid and possibly the alkalizing agent and/or the polymer component are gathered (are - mainly - present) in the lower phase (portion) (shown in lighter grey in the attached figures). More precisely but not necessarily, the upper phase and the lower phase are (substantially) immiscible (with each other).

[0063] In this context, advantageously but not necessarily, the inner composition 4 comprises one or more dyes (in particular, organic pigments) which is/are arranged so that the two phases are visually even more distinguishable.

[0064] It should be noted that when it is indicated that a component of the inner composition 4 is "mainly" arranged in a phase (portion), it is meant that the quantity of this component in that phase is greater than (in particular, it is at least double) the quantity of the same component in all the rest of the inner composition 4.

[0065] It should be noted that, according to some non-limiting embodiments, an air portion 5 (an air bubble), which tends to position itself above the inner composition 4 (more precisely, where present, of the aforesaid upper portion), is also arranged inside the chamber 3.

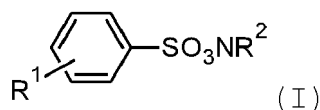
[0066] In some specific and non-limiting cases, the surfactant is selected from the group consisting of: ethoxylated alcohols (in particular C₈-C₃₈; more in particular, C₁₂-C₂₈), etho-propoxylated alcohols (in particular C₈-C₃₈; more in particular, C₁₂-C₂₈), alkyl polyglucosides (in particular C₉-C₃₈; more in particular, C₁₂-C₂₈), ethanolamides (in particular C₉-C₂₇; more in particular, C₁₈-C₂₄) of fatty acids (and a combination thereof).

[0067] Advantageously but not necessarily, the surfactant is selected from the group consisting of: ethoxylated alcohols (in particular C₈-C₃₈; more in particular, C₁₂-C₂₈), etho-propoxylated alcohols (in particular C₈-C₃₈; more in particular, C₁₂-C₂₈) (and a combination thereof).

[0068] According to some non-limiting embodiments, the surfactant is selected from the group consisting of: ethoxylated alcohols (in particular C₈-C₃₈; more in particular, C₁₂-C₂₈), etho-propoxylated alcohols (in particular C₈-C₃₈; more in particular, C₁₂-C₂₈), alkylbenzene sulfonates (in particular C₉-C₂₇; more in particular, C₁₈-C₂₄) (and a combination

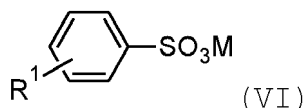
thereof).

[0069] In particular, the alkylbenzene sulfonates have the following structural formula (I):



wherein R^1 is a $\text{C}_9\text{-C}_{18}$ aliphatic (in particular, an alkyl); R^2 is a $\text{C}_1\text{-C}_4$ (in particular, $\text{C}_2\text{-C}_3$, more in particular C_2) an aliphatic (in particular, an alkyl). More precisely but not necessarily, R^1 is a linear aliphatic (in particular, an alkyl); R^2 is a linear aliphatic (in particular, an alkyl).

[0070] Alternatively, or in addition, in particular, the alkylbenzene sulfonate have the following structural formula (VI):

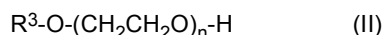


wherein R^1 is a $\text{C}_9\text{-C}_{18}$ aliphatic (in particular, an alkyl); M is a metal selected from sodium and potassium. More precisely but not necessarily, R^1 is a linear aliphatic (in particular, an alkyl).

[0071] In this text, by "aliphatic" it is meant a nonaromatic and unsubstituted (unless otherwise specified), saturated or unsaturated, linear, branched and/or cyclic hydrocarbon. Non-limiting examples of aliphatic groups are: t-butyl, ethenyl, 1- or 2-propenyl, cyclohexyl.

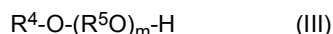
[0072] In this text, by "alkyl" or "alkyl-" it is meant a saturated aliphatic (i.e., an aliphatic group without double or triple carbon-carbon bonds). Non-limiting examples of alkyls are: methyl, n-propyl, t-butyl, cyclohexyl.

[0073] In particular, the ethoxylated alcohols have the following structural formula (II):



wherein R^3 is a $\text{C}_9\text{-C}_{18}$ aliphatic (in particular, an alkyl); n is an integer 1 to 9.

[0074] In particular, the etho-propoxylated alcohols have the following structural formula (III):



wherein R^4 is a $\text{C}_9\text{-C}_{18}$ aliphatic (in particular, an alkyl); m is an integer 1 to 9; and each R^5 is selected, each one independently of the other ones between $\text{-(CH}_2\text{)}_3\text{-}$ and $\text{-(CH}_2\text{)}_2\text{-}$.

[0076] In particular, the alkyl ethoxysulfates have the following structural formula (IV):



wherein R^6 is a $\text{C}_9\text{-C}_{18}$ aliphatic (in particular, an alkyl); a is an integer 1 to 9.

[0077] In particular, the alkyl sulfates have the following structural formula (V):



wherein R^7 is a $\text{C}_9\text{-C}_{18}$ aliphatic (in particular, an alkyl).

[0079] Advantageously but not necessarily, the inner composition 4 comprises from 1% (in particular, from 10%) to 30% (in particular, to 25%) by weight, with respect to the total weight of the inner composition 4, of the aforesaid surfactant.

[0080] Advantageously but not necessarily, once the product 1 is dissolved in demineralized water - i.e., osmotic and/or distilled (99 ml of water per each ml of the inner composition 4), the product 1 (in particular, the inner composition 4) has a pH ranging from 2 to 7.

[0081] According to some non-limiting embodiments, where the product 1 is for use as a dishwasher care, once the product 1 is dissolved in water (99 ml of water per each ml of the inner composition 4), the inner composition 4 has a pH up to 4 (in particular, up to 3; more in particular, up to 2.5).

[0082] Alternatively, where the product 1 is for use as a washing machine care and/or as an anti-scale product for washing machine, once the product 1 is dissolved in water (99 ml of water per each ml of the inner composition 4), the inner composition 4 has a pH ranging from 3 (in particular, from 6) up to 7 (in particular, up to 6.7).

[0083] According to some non-limiting embodiments, the casing has a thickness ranging from about $20\mu\text{m}$ to about

300 μ m (in particular, to about 150 μ m).

[0084] Advantageously but not necessarily, the casing 2 (is made of a material so that it) dissolves in water at 25°C within 10 minutes from immersion.

[0085] According to some non-limiting embodiments, the casing 2 is (mainly) of polyvinyl alcohol (PVOH).

[0086] In particular, the casing 2 is floppy. In other words, the casing 2 has a different shape when it is full (i.e., when the collecting chamber 3 is full) and when it is empty (i.e., when the collecting chamber 3 is empty). In other words, the casing 2, when full, assumes an expanded shape that is different (and volumetrically greater) than the shape assumed by the same empty casing 2.

[0087] Advantageously but not necessarily, the product 1 comprises from about 5 ml (in particular, from about 15 ml) to about 30 ml (in particular, to about 25 ml) of the inner composition 4.

[0088] It has been experimentally observed that the product 1 (as defined above) has several advantages relative to the state of the art. Among these we mention the following: the product 1 has a reduced environmental impact (in particular, the casing 2, being water-soluble and biodegradable, leaves no residues); it is easy to dose; it allows to improve the activity of the detergents relative to some types of dirt; in order to be used and, therefore, to make explicit its function it requires reduced energy, water, and time.

[0089] According to an aspect of the present invention, the use of the product 1 defined above is provided for the treatment of a washing appliance (for example, a dishwasher or a washing machine).

[0090] In particular, the appliance is configured for washing objects (items) selected from the group consisting of: kitchen utensils (more in particular, crockery and/or cutlery) and articles mainly made of fabric (more in particular, clothing and/or underwear).

[0091] Advantageously but not necessarily, during use, at least one of the aforesaid objects (in particular, a plurality of said objects) is present inside the appliance.

[0092] According to some non-limiting embodiments, the use comprises a treatment step during which the product 1 comes into contact with water (in particular, having a temperature below 40°C) inside the appliance and the casing (at least partially) dissolves.

[0093] Advantageously but not necessarily, during the treatment step, at least one aforesaid object (in particular, a plurality of said objects) is present inside the appliance.

[0094] According to some non-limiting embodiments, the appliance is a dishwasher.

[0095] Advantageously but not necessarily, the use provides that the product and a (further) detergent is used during the same washing cycle (in particular, during which at least one aforesaid object - more in particular, a plurality of said objects - is present inside the appliance). More precisely but not necessarily, the washing cycle comprises the aforementioned treatment step and (optionally) a washing step, during which the detergent is used to wash the object (s). Advantageously but not necessarily, the washing step takes place at a higher temperature than the treatment step. In particular, between the treatment step and the washing step there is a discharge step, during which the water used during the treatment step is removed (from the aforementioned appliance).

[0096] According to some embodiments, the use of the product 1 is as a dishwasher care. In addition, or alternatively, the use of the product 1 is as a washing machine care. In addition, or alternatively, the use of the product 1 is as an anti-scale product for washing machine.

[0097] As regards the use in the dishwasher, according to some embodiments, the product 1 can be placed, for example, in the cutlery basket and, considering the fast dissolution of the film, it starts working already in the pre-rinsing step (which in practice, corresponds to the aforementioned treatment step) allowing the dishwasher to be cleaned in preparation for washing.

[0098] In doing so, the product 2 never comes into contact with the real detergent, since the latter will outflow from the containment compartment only in the subsequent washing step. The product 1 therefore has the purpose of preparing the machine for washing, without having the need for unnecessary empty washing.

[0099] One of the most important problems to be overcome in the development of the product 1 was to realise a composition compatible with the water-soluble casing thereof. This implies that, unlike normal products, which envisage the use of high percentages of water, alternative solvents were to be chosen which, however, are able to solubilise the active ingredients. This is not at all simple since some ingredients, such as the weak acid, are well soluble in water, but poorly soluble in other means.

[0100] A common formulation basis was therefore identified for the various types of product (washing machine and dishwasher) which is based on the use of the aforesaid organic solvent (advantageously, a combination of the organic solvent and the alkalinizing agent).

[0101] Unless the contrary is explicitly indicated, the content of the references (articles, books, patent applications, etc.) cited in this text is referred to in full herein. In particular, the aforementioned references are incorporated herein by reference.

[0102] Further characteristics of the present invention will become apparent from the following description of merely illustrative and non-limiting examples.

Example 1

[0103] This example describes the realisation of some products in accordance with the present invention.

[0104] 20 millilitres of each of the inner compositions having one of the formulations ranging from A to E has been inserted between two sheets of MonoSol material (marketed by Kuraray WS Fil Division) whose perimeter edges were superimposed and subsequently welded by heat so as to enclose the formulations ranging from A to E. To facilitate welding, a very thin layer of water is applied between the edges before the superimposition thereof. These activities were carried out by a machine named Hydroforma supplied by the company Cloud Packaging Europe (L-8366 Hagen, Luxembourg).

[0105] In this way, five different products (single-dose) have been obtained, each of which (as described above) has a collecting chamber, which is delimited by a casing (obtained from the MonoSol material) and inside which an inner composition 4 having a respective of the formulations ranging from A to E is arranged.

Formulation A

Single-dose components	% by weight
Acrylic polymer	2
Citric acid	12
Sorbitol	12
Glycerol	46.3999
Triethanolamine	2
Etho-propoxylated alcohol	20
Colour	0.0001
Water	5.6
total	100

[0106] The product containing the composition with formulation A was mainly prepared as a dishwasher care product. This product is presented as biphasic.

Formulation B

Single-dose components	% by weight
Acrylic polymer	4
Citric acid	22
Sorbitol	12
Glycerol	34.9999
Monoethanolamine	2
Etho-propoxylated alcohol	15
Colour	0.0001
Fragrance	1
Water	9
total	100

[0107] The product containing the composition with formulation B was mainly prepared as a dishwasher care product. This product is presented as biphasic.

EP 3 825 391 A1

Formulation C

Single-dose components	% by weight
Acrylic polymer	2
Citric acid	6
Sorbitol	10
Glycerol	50.5
Monoethanolamine	20
Alkyl derivatives of benzenesulfonic acid with ethanolamine*	5
Water	6.5
total	100

[0108] The product containing the composition with formulation C was mainly prepared as an anti-scale product for washing machine. This product is presented as monophasic.

Formulation D

Single-dose components	% by weight
Citric acid	5
Sorbitol	10
Glycerol	45.4999
Triethanolamine	16
Ethoxylated alcohol	20
Colour	0.0001
Fragrance	0.5
Water	3
total	100

[0109] The product containing the composition with formulation D was mainly prepared as an anti-scale product for washing machine. This product is presented as biphasic.

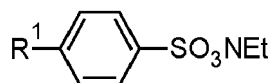
Formulation E

Single-dose components	% by weight
Citric acid	10
Acrylic polymer	5
Sorbitol	10
Glycerol	28.9999
Triethanolamine	16
Etho-propoxylated alcohol	20
Colour	0.0001
Water	10
total	100

[0110] The product containing the composition with the formulation E was mainly prepared as an anti-scale product for washing machines. This product is presented as biphasic.

[0111] The etho-propoxylated alcohols were one or more compounds having the following structure $R^4-O-(R^5O)_m-H$, wherein R^4 is a C_9-C_{18} aliphatic (in particular, an alkyl); m is an integer 1 to 9; and each R^5 is selected, each one independently of the other ones, between $-(CH_2)_3-$ and $-(CH_2)_2-$.

[0112] The alkyl derivatives of benzenesulfonic acid with ethanolamine had the following structure:



wherein R^1 is a C_9-C_{18} alkyl.

Example 2

[0113] This example describes the comparison between the capability of removing dirt from cotton patches of the detergent Dixan® alone (a detergent sold in Italy by Henkel® and marketed in other countries under the names Persil®, Wipp® and LeChat®) compared to the combination of the detergent Dixan® together with a single product in accordance with the present invention (the product with formulation D of the previous example).

[0114] The cotton patches were washed using the following parameters and devices:

Washing machine: Miele WMB 120

Water hardness: 20° f

Washing programme: cotton

Temperature: 30 °C

Spinning: 800 rpm

Time: 74 minutes

[0115] The measurements of the treated cotton patches were carried out using a Dr Lange LUCI 100 reflectometer by measuring the light reflected by the stains for the assessment of the dirt removal. Differences of less than 2 optical points are not perceived by the human eye and therefore were not considered as significant.

[0116] Each test was carried out by loading the washing machine with 10 towels, 2 bed sheets, 2 pillowcases, 1 specially stained patch (as required by the AISE - International Association for Soaps Detergents and Maintenance Products) and 2 ballast patches.

[0117] The differences between the results obtained are shown in the following table 1, in which the relative AISE code is shown together with the type of stain. The "+" signs indicate the stains for which the combination of the detergent Dixan® together with a single product in accordance with the present invention achieved a significant improvement. The "=" signs indicate that there is no substantial difference between the two treatments. The "-" signs indicate the stains for which there was a worsening using the combination of the detergent Dixan® together with a single product in accordance with the present invention.

Table 1

Washing at 30°C	Differences found	
Fruit juice CFT CS15	4.0	+
Te WFK 10J	8.1	+
Grass CFT CS08	-0.2	=
Car oil CFT C01	4.7	+
Make up CFT C01	4.2	+
Red Wine CFT H026	12.5	+
Coffee CFT KC-H109	11.7	+
Tomato sauce WE5TPWKC	9.1	+
Baby food WE5IACBFWKC	0.1	=
Blood WE5IACBFWKC	6.4	+

EP 3 825 391 A1

(continued)

Washing at 30°C	Differences found	
Mustard WE5FSMWKC	0.1	=
Chocolate CFT CS44	2.5	+
Grass/Mud WE5GMWKC	-5.9	-
Frying oil WE5BBWKC	-13.4	-

[0118] The table above shows how the use of the single dose has surprisingly allowed a significant improvement in washing performance for 9 stains out of 14.

Example 3

[0119] This example describes the comparison of the dirt removal capability of the combination of the detergent Dixan® together with a single product in accordance with the present invention (the product with formulation D of example 1) compared to the use of the detergent Dixan® together with another anti-scale product already present on the market.

[0120] The tests were carried out as described in the previous example. The results obtained are reported in the following table 2, in which the same symbols mentioned in the previous example were used.

Table 2

Washing at 30°C	Differences found	
Fruit juice CFT CS15	0.7	=
Te WFK 10J	5.2	+
Grass CFT CS08	2.6	+
Car oil CFT C01	-0.2	=
Make up CFT C01	-1.4	=
Red Wine CFT H026	5.1	+
Coffee CFT KC-H109	4.6	+
Tomato sauce WE5TPWKC	-4.3	-
Baby food WE5IACBFWKC	-0.4	=
Blood WE5IACBFWKC	4.1	+
Mustard WE5FSMWKC	-0.8	=
Chocolate CFT CS44	0.8	=
Grass/Mud WE5GMWKC	-7.7	-
Frying oil WE5BBWKC	-0.5	=

[0121] The table above shows how the use of the single dose has surprisingly allowed a significant improvement in washing performance for 5 stains out of 14; a worsening was observed in only two cases.

Example 4

[0122] This example describes a test carried out to assess the effect of a product in accordance with the present invention on limescale removal.

[0123] The tests were carried out using the following device and the following parameters:

Dishwasher: Whirlpool

Washing programme: pre-wash

Temperature: 20-30 °C

Litres: 4.0

Time: 14-16 minutes

Detergent: -

[0124] 25g of ballast dirt spread on the door of the dishwasher

[0125] Two tests were carried out by treating, in each case, a marble tile dimensioned: 7cm x 7cm x 0.1cm.

[0126] A test was carried out without using any product. The other test was carried out using a product in accordance with the invention (the product with formulation A of example 1).

[0127] At the end of the pre-wash cycle, the tiles were removed, dried, and weighed, assessing the removal of limescale by gravimetric method.

[0128] The results obtained have been reported in the following tables 3 and 4.

Table 3

	Initial weight	Final weight
Pre-wash without product	72.8694	72.8693
Pre-wash with product	72.0685	71.8543

Table 4

	Change	Change %
Pre-wash without product	-0.0001	=
Pre-wash with product	-0.2142	-0.30

[0129] As it can be observed, the use of the product allows a significant and surprising reduction of limescale.

Claims

1. A product for the treatment of a washing appliance;
the product (1) comprises a substantially water-soluble casing (2); a collecting chamber (3), which is delimited by said casing (2); and an inner composition (4), which is substantially liquid, is arranged inside the collecting chamber and comprises at least a weak acid and an organic solvent selected from the group consisting of:

alcohols, diols, triols, polyols and a combination thereof;

said inner composition (4) comprises 0% to 20% by weight, with respect to the total weight of said inner composition (4), of water; 2% to 40% by weight, with respect to the total weight of said inner composition (4), of said weak acid; and 10% to 95% by weight, with respect to the total weight of said inner composition (4), of said organic solvent.

2. A product according to claim 1, wherein said alcohols, diols, triols and polyols are, each one independently of the other ones, C₂-C₈; said weak acid has a pK_a in water measured at 25°C and 1 bar of more than 1 and up to 9; said inner composition (4) comprises 0% to 15% by weight, with respect to the total weight of said inner composition (4), of water; 5% to 35% by weight, with respect to the total weight of said inner composition (4), of said weak acid; and 25% to 80% by weight, with respect to the total weight of said inner composition (4), of said organic solvent; in particular, said weak acid is substantially in liquid phase.

3. A product according to claim 1 or 2, wherein 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; said weak acid is selected from the group consisting of: carboxylic acids (in particular, C₁-C₈; in particular, with 1 to 4 carboxylic groups), phosphoric acid and a combination thereof.

4. A product according to any one of the preceding claims, wherein said organic solvent is selected from the group

consisting of: glycerin, sorbitol and a combination thereof; said weak acid is selected from the group consisting of: citric acid, lactic acid, formic acid, phosphoric acid, and a combination thereof.

- 5 5. A product according to any one of the preceding claims, wherein said inner composition (4) comprises 1% to 40% by weight, with respect to the total weight of said inner composition (4), of an alkalinizing agent having a PK_b , in water at 25°C and 1 bar, ranging from 2 to 9.
- 10 6. A product according to any one of the preceding claims, wherein said inner composition (4) comprises 1% to 35% by weight, with respect to the total weight of said inner composition (4), of an alkalinizing agent selected from the group consisting of: C_1 - C_8 hydroxy-ammines, ammonia, potassium hydroxide and a combination thereof.
- 15 7. A product according to claim 5 or 6, wherein the alkalinizing agent is selected from the group consisting of: monoethanolamine, diethanolamine, triethanolamine and a combination thereof.
- 20 8. A product according to any one of the preceding claims, wherein said inner composition (4) comprises 1% to 10% by weight, with respect to the total weight of said inner composition (4), of a polymer component selected from the group consisting of: acrylic homopolymers, acrylic-maleic copolymers and a combination thereof.
- 25 9. A product according to claim 8, 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.
- 30 10. A product according to any one of the preceding claims, wherein said inner composition (4) comprises 1% to 50% by weight, with respect to the total weight of said inner composition (4), of a surfactant selected from the group consisting of: anionic surfactants, cationic surfactants, amphoteric surfactant, non-ionic surfactants, and a combination thereof.
- 35 11. A product according to claim 10, wherein said inner composition (4) comprises 1% to 30% by weight, with respect to the total weight of said inner composition (4), of said surfactant, which is selected from the group consisting of: alkyl ethoxysulfates, alkyl sulfates, salts of the dodecylbenzenesulfonic acid, alkylbenzene sulfonates, alkyl sulfonates, soaps, amine ethoxylates, quaternary ammonium salts, betaines, amine oxide, ethoxylated alcohols, ethopropoxylated alcohols, alkyl polyglucosides, ethanolamides of fatty acids and a combination thereof.
- 40 12. A product according to claim 11, wherein said inner composition (4) comprises 10% to 25% by weight, with respect to the total weight of said inner composition (4), of said surfactant, which comprises a non-ionic surfactant.
- 45 13. A product according to claim 12, wherein said surfactant is selected from the group consisting of: C_8 - C_{38} ethoxylated alcohols, C_8 - C_{38} etho-propoxylated alcohols, alkyl polyglucosides, ethanolamides of fatty acids and a combination thereof.
- 50 14. A product according to any one of the claims from 11 to 13, wherein said surfactant is selected from the group consisting of: C_8 - C_{38} ethoxylated alcohols, C_8 - C_{38} etho-propoxylated alcohols, C_9 - C_{27} alkylbenzene sulfonates and a combination thereof.
- 55 15. A use of a product according to any one of the preceding claims for the treatment of an appliance configured for washing objects (items) selected from the group consisting of: kitchen utensils (more in particular, crockery and/or cutlery) and articles mainly made of fabric (more in particular, clothing and/or underwear); in particular, the appliance is either a dishwasher or a washing machine; in particular, during use, at least one aforesaid object (in particular, a plurality of said objects) is present inside the appliance.
16. A use according to claim 15 and comprising a treatment step during which the product comes into contact with water having a temperature below 40°C inside said appliance and said casing (2) at least partially dissolves; in particular, during the treatment step, at least one aforesaid object (in particular, a plurality of said objects) is present inside the appliance; in particular, the appliance is a dishwasher.
17. A use according to claim 15 or 16, and which provides that said product and a (further) detergent are used during a same washing cycle (in particular, during which at least one aforesaid object - more in particular, a plurality of said objects - is present inside the appliance); in particular, the washing cycle comprises said treatment step and a washing step, during which the detergent is used to wash the object/s.

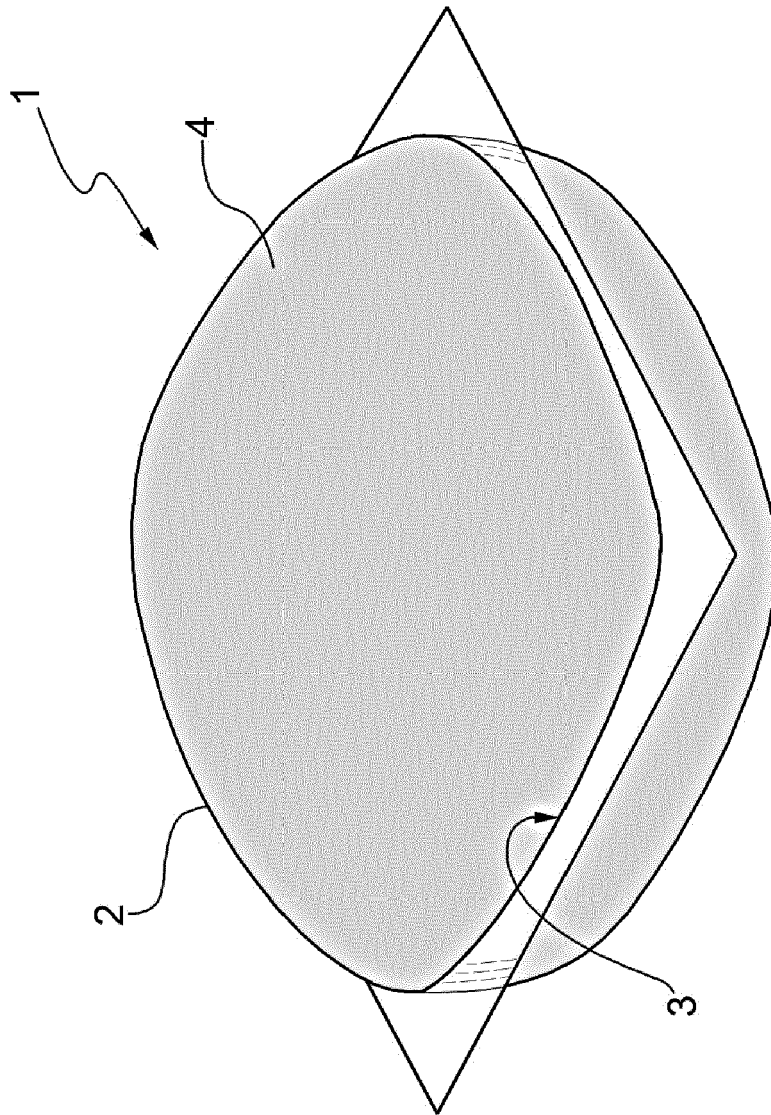


FIG. 1

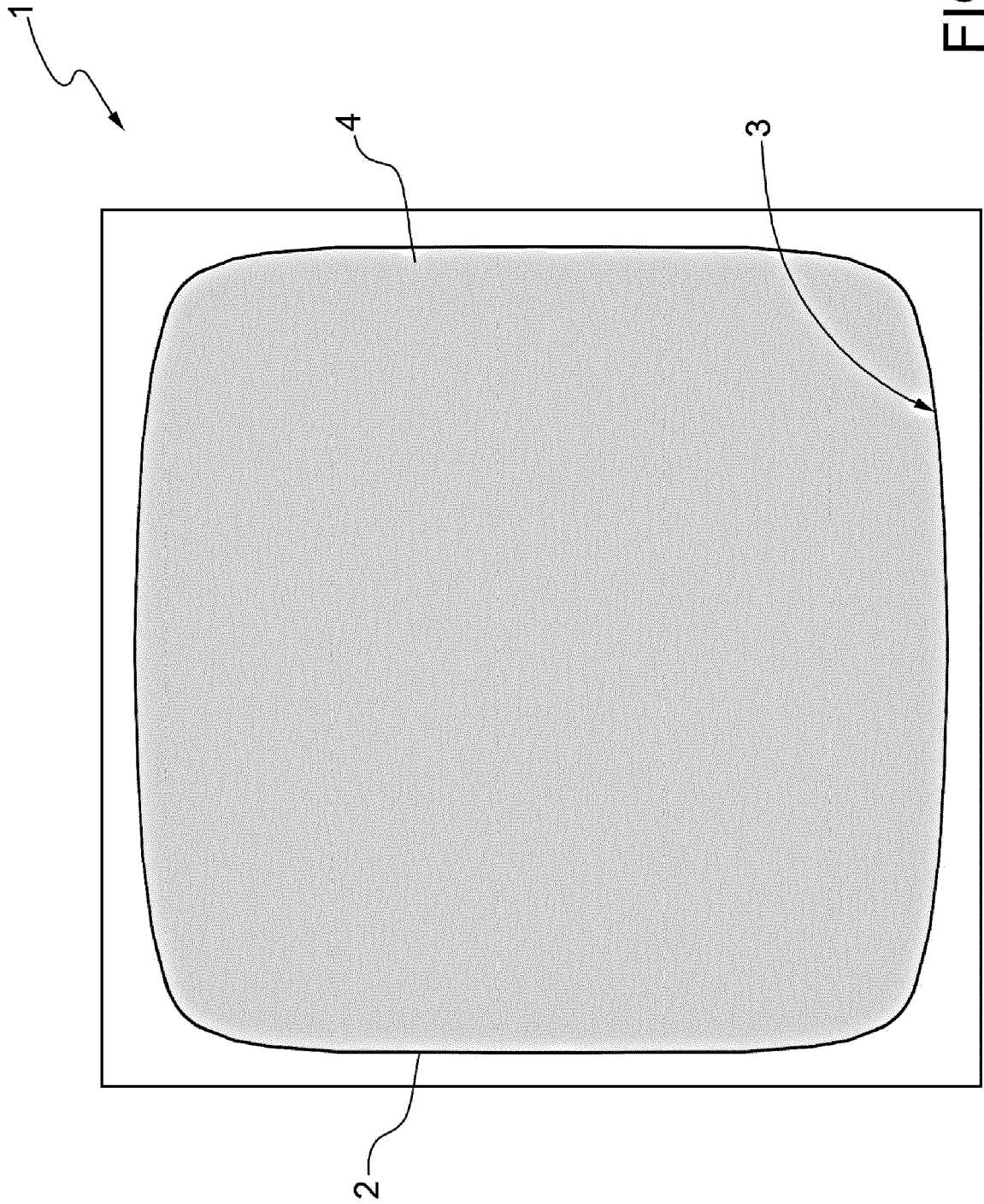


FIG. 2

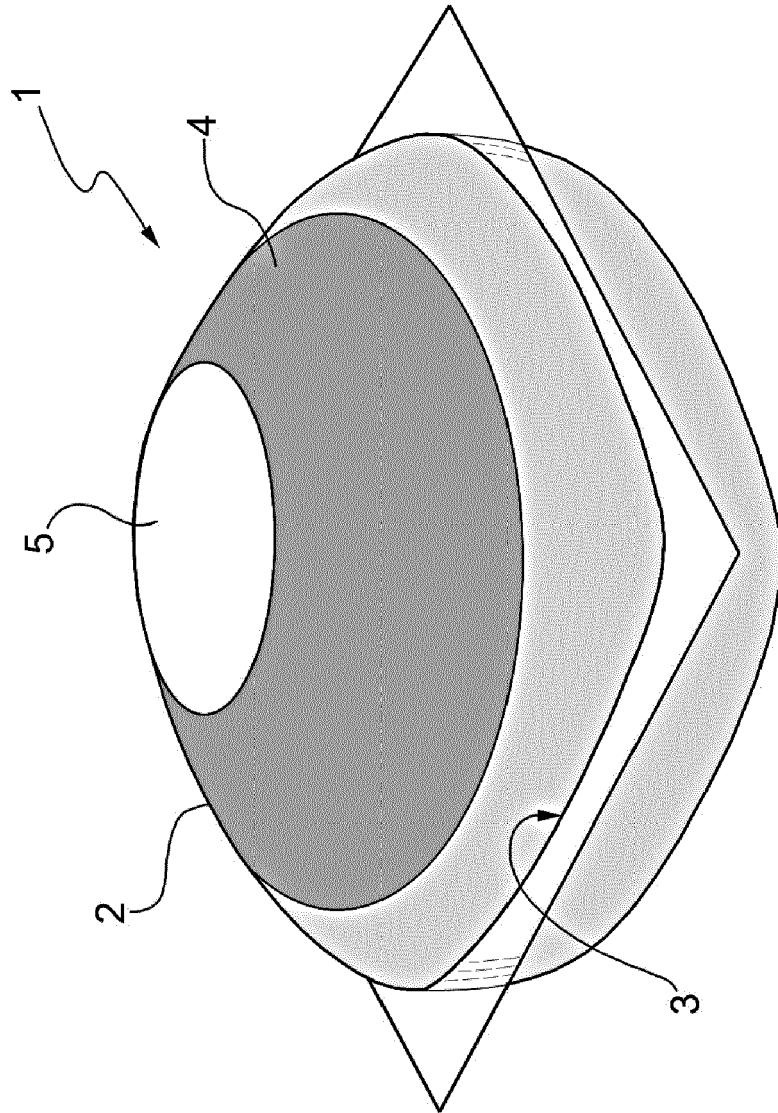


FIG.3

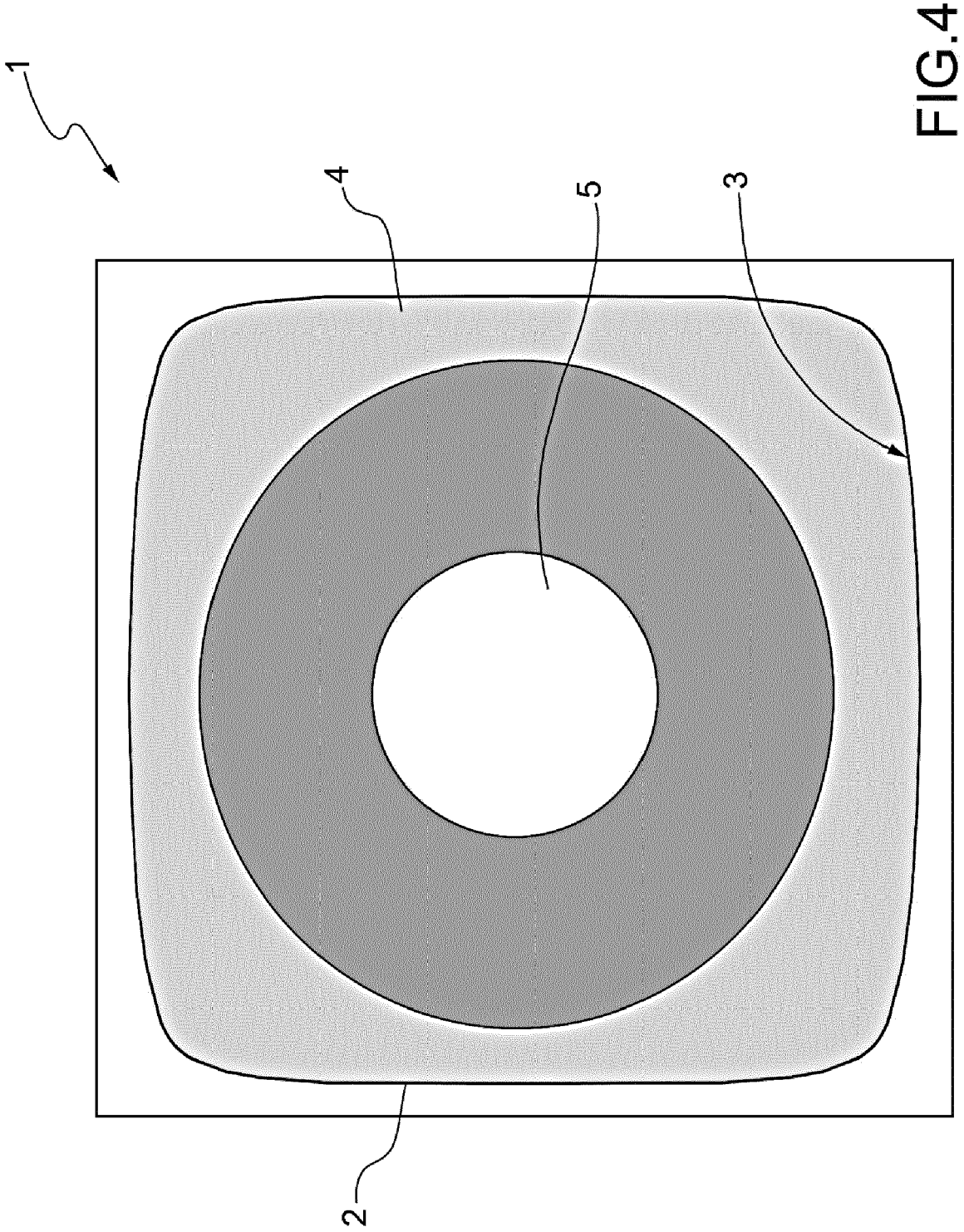


FIG. 4



EUROPEAN SEARCH REPORT

 Application Number
 EP 20 20 8761

5

10

15

20

25

30

35

40

45

50

55

DOCUMENTS CONSIDERED TO BE RELEVANT				
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)	
X	EP 1 679 362 A1 (PROCTER & GAMBLE [US]) 12 July 2006 (2006-07-12)	1-17	INV. C11D7/50 C11D7/04 C11D11/00 C11D7/08	
Y	* paragraphs [0014], [0015], [0016], [0018], [0024], [0031], [0033], [0035], [0040], [0041], [0054], [0061]; claims; examples *	1-17		
Y	EP 1 690 924 A1 (PROCTER & GAMBLE [US]) 16 August 2006 (2006-08-16) * paragraphs [0010] - [0018], [0022], [0027], [0030], [0042], [0062]; claims; examples *	1-17		
Y	WO 2015/017176 A1 (EASTMAN CHEM CO [US]) 5 February 2015 (2015-02-05) * paragraphs [0063], [0066], [0091]; claims *	1-17		
Y	US 5 981 449 A (RAPISARDA DARIO [IT] ET AL) 9 November 1999 (1999-11-09) * column 1 * * column 3, line 64 - column 4, line 27 * * claims; examples *	1-17		TECHNICAL FIELDS SEARCHED (IPC)
Y	US 4 465 612 A (ALTENSCHOEPFER THEODOR [DE] ET AL) 14 August 1984 (1984-08-14) * claims; examples *	1-17		C11D
Y	EP 0 256 148 A1 (BENCKISER GMBH JOH A [DE]) 24 February 1988 (1988-02-24) * column 1; claims; examples *	1-17		
A	WO 2006/023061 A1 (MALLINCKRODT BAKER INC [US]; KANE SEAN M [US]) 2 March 2006 (2006-03-02) * claims; examples *	1-17		
The present search report has been drawn up for all claims				
Place of search The Hague		Date of completion of the search 8 February 2021	Examiner Serbetsoglou, A	
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)

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 20 20 8761

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

08-02-2021

10

15

20

25

30

35

40

45

50

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1679362 A1	12-07-2006	AT 400643 T	15-07-2008
		CA 2593625 A1	17-08-2006
		EP 1679362 A1	12-07-2006
		ES 2308606 T3	01-12-2008
		JP 5270168 B2	21-08-2013
		JP 2008527111 A	24-07-2008
		US 2006172910 A1	03-08-2006
		WO 2006086109 A1	17-08-2006

EP 1690924 A1	16-08-2006	CA 2594638 A1	17-08-2006
		EP 1690924 A1	16-08-2006
		JP 2008528287 A	31-07-2008
		US 2006185697 A1	24-08-2006
		WO 2006086373 A1	17-08-2006

WO 2015017176 A1	05-02-2015	US 2015038391 A1	05-02-2015
		WO 2015017176 A1	05-02-2015

US 5981449 A	09-11-1999	NONE	

US 4465612 A	14-08-1984	AT 49339 T	15-01-1990
		AU 560696 B2	16-04-1987
		CA 1227423 A	29-09-1987
		DE 3240688 A1	30-05-1984
		DK 465283 A	05-05-1984
		EP 0111135 A2	20-06-1984
		US 4465612 A	14-08-1984
		US 4528110 A	09-07-1985
		ZA 838214 B	27-06-1984

EP 0256148 A1	24-02-1988	EP 0256148 A1	24-02-1988
		ES 2004799 A6	01-02-1989
		JP S6399295 A	30-04-1988

WO 2006023061 A1	02-03-2006	AT 450595 T	15-12-2009
		BR PI0514058 A	27-05-2008
		CA 2575991 A1	02-03-2006
		CN 1993457 A	04-07-2007
		DK 1789527 T3	08-03-2010
		EP 1789527 A1	30-05-2007
		ES 2335786 T3	05-04-2010
		JP 4625842 B2	02-02-2011
		JP 2008509554 A	27-03-2008
		KR 20070045224 A	02-05-2007
		MY 144284 A	29-08-2011
		PT 1789527 E	15-01-2010

EPO FORM P0459

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

55

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- IT 102019000021549 [0001]

Non-patent literature cited in the description

- **REIJENGA et al.** Developments of Methods for the Determination of pKa Values. *Analytical Chemistry Insights*, 2013, vol. 8, 53-17 [0029]
- **X. SUBIRATS et al.** Methods for pKa Determination (I): Potentiometry, Spectrophotometry, and Capillary Electrophore. *Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*, 2015 [0029]
- **SERJEANT, E. P.** Potentiometry and Potentiometric Titrations. Wiley, 1984 [0029]