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(54) PERFUMING AND/OR DETERGENT GEL TABLET

(57) A perfuming and/or detergent gel tablet is described, having improved performances and its use as a detergent and/or perfuming agent, by application through an open cage in sanitary appliances, household appliances, etc., preferably in WCs.

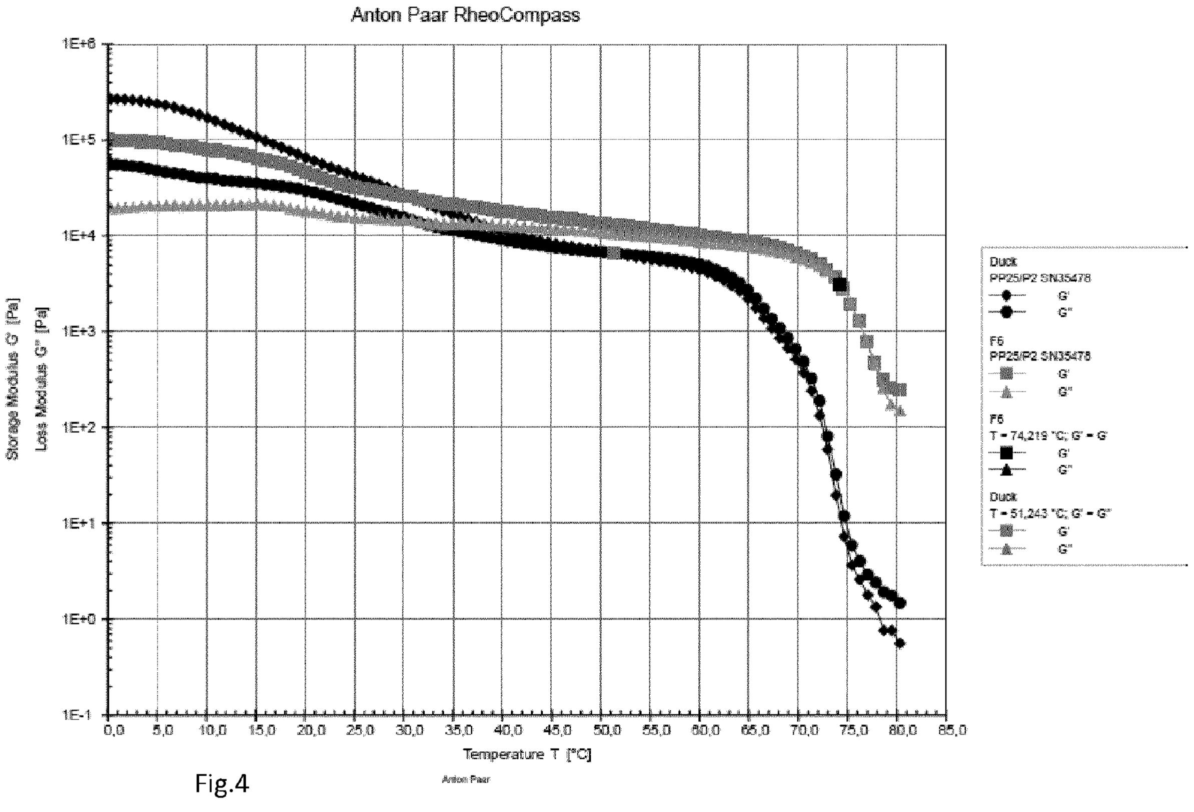

Fig.4

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Description

[0001] The present invention relates to a perfuming and/or detergent gel tablet, preferably for WC applications.

[0002] Most tablets for WCs are based on a solid matrix. This matrix has a composition based on anionic surfactants and, in a smaller quantity, non-ionic surfactants on a support of an inorganic salt: sodium carbonate and/or sodium sulfate and/or less frequently sodium chloride. Other additives such as, for example, polyethyleneglycols, can also be present in the composition, which modulate the hardness and mechanical properties of the composition and its behaviour in the extrusion process, and other ingredients such as dyes, fragrances, etc.

[0003] Water is present in very small percentages in these compositions and the critical aspects for the stability of these solid tablets mainly concern the aesthetic properties such as colour and fragrance. There are no known problems relating to the physical integrity of the block itself, which maintains its solid characteristics over time, also in open containers.

[0004] There are also other WC compositions in the form of gels or liquids. These compositions are also based on surfactants (anionic, non-ionic, amphoteric) and contain considerable quantities of water (30-75% by weight with respect to the total weight of the composition).

[0005] The structure of gels typically derives from the type and quantity of the surfactants, but also from further components: polyacrylates, cellulose, rheology modifiers, etc. The quantity of water in the composition significantly influences the physical properties of compositions in gel form such as, for example, the viscosity, the melting point or the temperature at which phase changes take place inside the structure. If not stored in a closed container, these compositions in gel form tend to gradually lose water and undergo profound physical changes during their useful life, a problem which, as already mentioned, does not arise in the case of solid tablets.

[0006] Examples of gels based on surfactants and for detergence applications are known in literature: see US 2011/0268683 or also EP 0 598 335 A2. These gels are in fact water-based and the concentration of water influences their physical properties such as viscosity, melting point or the temperature at which phase changes take place inside the structure, etc.

[0007] Other patents in literature describe gels whose function is to be applied directly to the wall of the WC. Examples of these solutions are described and claimed in patents EP1086199 or also EP1325103. These gels are conceived and used as tablets that adhere directly to the wall of the WC.

[0008] These gels are typically stored in closed containers and there are no particular problems of stability for two reasons. First of all, because the product, even if it has a relatively low melting point, cannot leave the closed container. Furthermore, even if high temperatures are reached (55°-60°C for example), which can lead to a transition of the liquid state, the gel is always stored in a closed container and once it is on the shelf of the supermarket or at the consumer's home, the product reacquires its original physical gel properties. Secondly, the type of container in which the gel is packaged, made of HDPE, PET or PP with a thickness of at least 1 mm, does not allow significant losses of humidity. The physico-chemical properties of the product are therefore preserved.

[0009] Problems arise when the production of gel tablets is proposed in application forms that require exposure of the product: a typical example relates to products in which the gel tablet is used as a sanitizing and/or cleaning and/or perfuming element in a WC cage, which evidently requires numerous openings. The use of a gel tablet in cage containers, in place of traditional solid tablets with a high content of inert products (such as sodium carbonate, calcium carbonate, sodium sulfate), has undoubted and evident advantages: it is in fact possible to combine a form of gel product, with aesthetics and perfuming performances definitely superior to traditional tablets, with a mode of use in cages. Application with the use of a cage is extremely advantageous with respect to the use of closed containers, which considerably limit the perfuming performances and interaction with the water of the WC, and also with respect to the use of adhesive forms which require particular formula expedients for making the gel adhesive with respect to the wall of the WC and wherein each application has a duration limited to 7-10 days.

[0010] A product for WCs composed of a tablet in a cage is typically marketed in blisters of thermoformed plastic material which allow the shelf contents to be viewed. These blisters are closed on the back with a welded plastic film or with cardboard, also applied by welding or gluing. As an alternative, these products in cages are marketed in flowpacks of plastic material, in turn closed in cartons.

[0011] These forms of packaging, however, are not very effective in retaining the water of the gel detergent composition, both in the long term and under high temperature conditions. Aqueous compositions preserved in blisters or in flowpacks and in cartons can lose considerable quantities of water, reaching a loss of water present in the composition of even 75% by weight with respect to the weight of the water present in the composition, for example when stored in a closed blister. This loss of water can take place in more or less lengthy times and evidently depends on the temperature, the material of the blister, the sealing film and the relative thicknesses.

[0012] This water loss is particularly significant in the case of compositions in gel form as it causes physical changes in the gel itself. In particular, as a result of the concentration of surfactants resulting from the loss of water, it is noted that the gel becomes liquid, i.e. it has a phase transition from gel to the liquid state at much lower temperatures with respect to the starting gel.

[0013] An objective of the present invention is therefore to identify a gel tablet that overcomes the drawbacks of the gel tablets of the state of the art.

[0014] A further objective of the present invention is to identify a table in gel form which can be used in open-cage applications, preferably for WCs.

[0015] These and further objectives that will appear evident from the text of the present patent application, have been achieved by the gel tablet according to the present invention.

[0016] The object of the present invention relates to a perfuming and/or detergent gel tablet characterized in that it has

a) an initial melting point or transition point from the gel state to the liquid state, ranging from 65°C to 90°C, and
b) a melting point or transition point from the gel state to the liquid state higher than or equal to 44°C, when the gel tablet is characterized by a reduction in the water content ranging from 75% to 95% by weight, preferably from 78% to 85% by weight, with respect to the water present in the initial gel tablet.

[0017] The melting or transition point is the temperature at which the composition in gel form becomes liquid and the product can therefore totally or partially come out of the cage containing it.

[0018] The initial melting or transition point from the gel state to the liquid state refers to the melting or transition point that characterizes the gel tablet having the initial composition, i.e. the composition in which no loss of water has occurred, due to use, with respect to the quantity of water present in the initial composition.

[0019] A gel tablet generally loses water in use, dehydrating and losing its initial gel structure, and consequently the second element that defines the gel tablet according to the present invention is particularly important as its specifies and requires as an essential feature that the gel tablet preserves a melting or transition point higher than or equal to 44°C, also when the gel tablet has reached a high dehydration degree (i.e. it has lost 75 to 95% by weight of water with respect to the initial quantity of water) due to use.

[0020] The perfuming and/or detergent gel tablet according to the present invention is therefore defined by two characteristics which, together, ensure that the product, during its useful life, always maintains its physical gel form, even as a result of the inevitable gradual loss of moisture during use.

[0021] This initial melting point or transition point value from the gel state to the liquid state within the range of 65°C to 90°C is also extremely convenient as it allows the tablet to be produced in gel form, operating with the composition in the liquid state, without causing damage to the product itself or to some of it components (for example the fragrance).

[0022] As already mentioned, the melting or transition point is the temperature at which the composition in gel form becomes liquid and the product can therefore either totally or partially come out of the cage containing it.

[0023] The melting or transition point can be measured empirically through an aging test in an oven, which evaluates the stability of the product over time. For a more specific and accurate evaluation of this property, a portion of gel is transferred to a test-tube, a calibrated thermometer is inserted in said test-tube and the bottom of the test-tube is immersed in a hot water bath. When the gel becomes liquid the temperature of the transition state is read.

[0024] More specifically, the measurement method used in the present patent application is the following: 10 g of composition are placed in a beaker having a diameter of 5 cm and a calibrated thermometer is inserted. Water is heated to a temperature of 40°C in a hot bath. The beaker is then immersed in the bath at 40°C and the temperature of the composition is read at the moment when the gel melts to become liquid.

[0025] This method is applied for measuring the melting or transition point of both the initial product that has not yet undergone any dehydration, and also the dehydrated product, i.e. which has lost from 75 to 95% by weight of water with respect to the initial quantity of water.

[0026] A further object of the present invention relates to the use of a gel tablet, as detergent and/or perfuming agent, by application through an open cage in sanitary appliances, household appliances, etc. preferably in WCs.

[0027] The gel tablet according to the present invention has a composition comprising:

- one or more hydrosoluble polymers;
- one or more non-ionic surfactants and
- water.

[0028] The hydrosoluble polymer has a structuring/viscosifying function, which allows the integrity of the structure of the composition to be maintained in the gel phase during the life of the product, under stress and also at high temperatures, thus allowing a high-quality gel tablet to be formulated, together with the other components.

[0029] The gel tablet according to the present invention is composed of a composition comprising:

- one or more polymers selected from cellulose polymers and/or their derivatives, polyvinylpyrrolidone polymers and/or their derivatives or a mixture of cellulose and/or polyvinylpyrrolidone polymers;

- one or more non-ionic surfactants selected from C_{16}-C_{18} ethoxylated alcohols with an ethoxylation degree ranging from 20 to 50, preferably from 20 to 30 and,
- water.

[0030] The cellulose polymers and/or their derivatives are selected from carboxymethyl cellulose (CMC), high-purity CMC, preferably carboxymethyl cellulose. The molecular weight of the cellulose polymers ranges from 1,000,000 to 1,500,000 g/mol.

[0031] The polyvinylpyrrolidone polymers and/or their derivatives are selected from polyvinylpyrrolidone having a molecular (g/mol) ranging from 40,000 to 3,000,000, preferably polyvinylpyrrolidone having a molecular weight (g/mol) ranging from 900,000 to 1,500,000.

[0032] The gel tablet according to the present invention comprises one or more hydrosoluble polymers selected from cellulose polymers and/or their derivatives, polyvinylpyrrolidone polymers and/or their derivatives or mixtures of cellulose and/or polyvinylpyrrolidone polymers, in a quantity ranging from 0.01% to 10% by weight with respect to the total weight of the gel tablet.

[0033] The gel tablet according to the present invention preferably comprises a polyvinylpyrrolidone polymer having a molecular weight (g/mol) ranging from 900,000 to 1,500,000, in a quantity ranging from 0.01% to 10% by weight with respect to the total weight of the gel tablet, preferably in a quantity ranging from 1% to 5%, even more preferably from 1.5% to 3% by weight with respect to the total weight of the gel tablet.

[0034] In the gel tablet according to the present invention, the C_{16}-C_{18} ethoxylated alcohol with an ethoxylation degree ranging from 20 to 30, is selected from cetylstearyl alcohol 20 EO or cetylstearyl alcohol 29 EO, and is preferably cetylstearyl alcohol 20 EO.

[0035] The C_{16}-C_{18} ethoxylated alcohol with an ethoxylation degree ranging from 20 to 50, preferably from 20 to 30, is present in a quantity ranging from 20% to 60% preferably from 30% to 45% by weight with respect to the total weight of the gel tablet.

[0036] The weight ratio water/non-ionic surfactant in the gel tablet according to the present invention ranges from 65/20 to 20/65, preferably from 60/30 to 30/60.

[0037] An example of a gel tablet according to the present invention which is particularly performing, has the following composition:
water, polyvinylpyrrolidone having a molecular weight (g/mol) ranging from 900,000 to 1,500,000, cetylstearyl alcohol 20 EO, benzisothiazolinone, dye and fragrance.

[0038] A preferred example of a gel tablet according to the present invention, which is particularly performing, has the following composition:

- water in a quantity ranging from 25 to 65% by weight,
- polyvinylpyrrolidone having a molecular weight (g/mol) ranging from 900,000 to 1,500,000 in a quantity ranging from 1 to 5% by weight,
- cetylstearyl alcohol 20 EO in a quantity ranging from 20 to 60% by weight,
- benzisothiazolinone in a quantity ranging from 0.01 to 3% by weight,
- dye in a quantity ranging from 0.001 to 0.01% by weight and
- fragrance in a quantity ranging from 1 to 10% by weight,

each weight quantity being indicated with respect to the total weight of the gel tablet.

[0039] An even more preferred composition of a gel tablet according to the present invention is the following:

- water in a quantity equal to 59.36% by weight,
- polyvinylpyrrolidone having a molecular weight (g/mol) ranging from 900,000 to 1,500,000 (PVP K90) in a quantity equal to 1.5% by weight,
- cetylstearyl alcohol 20 EO in a quantity equal to 35.0% by weight,
- benzisothiazolinone in a quantity equal to 0.1% by weight,
- dye in a quantity equal to 0.04% by weight and
- fragrance in a quantity equal to 4% by weight,

each quantity being indicated with respect to the total weight of the gel tablet.

[0040] The main and surprising advantage of the gel tablet according to the present invention is that it maintains the physical gel state even after a substantial loss of moisture. The insertion of cellulose and/or polyvinylpyrrolidone polymers, combined with specific ethoxylated alcohols surprisingly allows a clear improvement in terms of stability, allowing the phase transition to the liquid state to be avoided even in the face of significant water losses.

[0041] The gel tablets according to the present invention surprisingly maintain the physical gel form for much longer times, even after substantial moisture losses. The phase transition from gel to the liquid state consequently takes place, under the same conditions, in much longer times with respect to the tablets of the state of the art, therefore resulting in an improved stability.

[0042] The gel tablet according to the present invention is also particularly advantageous in a condition of non-reception of water flows after application in the WC. Also under this condition of use, the presence of polyvinylpyrrolidone or cellulose polymer leads to a greater general stability of the composition in terms of daily moisture loss and consequent removal, in terms of time, of the phase transition phenomenon to liquid.

[0043] The gel tablet according to the present invention also has the advantage of an improved stability also in the presence of strongly destabilizing agents such as foaming surfactants with a negative charge. Also in the presence of sodium lauryl sulfate, in fact, i.e. an anionic foaming surfactant, no decrease in the stability is observed. This allows the production of gel tablets having a sufficient stability and an increased foaming activity.

[0044] Furthermore, it is also particularly advantageous to use combinations of blisters and sealing films with particular barrier properties. In this way, the loss of moisture over time is significantly slowed down and the useful life of the product is further extended, combining the advantages linked to the compositions described above and object of the present invention, which maintain their physical integrity even after a strong losses of moisture, and the advantages linked to the properties of the blister and the sealing film that slow down the loss of moisture over time. The combination of these two effects advantageously extends the shelf-life of the finished product.

[0045] Some examples are provided of particularly advantageous blisters and sealing films (materials and thicknesses).

Blister:

PVC 500 microns

PET 500 microns

Coupled material: PET/EvOH/PE 500 microns

Sealing film:

Coupled material: PETalox/PET.EvOH.PE 30 microns (transparent metallized polyester with a further EvOH barrier)

PET/PE.EvOH.PE 72 microns

[0046] The following examples are provided for purely illustrative purposes.

[0047] In all the examples described hereunder, the gel tablet was prepared as follows:

- a mixer was charged with deionized water and the whole mixture heated to a temperature of 85-90°C;
- the polymer was then added until complete dissolution of the same;
- the anionic surfactant was subsequently added, depending on the composition;
- a premix was then added comprising non-ionic surfactant and fragrance;
- a premix of preservative, colour and water was subsequently added;
- finally, the remaining weight percentage of non-ionic surfactant, depending on the composition, was added, and the whole mixture was brought to volume with water.

[0048] Ten gel tablets were tested in the examples, whose qualitative and quantitative compositions are indicated in Table 1 hereunder.

Table 1

Components	F1 (%)	F2 (%)	F3 (%)	F4 (%)	F5 (%)	F6 (%)	F7 (%)	F8 (%)	F9 (%)	F10 (%)
Water	**50.87**	**55.57**	**53.86**	**59.36**	**60.86**	**47.86**	**50.36**	**59.86**	**50.86**	**54.9**
High-purity CMC		**0.3**								
PVP K-90			**1.5**	**1.5**		**3.0**				
Xanthan gum							**0.5**	**1.0**		**0.5**
Cetylstearyl alcohol 20EO			**40.0**	**35.0**	**35.0**	**35.0**	**35.0**	**35.0**	**35.0**	
Cetylstearyl alcohol 29EO	**40.0**	**35.0**								
Ethoxylated Alkyl (C22) 35EO										**20.0**
Coconut amidopropyldimethylamino-oxide										**2.0**
Sodium Lauryl Sulfate						**10.0**	**10.0**		**10.0**	
α-olefinsulfonate										**2.5**
Benzisothiazolinone	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**	**0.1**
Colour	**0.03**	**0.03**	**0.04**	**0.04**	**0.04**	**0.04**	**0.04**	**0.04**	**0.04**	
Fragrance	**4.0**	**4.0**	**4.5**	**4.0**	**4.0**	**4.0**	**4.0**	**4.0**	**4.0**	**20.0**
Amine N-oxide	**5.0**	**5.0**								

[0049] The gel tablets F2, F3, F4 and F6 are tablets according to the present invention, whereas the tablets F1, F5, F7, F8, F9 and F10 are tablets according to the state of the art or in any case not representative of the present invention. More specifically, the tablet F10 represents a compound according to the example of the document US 6,667,286, corresponding to European patent EP1086199.

Example 1

[0050] The composition F1 indicated in Table 1, has a melting point of 70°C. The same composition F1, placed in a blister with sealing film PET/PE.EVOH.PE and a thermoformed PE/PET valve in an oven at 40°C, has a phase transition to the liquid state at a temperature lower than 40°C after 5 weeks, having lost about 43.8% of water, as indicated in Table 2 hereunder.

[0051] The loss of water was measured by weighing the sample before the experiment and subtracting the weight measured from week to week, from the initial weight. The difference in weight between the initial weight and the weight per week 1 (2, 3, 4 or 5) represents the moisture/water lost during the same week.

Table 2: The experiment was carried out at a fixed temperature of 40°C.

F1	**Week 1**	**Week 2**	**Week 3**	**Week 4**	**Week 5**
Moisture loss percentage (Physical state)	**9.3% (Gel)**	**18.8% (Gel)**	**26.1% (Gel)**	**34.4% (Gel)**	**43.8% (Liquid)**

[0052] The same test was carried out comparing the gel tablet having formulation F1 with the gel tablets according to the present invention, having formulations F2, F4 and F6.

[0053] The results are indicated in Table 3 hereunder.

Table 3: the compositions were kept at a fixed temperature of 40°C.

Composition	**F1**	**F2**	**F4**	**F6**	**F9**
Moisture loss percentage 5th week (Physical state)	**43.8% (Liquid)**	**41.1% (Gel)**	**38.2% (Gel)**	**40.2% (Gel)**	**40.2% (Gel)**
Moisture loss percentage 10th week (Physical state)		**74.3% (Liquid)**	**69.6% (Gel)**	**73.5% (Gel)**	**70.1% (Gel)**
Moisture loss percentage 11th week (Physical state)			**82.1% (Gel)**	**81.7% (Liquid)**	
Moisture loss percentage 13th week (Physical state)			**91.1% (Liquid)**		

[0054] The results indicated in Table 3 show that the composition F2 has a better stability profile with respect to the composition F1. The phase transition to the liquid state at 40°C is postponed by 5 weeks compared to F1, bringing the stability in blisters with PET/PE.EVOH.PE sealing film and thermoformed PE/PET valve, from 5 to 10 weeks. The effect is even more evident for F4 and F6.

[0055] The presence of cellulose (F2) or polyvinylpyrrolidone (F4 and F6) polymers in the gel tablet according to the present invention has in fact brought about a significant improvement. The stability data of Table 3 show maintenance of the physical state of the gel for a longer time, as the moisture loss increases.

[0056] The previous test actually shows that the gel tablet according to the present invention, comprising cetyl stearyl ethoxylated alcohols with an ethoxylation degree of 20 EO combined with a polyvinylpyrrolidone polymer PVP-K90 (F4 and F6), maintains the physical gel state also after significant moisture losses. The insertion of the polyvinylpyrrolidone polymer PVP-K90 surprisingly produces an evident improvement in terms of stability. The stability profile, in fact, is further improved bringing the phase transition to the liquid state to the thirteenth week. Table 3 above also shows an improved stability profile also for compositions, such as the composition F6, in which a strongly destabilizing agent is present, such as foaming surfactants with a negative charge.

[0057] The composition F6, also comprising sodium lauryl sulfate, i.e. an anionic foaming surfactant, does not show a decrease in the stability: the phase transition to the liquid state of F6 becomes evident at the tenth week, with a definite improvement with respect to F1, a composition that does not include either polyvinylpyrrolidone polymers or cellulose polymers, and also with respect, for example, to F2, a composition according to the present invention in which the polymer is a cellulose polymer and does not contain however the destabilizing agent.

[0058] The composition F9 (i.e. the same composition as F6, but without the polymer PVP-K90) incorporates the concept of modification of the composition without the stabilizing agent PVP-K90. The data indicated in Table 3 show an improvement in terms of stability, bringing the phase transition from gel to liquid from 81.7% for a composition F6 with PVP-K90, to 70.1% of moisture loss for a composition F9 without PVP-K90, the anionic surfactant being present in both cases.

[0059] The previous data therefore show that the improvement effect of the polyvinylpyrrolidonic polymer is greater than the improvement effect of a cellulose polymer.

[0060] This improvement in terms of stability was also tested under a condition of non-reception of water flows after application inside the WC. The presence of the polymer PVP-K90 allowed a greater general stability of the composition in terms of daily moisture loss and a consequent removal, in terms of time, of the phase transition phenomenon to liquid.

[0061] The composition F4 showed the above-mentioned phenomenon on the sixth day of application without use, whereas the formulation F5 showed the same phase transition on the second day of application.

[0062] In order to better illustrate this result, figure 1 shows the formulation F5 which undergoes destructuring after 2 days under a condition of non-reception of water flows. The importance of the result in the formulation F4 which maintains stability up to the sixth day, is therefore clearly evident.

Example 2

[0063] As further evidence of what is shown in Example 1 and in Table 3, a stability test method was developed, with the aim of ascertaining, in an accelerated way, the outcome of the stability tests, and the following surprising results, indicated in Table 4, were obtained.

[0064] The method provides for the positioning of a cage in an open Doypack made of PET/AL/PE material with a fixed dimension of the opening and kept at 40°C (represented in Figure 2).

[0065] The formulations according to the present invention F2, F3, F4 show maintenance of the physical gel state, for a greater number of days with respect to the formulations of the state of the art F1 and F7.

[0066] The results for the composition F7 are of particular interest, where it is shown that not all the classes of polymers allow the technical problem addressed by the present invention to be solved, i.e. obtaining an improved stability over time.

[0067] A much better performance is evident, in fact, for the compositions F3 and F4 with polyvinylpyrrolidone polymers with respect to the formulation F7 with a polymer such as xanthan gum.

Table 4: the compositions were kept at a fixed temperature of 40°C.

Formulation	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6
F1	**Gel**	**Liquid**				
F2	**Gel**	**Gel**	**Gel**	**Liquid**		
F3	**Gel**	**Gel**	**Gel**	**Gel**	**Gel**	**Liquid**
F4	**Gel**	**Gel**	**Gel**	**Gel**	**Gel**	**Liquid**
F7	**Gel**	**Liquid**				

Example 3

[0068] In order to further confirm the results obtained with the method described in Example 2, aimed at rapidly ascertaining the result of the stability tests, a further test was carried out in a closed and more easily repeatable system under identity conditions: the gel tablet to be tested, arranged in a cage, was positioned in sachets of PE-LD material with a thickness of 65 μm with the possibility of closing with a front zip, commercially known on the French market with the name Zipper Albal Sacs multi-usages, commonly used as containers for food or various kinds of objects and kept at 50°C (represented in figure 3).

[0069] The results obtained at the end of this test are indicated in Table 5 hereunder.

Table 5: the compositions were kept at a fixed temperature of 50°C.

Formulation	Day 2	Day 4	Day 6	Day 8	Day 10	Day 12	Day 13
F1	**Gel**	**Gel**	**Liquid**				
F2	**Gel**	**Gel**	**Gel**	**Gel**	**Gel**	**Liquid**	
F3	**Gel**	**Gel**	**Gel**	**Gel**	**Gel**	**Liquid**	

(continued)

Formulation	Day 2	Day 4	Day 6	Day 8	Day 10	Day 12	Day 13
F4	Gel	Gel	Gel	Gel	Gel	Gel	Liquid
F5	Gel	Gel	Gel	Gel	Liquid		
F6	Gel	Gel	Gel	Gel	Gel	Liquid	
F7	Gel	Gel	Gel	Gel	Gel	Liquid	
F8	Gel	Gel	Gel	Gel	Gel	Liquid	
F10	Liquid						

[0070] The formulations according to the state of the art, i.e. without cellulose or polyvinylpyrrolidone polymer, F1 and F5, provide less performing results in terms of water loss percentage and therefore stability over time with respect to the composition F4 with PVP polymer.

[0071] The tablet F10, as indicated above, represents a compound according to the example of the document US 6,667,286, having the formulation indicated in Table 1: when subjected to the test described above, and specifically Zipper Albal of PE-LD material at 50°C continuously over time, it begins to show destructuring of the gel already after a day of storage and with a much lower water loss, equal to 7.15% of the total water present in the composition.

[0072] The same test described above was repeated and Table 6 shows that the phase transition to the liquid state of F4 takes place at the thirteenth day, whereas the compositions without the polymer F1 are already liquid at the fifth day.

[0073] In particular, Table 6 also shows that the composition F5 according to the state of the art, although comprising the same cetyl stearyl ethoxylated alcohol with an ethoxylation degree of 20 EO, is however less stable with respect to the composition F4 in which said alcohol is present in a combination with polyvinylpyrrolidone polymer. This demonstrates the synergistic effect associated with the presence of both components.

[0074] It is interesting to observe the behaviour of the product Duck Fresh Discs, having a composition indicatively comprising (as indicated in the producer's site): water, Ceteareth-30, glycerine, fragrance, poly(oxy-1,2-ethandiyl)-alpha-isotridecyl-omega-hydroxy-, mineral oil, coumarin, eugenol, limonene, citral, dyes, sodium sulfate, iodopropynyl butyl carbamate.

[0075] The gel composition of Duck Fresh Discs, without polymers, shows a transition to the liquid state within eight days of the start of the test, almost totally losing the water present in the composition.

Table 6: the compositions were kept at a fixed temperature of 50°C.

Composition	F1	F4	F5	Duck Fresh Discs
Water loss percentage 5th day (Physical state)	42.1% (Liquid)	37.1% (Gel)	35.3% (Gel)	35.3% (Gel)
Water loss percentage 8th day (Physical state)		54.9% (Gel)	54.5% (Gel)	59.7% (Liquid)
Water loss percentage 10th day (Physical state)		68.7% (Gel)	62.4% (Liquid)	
Water loss percentage 13th day (Physical state)		91.2% (Liquid)		

[0076] The test with the product Duck Fresh Discs was carried out under conditions completely comparable with the conditions used and indicated above for the formulations F1, F4 and F5, placing a weight of 27 grams of product in a cage, subsequently positioned in a sachet of PE-LD material having a thickness of 65 μm with the possibility of closing with a front zip (Zipper Albal Sacs multi-usages) and kept at 50°C. The gel undergoes phase transition passing from the liquid state at the eighth day in an oven at 50°C, with a moisture loss of 59.7%. This test is therefore a further confirmation of the superior and surprising results of the formulations according to the present invention.

[0077] The data indicated in Table 6 are further confirmed by the graph of figure 4: the graph shows the rheological profile through an oscillatory test, rheometer Modular Compact Rheometer MCR102, of the composition F6 of Table 1 and the product Duck Fresh Discs previously mentioned. This test is independent of the weight of the product and is an objective test that demonstrates that, in the case of the tablet according to the present invention, more energy is required for effecting the phase inversion.

[0078] The graph shows, in fact, that, with the same moisture loss, there is an inversion of the elastic module to viscous (flow point) at a temperature higher than F6 with respect to the other composition. This therefore confirms that, with the same conditions, the loss of structure and therefore the transition to the liquid state takes place for the composition F6 (black line) at 75°C and for the Duck composition (grey line) at 51°C, further confirming the greater stability of the structure guaranteed by the use of the PVP polymers according to the present invention.

Example 4

[0079] Using the same method described in Example 3, the formulations F4 according to the present invention and F8 according to the state of the art were tested and compared.

[0080] The composition F4 showed a significantly improved stability with respect to the composition F8 as indicated in Table 7, re-confirming the better performances of the PVP polymer according to the invention present in the composition F4, with respect to the xanthan gum present in the composition F8.

Table 7: the compositions were kept at the same fixed temperature of 50°C.

Composition	**F4**	**F8**
Moisture loss with transition to the liquid state	**91.2%**	**78.5%**

[0081] The datum indicated in Table 7 is particularly relevant. The storage conditions, in fact, specifically studied for the present method, are characterized by being particularly stressed conditions to be able to obtain a stability result in rapid time. By transposing the moisture loss datum to a storage condition that approaches the daytime and nighttime temperature cycle, it is clear that the difference in moisture can be appropriately evaluated as an increase in the stability of the formulation F4 with respect to the formulation F8, in a blister with sealing film PET/PE.EVOH.PE and a thermoformed PE/PET valve, equal to about 11 weeks.

[0082] The result in terms of percentage of moisture loss relating to the composition F8 is of particular interest, wherein the polyvinylpyrrolidone polymer has been replaced by xanthan gum. When subjected to the test described in Example 3, i.e. in Zipper Albal of PE-LD material at 50°C continuously over time, the formulation F8, very similar to the preferred formulation F4 from which it differs only in the substitution of polyvinylpyrrolidone with xanthan gum, in any case shows a considerable deterioration in the performances (see Table 7 above).

[0083] Particularly important is the result obtained with the formulation F10, representative of the prior document EP1086199 (corresponding to US 6,667,286), representative of the example shown in the table of EP1086199 as: *"example recipe for a sanitary medium such as pasty gel"* which, when subjected to the test described in Example 3, i.e. in Zipper Albal of PE-LD material at 50°C continuously over time, begins to undergo destructuring of the gel already after one day of storage and with a much lower water loss, equal to 7.15% of the total water present in the composition. This result can only prove that the gel tablet according to the present invention has no characteristic in common with the gel tablet according to this state of the art.

Example 5

[0084] In order to re-confirm the properties of the gel tablet formulations according to the present invention, a further storage test was carried out in a container made of plastic material, specifically HDPE, plugged with a PP cap, kept at a temperature of 60°C. Said container is the same container used and marketed for analogous gel compositions that have similar applications such as, for example, Duck Fresh Discs.

[0085] The compositions F3 and F4 according to the present invention, compared with the compositions F1 and F5, without polymers, surprisingly maintained a rigid gel structure for a greater number of weeks.

Table 8: the compositions were kept at a fixed temperature of 60°C.

Formulation	**Week 1**	**Week 2**	**Week 3**	**Week 4**	**Week 5**
F1	**Gel**	**Gel**	**Liquid**		
F3	**Gel**	**Gel**	**Gel**	**Gel**	**Liquid**
F4	**Gel**	**Gel**	**Gel**	**Gel**	**Liquid**
F5	**Gel**	**Gel**	**Liquid**		

[0086] The stability over time, evaluated as the capacity of maintaining a rigid structure with an increasing moisture loss of the gel, is unequivocally correlated with the presence of PVP or cellulose polymers within the gel tablet formulation and, in particular, is maximum when the polymer is polyvinylpyrrolidone with a molecular weigth (g/mol) ranging from 900,000 a 1,500,000 (PVP K90).

[0087] Other factors contribute to the stability and the previous tests show how the number of carbon atoms of the aliphatic chain of the non-ionic surfactant, the number of ethoxylations of the non-ionic surfactant and the correct water/surfactant ratio, are also fundamental.

[0088] When the ethoxylation number changes, in fact, the structure of the gel can vary greatly. With an ethoxylation number ranging from 10 EO to 20 EO, the phase transition to the liquid state already takes place at a temperature lower than 40 degrees whereas with an ethoxylation number ranging from 20 EO to 80 EO, the stability of the gel is always maintained, at a temperature of 40 degrees. With a variation in the carbon atoms of the aliphatic chain of the non-ionic surfactant, there is a consequent variation in the physico-chemical characteristics of the gel. Aliphatic chains having an overall length of C16-C18 maintain a good stability at a temperature of 40 degrees, whereas aliphatic chains having an overall length of C12-C14 already have a transition to the liquid state at 40 degrees.

[0089] It has been surprisingly found that by specifically using the non-ionic surfactants according to the present invention and precisely C_{16}-C_{18} ethoxylated alcohols with an ethoxylation degree ranging from 20 to 50, preferably from 20 to 30, combined with the specific polyvinylpyrrolidone or cellulose polymers, a gel tablet is obtained with the maximum stability over time, evaluated as the capacity of maintaining a rigid structure with an increasing moisture loss of the gel.

[0090] Furthermore, the tests presented in the examples according to the present invention also demonstrate how the choice of the specific polymer is essential, as polymers such as xanthan gum and polymers of the polyvinylpyrrolidone type having a lower molecular weight such as, for example, PVP K30, although allowing a certain advantage in terms of stability with respect to the complete absence of polymer, have problems of another nature however, that do not allow them to be considered as a suitable solution for solving the technical problem according to the present invention. More specifically, for example, the use of PVP K30 in the compositions previously described, leads to a persistent, aesthetically unacceptable flocculation at the end of processing. Polymers such as xanthan gum lead to a lowering of the level of foam produced inside the WC, such as to reduce the cleaning and sanitizing performances. In both cases, although there may be an improvement in terms of stability, not comparable however with the stability of the gel tablet according to the present invention, the compositions would not be acceptable in terms of product quality in its entirety.

Claims

1. A perfuming and/or detergent gel tablet **characterized by** having

   a) an initial melting point or transition point from the gel state to the liquid state, ranging from 65°C to 90°C; and
   b) a melting point or transition point from the gel state to the liquid state higher than or equal to 44°C, when the gel tablet is **characterized by** a reduction in the water content ranging from 75% to 95% by weight, preferably from 78% to 85% by weight with respect to the water present in the initial gel tablet.

2. The gel tablet according to claim 1, wherein said tablet has a composition comprising:

   - one or more hydrosoluble polymers;
   - one or more non-ionic surfactants and
   - water.

3. The gel tablet according to claim 1 or 2, wherein said tablet has the following composition which comprises:

   - one or more hydrosoluble polymers selected from cellulose polymers and/or their derivatives, polyvinylpyrrolidone polymers and/or their derivatives or a mixture of cellulose and/or polyvinylpyrrolidone polymers;
   - one or more non-ionic surfactants selected from C_{16}-C_{18} ethoxylated alcohols with an ethoxylation degree ranging from 20 to 50, preferably from 20 to 30 and,
   - water.

4. The gel tablet according to claim 3, wherein the composition comprises one or more hydrosoluble polymers selected from carboxymethyl cellulose (CMC), high-purity CMC, preferably carboxymethyl cellulose having a molecular weight ranging from 1,000,000 to 1,500,000 g/mol; polyvinylpyrrolidone having a molecular (g/mol) ranging from 40,000 to 3,000,000, preferably polyvinylpyrrolidone having a molecular weight (g/mol) ranging from 900,000 to 1,500,000, or mixtures thereof.

5. The gel tablet according to any of the claims 2-4, wherein the composition comprises one or more hydrosoluble polymers selected from cellulose polymers and/or their derivatives, polyvinylpyrrolidone polymers and/or their derivatives or mixtures of cellulose and/or polyvinylpyrrolidone polymers, present in a quantity ranging from 0.01% to 10% by weight with respect to the total weight of the gel tablet.

6. The gel tablet according to any of the claims 2-5, wherein the composition comprises a polyvinylpyrrol-idone polymer having a molecular weight (g/mol) ranging from 900,000 to 1,500,000, in a quantity ranging from 0.01% to 10% by weight with respect to the total weight of the gel tablet, preferably in a quantity ranging from 1% to 5%, even more preferably from 1.5% to 3% by weight with respect to the total weight of the gel tablet.

7. The gel tablet according to any of the claims 2-6, wherein the composition comprises C_{16}-C_{18} ethoxylated alcohol with an ethoxylation degree ranging from 20 to 50, preferably from 20 to 30, in a quantity ranging from 20% to 60% preferably from 30% to 45% by weight with respect to the total weight of the gel tablet.

8. The gel tablet according to any of the claims 2-7, wherein the composition comprises C_{16}-C_{18} ethoxylated alcohol with an ethoxylation degree ranging from 20 to 30, preferably selected from cetylstearyl alcohol 20 EO or cetylstearyl alcohol 29 EO, even more preferably cetylstearyl alcohol 20 EO.

9. The gel tablet according to one or more of the previous claims, wherein the water/surfactant weight ratio ranges from 65/20 to 20/65, preferably from 60/30 to 30/60.

10. The gel tablet according to one or more of the previous claims, wherein the tablet has the following composition: water, polyvinylpyrrolidone having a molecular weight (g/mol) ranging from 900,000 to 1,500,000, cetylstearyl alcohol 20 EO, benzisothiazolinone, dye and fragrance; the tablet preferably has the following composition:

- water in a quantity ranging from 25 to 65% by weight,
- polyvinylpyrrolidone having a molecular weight (g/mol) ranging from 900,000 to 1,500,000 in a quantity ranging from 1 to 5% by weight,
- cetylstearyl alcohol 20 EO in a quantity ranging from 20 to 60% by weight,
- benzisothiazolinone in a quantity ranging from 0.01 to 3% by weight,
- dye in a quantity ranging from 0.001 to 0.01% by weight and
- fragrance in a quantity ranging from 1 to 10% by weight,

each weight quantity being indicated with respect to the total weight of the gel tablet; and even more preferably the tablet has the following composition:

- water in a quantity equal to 59.36% by weight,
- polyvinylpyrrolidone having a molecular weight (g/mol) ranging from 900,000 to 1,500,000 (PVP K90) in a quantity equal to 1.5% by weight,
- cetylstearyl alcohol 20 EO in a quantity equal to 35.0% by weight,
- benzisothiazolinone in a quantity equal to 0.1% by weight,
- dye in a quantity equal to 0.04% by weight and
- fragrance in a quantity equal to 4% by weight,

each quantity being indicated with respect to the total weight of the gel tablet.

11. The gel tablet according to one or more of the previous claims, wherein the tablet is packaged in a blister and sealing film, preferably having the following composition and thicknesses:

Blister:

PVC 500 microns
PET 500 microns
Coupled material: PET/EvOH/PE 500 microns

Sealing film:

coupled material: PETalox/PET.EvOH.PE

PET/PE.EvOH.PE 72microns.

12. Use of a gel tablet according to any of the claims from 1 to 11, as a detergent and/or perfuming agent, by application through an open cage in sanitary appliances, household appliances, etc., preferably in WCs.

Fig.1

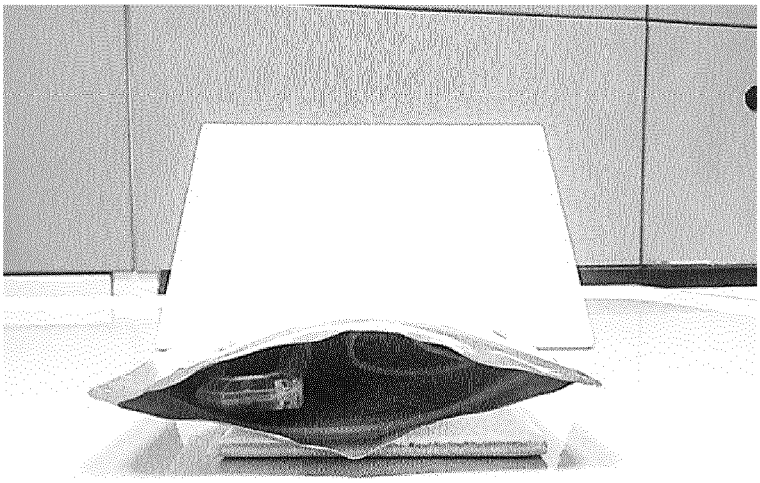
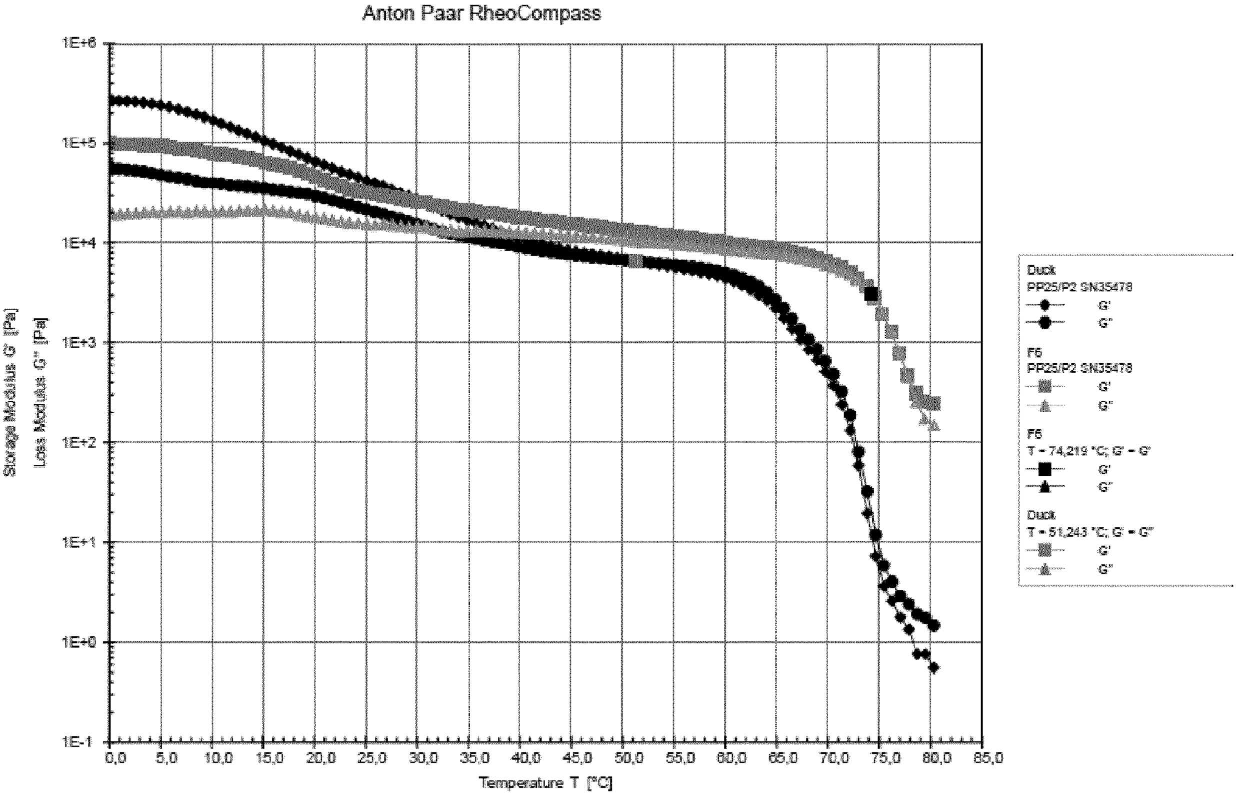


Fig.2

Fig.3


Anton Paar RheoCompass
1E+6
1E+5
1E+4
1E+3
1E+2
1E+1
1E+0
1E-1
Storage Modulus G' [Pa]
Loss Modulus G'' [Pa]
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5,0
10,0
15,0
20,0
25,0
30,0
35,0
40,0
45,0
50,0
55,0
60,0
65,0
70,0
75,0
80,0
85,0
Temperature T [°C]
Duck
PP25/P2 SN35478
G'
G''
F6
PP25/P2 SN35478
G'
G''
F6
T = 74,219 °C; G' = G''
G'
G''
Duck
T = 51,243 °C; G' = G''
G'
G''
Anton Paar

Fig.4

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des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 18 16 4121

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A	US 6 192 524 B1 (BLACK ROBERT H [US]) 27 February 2001 (2001-02-27) * column 5, line 31 - line 41 * -----	1-12	INV. C11D1/72 C11D3/22 C11D3/37 C11D17/00 C11D17/04
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			C11D

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	13 July 2018	Culmann, J

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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