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(71) Applicant: **Bolton Manitoba SpA  
20124 Milano (IT)**

(72) Inventors:

- NOVITA', Luciano  
20090 Segrate (MI) (IT)**
- PIMAZZONI, Massimiliano  
21042 Caronno Pertusella (VA) (IT)**
- BRIGNOLI, Cinzia  
20135 Milano (MI) (IT)**

(74) Representative: **De Gregori, Antonella et al  
Studio Legale Bird & Bird  
Via Borgogna, 8  
20122 Milano (IT)**

### (54) OPTIMIZED METHOD FOR WASHING IN WASHING MACHINES

(57) An optimized method for washing in washing machines is described, which comprises a step for adding a stain-removing/cleaning additive during the last rinsing step of any washing cycle, wherein said additive

is withdrawn and brought into contact with the clothes to be washed by the water passing through the dispenser compartment of the softening additive.

**Description**

[0001] The present invention relates to an optimized method for washing in washing machines.

5 [0002] The present invention falls within the technical field of additives for washings in washing-machines, i.e. products that are substantially washing adjuvants that integrate the use of detergents, with a specific function, different from the cleaning action itself of detergents: examples of these additives are stain-removing additives, softeners, colour additives, whiteners, anti-lime additives, antibacterial agents, bleaches, perfuming agents, etc. and washing methods that use these additives.

10 [0003] Additive products to be used in addition to the detergent and that can exert various functions are in fact known and widely marketed.

[0004] These additive products are added according to their characteristics and function at different times/stages of the washing process of clothes in a washing machine.

15 [0005] Certain additives are added in the pre-washing or washing step, as is the case for example of stain-removing additives, bleaches, anti-lime additives, antibacterial agents, whereas other additive products are added in the final washing phase, i.e. in the last rinse: this is the case of softeners and, in some cases, also antibacterial agents.

20 [0006] As previously indicated, the different addition time of the additive product depends on its physico-chemical characteristics and its function: it is clear, in fact, that a softening additive must be added in the final washing stage to prevent losing or minimizing the desired softening and perfuming effect due to the subsequent rinsing phases of the clothes. More specifically, a softener acts in the following way: the molecules of the softening product become bound to the fibers of the fabrics, creating a thin film and the final effect is a greater softness of the garment, combined with its possible fragrance and, again thanks to the composition of the softening product and reduction in friction between the fibers, said additive also facilitates the ironing of the garment. The use of the softening product also reduces the static electricity of the freshly washed garments.

25 [0007] Softeners are therefore basically washing adjuvants that integrate the use of detergents. Historically, the composition of softeners comprises the use of quaternary ammonium compounds with one or more fatty chains. Examples of softening additives used in the past are DSDMAC (distearyldimethylammonium chloride), DHTDMAC (dihydrogenated tallow dimethylammonium chloride). Nowadays, the composition of all the main softeners on the market comprises esterquat (inci definition: Distearoylethyl Hydroxyethylmonium Methosulfate), as essential component: these are positively charged softening molecules, obtained by the esterification of ethoxylated quaternized amines with long-chain fatty acids. The other components are almost always additives, fragrances, thickeners or pearlizing agents, dyes, etc.

30 [0008] It is also evident that the moment of use of a stain-removing additive, again referring to a washing adjuvant that integrates the use of detergents, is substantially different from that of the softening additive described above.

35 [0009] A stain-removing additive is in fact generally used by applying it directly to the garment and specifically on the stain to be treated, before washing, or it is generally added as additive in the pre-washing or washing step in the washing cycle of the washing machine.

40 [0010] The composition of liquid stain-removing additives is generally based on an appropriate mixture of nonionic, anionic, amphoteric surfactants, amine oxide, enzymes or hydrogen peroxide or other oxidizing agents, such as, for example, sodium hypochlorite (the latter only to be used on white garments).

[0011] In order to facilitate the task of the end user, various products called "multifunction" or with integrated action have been recently introduced onto the market, i.e. products characterized by contemporaneously exerting two or more functions among those previously listed: colour and anti-lime additives, stain-removers and bleaches, softeners and optical whiteners, etc., can in fact be found on the market, in addition to the "obvious" softening and perfuming additive.

45 [0012] The production of these "multifunction" compositions or additives is not as easy and trivial as might seem to the eye of a simple user. Skilled persons in the field, in fact, are well aware of the difficulties encountered in producing these additives as the ingredients used for one function are often in conflict with those that exert other functions and their combination can lead to a partial/total inactivity of the end-product in one or more of the desired functions.

50 [0013] It is also evident that the production of an effective "multifunction" additive has a further fundamental basic requirement: not only must the physico-chemical characteristics of the various components be such as to allow the stability and functioning of the final additive for each function desired, but the functions of the "multifunction" additive must also be contemporaneous, i.e. they must be functions that are exerted in the same washing step(s). The multifunction additives currently on the market are in fact specifically additives that combine two or more additive functions which, in the past, were added individually and separately in the same washing step of the garment.

55 [0014] Multifunction additives that combine the softening action to be exerted in the last rinsing phase with the stain-removing or bleaching action (for example), which, by their very nature, are exerted in different phases of the washing cycle (pre-washing or actual washing), are neither known nor commercialized.

[0015] The Applicant has now surprisingly found that, contrary to what has so far been considered, an optimized washing method can be provided, which allows an improved cleaning effect to be obtained, that overcomes the preconception of the state of the art. The main objective of the present invention is therefore to find an optimized method for

washing in washing machines, which allows an improved cleaning effect to be obtained.

[0016] A further objective of the present invention is to find an optimized method for washing in washing machines, which allows a different use of cleaning/stain-removing compositions or additives present on the market.

[0017] An object of the present invention therefore relates to an optimized method for washing in washing machines, characterized by a step for adding a stain-removing/cleaning additive in the last rinsing step of any washing cycle, wherein said additive is withdrawn and brought into contact with the garments to be washed by the water passing through the dispenser compartment of the softening additive.

[0018] A further object of the present invention relates to the use of a stain-removing/cleaning additive as additive in the last rinsing step of any laundry washing cycle.

[0019] This is achieved by the use of the stain-removing/cleaning additive in the compartment/space of the washing machine normally reserved for the insertion of softening additives, i.e. additives withdrawn by the washing machine in the last rinsing step.

[0020] The Applicant has in fact very surprisingly found that, contrary to what is believed, i.e. that a cleaning/stain-removing additive necessarily requires completely different times, temperatures and washing dilutions from the times, temperatures and dilutions necessary for a softening/perfuming additive that is added in the final rinse of the whole washing cycle, a stain-removing/cleaning additive, when added in the final rinse, is capable of exerting its specific cleaning/stain-removing function, i.e. it is effectively able to ensure a significant cleaning action under said time, temperature, shaking/friction and dilution conditions, that is to say in a cold water dilution whose purpose is simply to remove the last detergent residues and distribute the softening additive. More specifically, the effectiveness of the cleaning action of cleaning/stain-removing additives added in the softener compartment, has been verified with a wide range of technologies/washing and stain-removing products.

[0021] The experimental data indicated in the examples of the present patent application, in fact, show that effective performance results are obtained with different types of product added in the softener compartment: enzymatic products, products based on hydrogen peroxide, products based on surfactants and enzymes. The use of formulations typical of liquid detergents (surfactants and enzymes), pre-treating agents (surfactants and enzymes), laundry additives (surfactants and hydrogen peroxide), leads to a significant increase in the stain-removing performance with respect to the use of a detergent alone.

[0022] In short, the stain-removing/cleaning additive used in the softener compartment can be any composition comprising one or more of the following components: surfactants (nonionic, anionic, amphoteric, cationic) and/or soaps and/or enzymes and/or sequestering agents such as, for example, phosphonates, EDTA or amino-acid derivatives and/or oxygen-based whiteners and/or chlorine-based whiteners and/or species which, without being themselves washing agents, improve the performances of surfactants or other washing components such as, for example, performance booster polymers (such as for example ethoxylated polyethyleneimines such as Sokalan HP 20).

[0023] The stain-removing/cleaning additive can be selected from enzymatic products, products based on hydrogen peroxide, products based on surfactants and enzymes, possibly products containing sodium hypochlorite whose use, however, is limited to white or particularly resistant garments. By way of example, liquid detergents comprising surfactants and enzymes, pre-treating additives comprising surfactants and enzymes, stain-removing additives for laundry comprising surfactants and hydrogen peroxide, can be mentioned.

[0024] These additives however can contain perfuming substances, dyes, or optical whiteners and possibly softeners for providing the garments with sensory benefits, in addition to cleaning/stain-removing additives.

[0025] Furthermore, although the cleaning/stain-removing additive is only introduced in the final rinsing step, the tests carried out showed the absence of significant residues of additive on the washed garments at the end of the washing program.

[0026] The optimum dosing of the cleaning/stain-removing additive in the softener compartment can naturally vary depending on the type of formula or technology used. It is of course also limited by the capacity of the softener compartment which can vary, but which is normally not greater than 100 ml. The dosage of the cleaning/stain-removing additive in the softener compartment can range from 20 to 100 ml, more specifically from 30 to 75 ml.

[0027] The following examples are provided for purely illustrative purposes.

## 50 Example 1

[0028] Example 1 was carried out on standard WFK, EMPA and CFT pieces commonly used in standard washing tests according to the AISE protocol, which have been subjected to a washing cycle effected in Miele Novotronic W1513 washing machines at 40°C, using, in all the tests, the same detergent and under the same washing conditions. Three different stain-removing/cleaning additives were used in the following tests 1-3, which were added in the final step of the last rinse of a washing cycle.

[0029] In the comparative test, the detergent alone was used, under the same washing conditions.

[0030] The additives in the optimized washing tests 1-3 according to the present invention were withdrawn and brought

into contact with the garments to be washed through the water passing through the dispenser compartment of the softening additive in the final rinse.

[0031] The washing program carried out is a washing program at 40°C, but the rinse is always effected in cold water, this term referring to water having the "ambient" supply temperature from the pipes.

5 [0032] Test 1: 65 ml of washing-machine detergent were used, containing 4.5% of sodium LAS, 4.5% of ethoxylated C<sub>12</sub>-C<sub>14</sub> alcohol 7 EO, 1.5% sodium soap, phosphonate sequestering agents and ethoxylated polyethyleneimine, commercialized under the trade-name of Omino Bianco, and 75 ml of the following stain-removing/cleaning composition to be added in the washing step:

10 12.5% anionic surfactant, 6.0% ethoxylated alcohol, 2.5% soap; enzymes: protease, cellulase, amilase. This is the detergent "Dash Actilift" commercialized by P&G.

15 [0033] Test 2: 65 ml of the washing-machine detergent of test 1 were used, and 75 ml of the following stain-removing/cleaning composition for pre-treating the stain: 10.5% ethoxylated alcohols; enzymes: protease. This is the pre-treating additive "Bio shout" commercialized by SC Johnson.

[0034] Test 3: 65 ml of the washing-machine detergent of test 1 were used, and 75 ml of the following stain-removing/cleaning composition for pre-treating the stain: Sodium LAS 3.0%, ethoxylated alcohol 12.4% and hydrogen peroxide 5.0%; commercialized under the trade-name of Omino Bianco Smacchiatore Gel.

[0035] Comparative Test: 65 ml of the washing-machine detergent of test 1 alone were used.

20 [0036] The cleaning performance results are indicated in Table 1 below:

- Type of test
- Agreed protocol AISE 2013  
(<https://www.aise.eu/our-activities/standards-and-industry-guidelines/detergent-test-protocol.aspx>)
- 25 A.I.S.E. Working group "Laundry Detergent Testing" published in November 2013;
- Temperature: 40°C
- Washing cycle: Standard for cotton
- Washing machine: Miele Novotronic

30 [0037] The type and number of stains verified are those provided under this protocol.

[0038] The results in Table 1 show the significant differences in cleaning power on the single stain between the products of the various tests: a product marked with the letter B, for example, is characterized by a cleaning/stain-removing power on that type of stain: statistically lower with respect to a product marked with the letter A, statistically higher with respect to a product marked with the letter C, statistically equal with respect to a product marked with the letter B.

[0039] The three subsequent lines of the table indicate the score, in terms of number of stains, between two products: more specifically, the method according to the present invention of test 1 is better in the treatment of eleven stains and is equal in the treatment of the remaining stains with respect to the washing method with detergent alone (comparative example); the method according to the present invention of test 2 is better in the treatment of nine stains and equivalent in the treatment of the remaining stains, with the exception of only one stain (blood) with respect to the washing method with detergent alone (comparative example); the method according to the present invention of test 3 is better in the treatment of five stains and equivalent in the treatment of the remaining stains, with the exception of only two stains (carrot baby food and tomato puree) with respect to the washing method with detergent alone (comparative example).

[0040] The results are also expressed as y index in the last line of Table 1: the higher the Y index value, the greater the stain-removing effectiveness.

	Comparison	Test 1	Test 2	Test 3
Fried fat	C	B	A	B
Grass and mud	B	A	B	A
French mustard	B	A	A	B
Carrot baby food	C	A	B	D
Chocolate	C	A	AB	B
Blood	AB	BC	C	A
Cooked steak fat	B	A	B	B

(continued)

	Comparison	Test 1	Test 2	Test 3
5	Engine oil	C	A	B
	Makeup	A	A	A
10	Tomato puree	C	A	B
	Fruit juice	C	A	A
	Red wine	C	AB	A
	Coffee	AB	B	B
15	Tea	B	A	AB
	Results	0	11	
		1		9
		2		5
20	Y Index	100	104	102
				101

Example 2

[0041] Some pieces of EMPA 221 (white cotton) were subjected to washing at 20°C in a Miele Novotronic V1513 washing machine, together with 3 Kg of ballast. The washing was effected with a washing-machine detergent, commercialized with the trade-name Omino Bianco and the cleaning/stain-removing product "Dash Actilift", also used in test 1 of Example 1, was added in the softener compartment, dosed in the same in a quantity equal to 65 ml.

[0042] The content of residual enzymes on the washed pieces was controlled with the aid of the kit Protazyme AK Tablets. Water was added to portions of washed and dried EMPA 221 fabric, the solution was treated with Protazyme AK according to the instructions of use and the absorbance of the solution at 590 nm was measured with a spectrophotometer.

[0043] The absorbance values show the presence or absence of residues of protease enzyme on the piece. The results are as follows:

	Absorbance	
35	EMPA 221 not treated, cut into dimensions of 1x19cm	0.000
	Liquid detergent Dash Actilift (1 ml)	1.328
40	EMPA 221 subjected to cycle (Example 2) cut into dimensions 1x19cm	0.000
	EMPA 221 cut into dimensions of 1x19cm Non-rinsed fabric	0.072
	EMPA 221 cut into dimensions of 9x9cm Non-rinsed fabric	0.184

[0044] The tests carried out showed the presence of protease enzyme both in the detergent as such, and on pieces treated and not subjected to the final rinsing step.

[0045] The pieces treated in the washing machine with the method according to the present invention and specifically with the use of the cleaning/stain-removing additive in the softener compartment, i.e. in the final rinsing step, on the contrary, showed the absence of protease.

**Claims**

1. An optimized method for washing in washing machines, characterized by a step of adding a stain-removing/cleaning additive during the last rinsing step of any washing cycle, wherein said additive is withdrawn and brought into contact with the clothes to be washed by the water passing through the dispenser compartment of the softening additive.
2. The method according to claim 1, wherein the stain-removing/cleaning additive is added in an amount ranging from

20 to 100 ml, preferably from 30 to 75 ml, during the last rinsing step of any washing cycle.

3. The method according to one or more of the previous claims, wherein the stain-removing/cleaning additive is a composition comprising one or more of the following components: nonionic, anionic, amphoteric, cationic surfactants and/or soaps and/or enzymes and/or sequestering agents such as for example phosphonates, EDTA or amino-acid derivatives and/or oxygen-based whiteners and/or chlorine-based whiteners and/or performance booster polymers.
4. Use of a stain-removing/cleaning additive as an additive in the last rinsing step of any laundry washing cycle.
- 10 5. Use of a stain-removing/cleaning additive according to claim 4, where the stain-removing/cleaning additive is added in the compartment/space of the washing machine commonly normally reserved for introducing softening additives withdrawn by the washing machine during the last rinsing step.
- 15 6. Use of a stain-removing/cleaning additive according to one or more of claims 4 and 5, where the stain-removing/cleaning additive is added in an amount ranging from 20 to 100 ml, preferably from 30 to 75 ml, during the last rinsing step of any washing cycle.
- 20 7. Use of a stain-removing/cleaning additive according to one or more of claims from 4 to 6, where the stain-removing/cleaning additive is a composition comprising one or more of the following components: nonionic, anionic, amphoteric, cationic surfactants and/or soaps and/or enzymes and/or sequestering agents such as for example phosphonates, EDTA or amino-acid derivatives and/or oxygen-based whiteners and/or chlorine-based whiteners and/or performance booster polymers.

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Application Number

EP 17 19 2255

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15 A	----- EP 1 580 313 A1 (SHARP KK [JP]) 28 September 2005 (2005-09-28) * paragraph [0098] - paragraph [0106]; figure 14 * * paragraph [0122] - paragraph [0125]; figure 14 *	1-7	
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CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document			

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

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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.

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